KONINKLIJKE AKADEMIE
VAN WETENSCHAPPEN
-:- TE AMSTERDAM -:-

PROCEEDINGS OF THE SECTION OF SCIENCES

VOLUME XVIII
(— 1ST PART —)
(N°. 1—5)

JOHANNES MÜLLER :—: AMSTERDAM
:————: JANUARY 1916 :————:

(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling Dl. XXIII en XXIV.)

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Vol XVIII. — Part 1st.

N°. 1—5.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday May 29, 1915.

VOL. XVIII.

President: Prof. H. A. LORENTZ.

Secretary: Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 29 Mei 1915, Dl. XXIV).

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Anatomy. — *"On the structure and the innervation of the musculus sphincter pupillae and the musculus ciliaris of the bird's eye."* By Prof. J. Boeke. (With 12 figures).

(Communicated in the meeting of April 23, 1915).

In a former communication [1] I described the innervation, the relations between the muscle-cells and the nerve-endings, of the ciliary muscle of the human eye, as a type of plain muscular tissue. A subsequent examination of frontal sections through the iris-muscles taught me, that, as far as my preparations showed me, the relations between the efferent nerve-endings and the muscle-cells of the sphincter pupillae in the iris of the human eye are essentially the same as in the ciliary muscle. In connection with these observations it seemed to be of interest to study somewhat more closely the structure and the innervation of the intrinsic eye-ball-muscles (sphincter and dilatator pupillae, ciliary muscles) of the bird's eye.

For indeed, both from the physiological and the morphological point of view, this comparison of the iris- and ciliary muscles of mammals and birds seems to be of interest. The swift and complex accomodation (lens and cornea), the swift and varying play of the muscles of the iris and their rôle in accomodation, the peculiar differences in the function of the eyes in birds of different kinds and habits (birds of prey, fastflying birds, day- and night-birds, diving birds etc.) make such a comparison of the details of the nerve-supply tempting. And beside these physiological differences the ciliary and iris-muscles of birds present such striking morphological characteristics, that these alone would make a comparison of the avian and mammalian eye-muscles valuable.

The intrinsic muscles of the avian eye, both the muscles of the iris (with the exception of the dilatator pupillae) and the ciliary muscle, are distinguished from the homologous muscles of mammals by their being composed of striated muscle-fibres, as was known since the classical researches of Brücke and Müller.

In the vertebrate series this cross-striation of the inner muscles of the eye-ball is only found in reptiles and birds. As was mentioned above, it is met with both in the muscles of the iris and of the corpus ciliare. Only the so-called dilatator pupillae of the membrane of Bruch, as it was shown by the interesting and thorough researches of Grynfellt, Andreae, Zietzschmann, von Szily and others, does not show any vestige of cross-striation.

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[1] Proceedings of the meeting of Jan. 30, 1915. Royal Academy of science, Amsterdam, p. 982—989.

By this cross-striation the muscle-fibres of the iris and the corpus ciliare may be compared with the group of voluntary muscle-fibres, but when we study somewhat more closely their form and structure, there appear quite a number of minor differences, which bring them into a closer vicinity to the heart-muscle fibres.

In the first place the muscle-fibres of the iris and the corpus ciliare, as was shown as far back as 1883 by Geberg, do not possess the tough, thickened cellmembrane commonly known as sarcolemma. Here the plasma and the myofibrilla contained in the sarcoplasma are surrounded by an extremely thin and delicate membrane, reinforced by the closely applied bodies of connective-tissue cells, and often it is practically impossible to demonstrate the membranous covering of the fibres, which might be called a sarcolemma apart from this connective tissue.

In the second place these muscle-fibres contain a very considerable amount of sarcoplasm and only a comparatively small number of contractile striated fibrillae. These fibrillae are usually gathered together into a number of columnlike or platelike bundles, which we may call with Schäfer among others the sarcostyles.

In thin muscle-fibres these fibrilbundles are distributed rather regularly throughout the whole muscle-fibre, and, when cut in transverse sections, present the picture of fig. 1 and fig. 3.

In the larger muscle-fibres these fibrilbundles or sarcostyles are arranged in a curious manner, in flattened bundles, folded or curved round, and lying in a large amount of sarcoplasm; the structure

Fig. 1. Fig. 2.

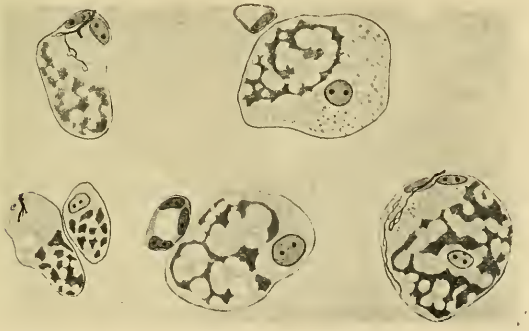

Fig. 3. Fig. 4. Fig. 5.

Fig. 1—5 cross sections of muscle-fibres of the musc. sphincter pupillae of a full-grown fowl. Magn. 1600.

and arrangement of the contractile elements of these large fibres is better elucidated by regarding the cross-sections figured in fig. 2, 4, and 5 than by a long-winded description. Especially in the transverse sections of the larger muscle-fibres of the sphincter pupillae of full-grown fowls this arrangement of the sarcostyles in flattened and curved bundles is clearly shown.

The sarcoplasm between the folded and curved sarcostyles is in most cases of a very loose reticular slightly granular appearance. Outside the column of fibrilbundles and platelike bands the sarcoplasm is generally of a more coarsely granular structure and surrounds the contractile elements on all sides, often in a thick layer. Sometimes this granular appearance is seen throughout the whole of the transverse section of a muscle-fiber. At intervals this layer of sarcoplasm lying outside the column of sarcostyles is so thick, that it not only surrounds the bundle of sarcostyles at all sides, but is seen projecting beyond the line of the surface of the fibre, forming a sort of protuberance on the side of the fibre (fig. 2, fig. 6); this accumulation of sarcoplasm always contains several nuclei; which however, are found also here and there in the loosely reticulated sarcoplasm between the sarcostyles (fig. 5). These sarcoplasmatic protuberances may be compared with the granular expansions first

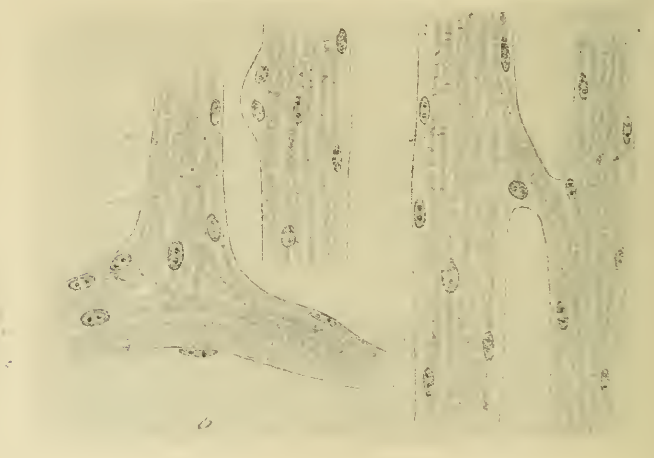

Fig. 6. Fig. 7.

Fig. 6 and 7 Longitudinal sections of striated muscle-fibres of the iris of the fowl's eye noticed by Doyère in insects, and with the "soles" of the muscle-fibres of the vertebrates. Only here they are found in a large number on the same muscle-fibre, and only one or two of them serve as a "bed" or "sole" for the efferent nerve-endings (fig. 1, fig. 5, fig. 8).

Through this abundance of sarcoplasm, the curious arrangement of the sarcostyles and the local protuberances of sarcoplasm on the side of it, the muscle-fibre already acquires a very curious appearance. This is still accentuated by the third fact to be mentioned here, viz. that the muscle-fibres are not the independent, threadlike, straight elements, running from one end of the muscle to the other, as is the case in most of the sceletal muscles, but that in the iris of the birds the muscle-fibres are branched, interwoven, and not only that they divide, but the fibres anastomose through these side-branches (cf. Geberg), so that there is established a continuity of the fibres throughout the whole ring of the iris instead of a tissue containing only distinct separate fibres. This syncytium of sarcoplasmatic elements with bundles of fibrillae running through it in complete continuity over a great distance gives the muscles of the avian iris a striking resemblance to the cardiac muscle-fibres of the mammalian or avian heart, with the only restriction that in the sphincter iridis the connections between the different musclefibres do not come so much to the foreground as in the heart muscle, and that the individuality of the musclefibres is better preserved than it is the case in the myo-cardium.

In connection with this branching, dividing and anastomosing of the different muscle fibres of the iris muscle a curious phenomenon may be mentioned here, of which an example is drawn in fig. 6. When we study tangential (frontal) sections of the iris, in which the whole system of the fibres of the sphincter pupillae is shown parallel to the surface, we meet in these sections both the circular fibres running around the pupil (the sphincter pupillae) and the radiating fibres, cut in longitudinal direction. We can state in these sections throughout the whole depth of the sphincter muscle, but especially in the dorsal part of the stroma iridis, the presence of a number of radiating fibres running between the bundles of the circular fibres, at right angles to the direction of the circular fibres, but lying in the same plain. These radiating muscle fibres are apparently independent of the circular fibres, and this is what we should expect, in correspondence with the antagonistic function, which we should be inclined to ascribe to the two sorts of fibres. But then this independency is often only apparent, and one often finds a connection between the two sets of fibres, even in the way figured in fig. 6, where a muscle-fibre belonging to the circular system of the sphincter pupillae divides into two branches running at right angles to the motherfibre, and thus forming a radiating fibre of the second system. The curving round of the sarcostyles, the place of these fibril-bundles in the sarcoplasm, the whole aspect of the T-shaped muscle-fibre, drawn in the figure as accurately as possible, leave as it seems no doubt as to the accuracy of the observation. And indeed, even GEBERG as long ago as 1883, seems to have seen something like it, where he says: "wo wir es, wie es so oft an unseren Object der Fall ist, mit vielfach und mitunder senkrecht gegen einander sich verzweigenden Muskelfasern zu thun haben", . . . (l.c. p. 14).

Thus we must regard the muscular system of the iris in a certain sense as a syncytium, composed of elements, connected with each other, and in which the fibres of the circular system are in an organic connection with the radiating fibres of the iris musculature.

Entirely independent of this system remains the so-called membrane of BRUCH, composed of fibres (or elongated cells) running only in a radiary direction and remaining through life in close connection with the epithelium of the iris, which do not show any vestige of cross-striation, and to which must be ascribed exclusively, according to ZIETZSCHMANN, the function of a real dilatator pupillae.

In the muscular sheet of the iris of the human eye, being composed of plain muscle-cells, this organic connection between the sphincter muscle and the dilatatory fibres converging towards the pupil, is of course not easily to be stated with accuracy. But the study of thin tangential (frontal) sections through the iris gives one the impression, that even here similar relations exist.

In my former communication I described the interesting relations existing between the efferent nerve-endings and the muscle-cells of the musculus ciliaris of the human eye. The small dimensions of the muscular elements of the human corpus ciliare and the closely interwoven nerve plexus make it very difficult to get a clear picture of the numerical relations between the nerve-endings and the muscle-cells. The terminations of the efferent nerves seemed to be present in two distinct types (compare the figures of the communication mentioned above), as small rings or loops and as small networks, but I could not get a distinct answer to the question whether these two types of intraplasmatic nerve-endings belong to two different kinds of efferent nerves or to nerve-fibres of the same kind and the same source.

Easier to determine are the relations between the efferent nerves and the muscular elements in the bird's eye.

According to the current opinion, in man and mammals, in which the relations between the nerves and the muscle-cells of the iris are studied profoundly. the sphincter pupillae is innervated by means of the ganglion ciliare and the third nerve, the dilatator pupillae however gets its nervous supply from the sympathetic nerve, by means of the superiorcervical ganglion, the ganglion ciliare and the nervi ciliares longi. Stimulation of the nervus oculomotorius causes the pupil to contract, stimulation of the cervical sympathetic causes the pupil to enlarge. The real innervation of the membrane of Bruch is not known. Only Retzius (1893) asserts to have seen in albinotic rabbits very delicate non-medullated nerve-fibres running towards the fibres or cells of this membrane and ending in very small knobs lying against the surface of the membrane. In birds, where the structure of the iris-muscles and the function of the sphincter and dilatata pupillae have been studied very profoundly of late years, there is no unanimity of opinion about the relations between efferent nerves and the different muscular systems. Geberg and Melkich are of opinion that both the circular and the radiating muscle-fibres of the iris are innervated by medullated nerve-fibres coming from the same source. About the innervation of the membrane of Bruch in the bird's eye we know nothing exactly.

Cross sections and especially longitudinal (frontal) sections through well-impregnated preparations of the iris of fowls and pigeons stained after the method of Bielschowsky and treated afterwards with chloride of gold, haematoxylin and eosin showed the following facts.

In the iris-stroma we find the bundles and plexus of nerve-fibres, containing medullated and non-medullated fibers, as they were described by Geberg and others.

The thick medullated nerve-fibres running between the muscular elements of the sphincter pupillae supply them with terminations, which may be compared with the motor nerve-endings (end-plates of Kuenen) of the voluntary muscle-fibres.

On the muscle-fibres both of the musculus ciliaris and of the sphincter pupillae these efferent nerve-terminations are loose, provided with only a few branches and small endrings or delicate endnets. The motor nerve-fibre usually enters the muscle-fibre at one of the sarcoplasmatic protuberances described above (fig. 9 and 10) and in transverse sections through the muscle-fibres the hypolemmal position of these nerve-endings is clearly to be seen (fig. 1 and 5). Under a very high power even in these muscles the existence of a periterminal network in the sarcoplasm and the intimate connections between this periterminal network and the nerve-termination on one

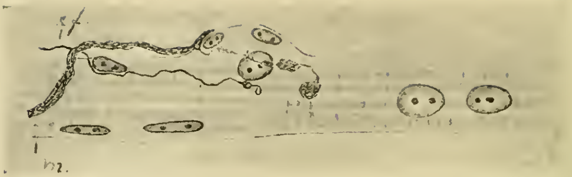

Fig. 8. Muscle-fibre from the musculus ciliaris of a full-grown fowl with double innervation. af = accessory nerve-termination. m = common motor nerve-ending.

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Fig. 9 and 10. Muscle-fibres of the sphincter pupillae of the eye of a full-grown fowl, showing double innervation.

hand and the contractile fibrils, the sarcostyles on the other hand, could be stated with accuracy. I often got the impression that the delicate nerve-fibrils of the motor nerve-ending, after entering the muscle-fibre, run round the sarcoplasmatic prominence, encircling it, and then follow the direction of the sarcostyles for some distance before breaking up in endrings or endnets. These motor nerve-endrings I found both in the circular fibres of the sphincter pupillae and in the radiating fibres. The innervation of the membrane of Bruch I could not make out.

Beside these motor nerve-endings at the end of medullated nerve-fibres there exist in the sphincter pupillae and in the musculus ciliaris of the bird's eye just as in the voluntary sceletal muscles the very delicate, non-medullated nerve-fibres with their small, loosely arranged, delicate endings, entering the muscle-fibers independently of the motor nerve-terminations mentioned above, which I described in the voluntary muscles of the body as "accessory nerve-terminations", and which could be traced to the nervus sympathicus. In fig. 8, 9, and 10 are given some examples of these accessory nerve-endings on muscle-fibres of the sphincter pupillae and the musculus ciliaris.

As far as I could gather from my preparations, the delicate non-medullated nerve-fibres ending in the small "accessory" terminations on the muscle-fibres, remained independent of the medullated nerves.

Whether we are entitled to ascribe to these accessory nerve-fibres even here an influence on the tonus of the iris- and ciliary muscles, and what are the relations of these nerve-fibers to the sympathetic nerve, are questions not to be debated here. There is here a wide field lying open for experimental study.

In conclusion some words may be added about the question, whether ganglioncells are present in the corpus ciliare or in the stroma of the iris or not. Several authors (e. g. Retzius) denied the existence of these ganglioncells, others, as C. Krause, H. Müller, and in later years especially Geberg, described small groups of ganglioncells and separate cells appearing alongside the nerve-fibre bundles, others, as Agababow, found ganglioncells only in the course of the vasomotor nerves. Finally Inglis Pollock found in 1912 that after the exstirpation of the ganglion ciliare or of the superior cervical sympathetic ganglion the nerves of the corpus ciliare and iris did not degenerate. This fact would point to the conclusion, that in the corpus ciliare and the iris the ganglioncells are as abundant as they are in the terminal sympathetic ganglia in the intestinal wall in the nerve plexus of Auerbach and Meissner.

In my preparations of the corpus ciliare and iris, stained after the method of BIELSCHOWSKY, ganglioncells were scarce, and in fact I often looked in vain for them. It was only in the nerve plexus of the corpus ciliare that ganglioncells were to be found, of the type figured in fig. 11, 12 and 13. It therefore seems improbable that they should exist in the numbers required for the theory of INGLIS POLLOCK. So from this point of view too renewed research is necessary and especially it will be necessary to verify the interesting results of the last-named author.

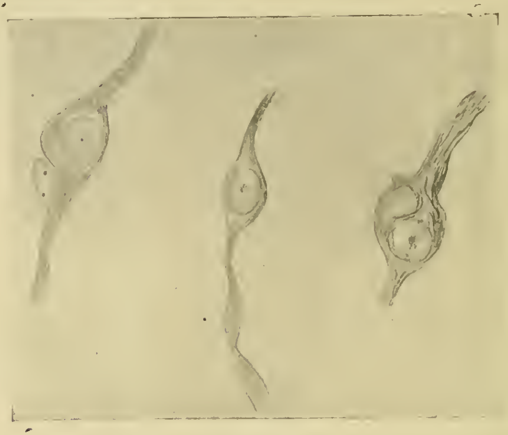

Fig. 11, 12 and 13. Ganglioncells from the plexus ciliaris of the human eye.

Leiden, April 1915.

Geology. — "*How volcanism might be explained.*" By Dr. C. G. S. SANDBERG. (Communicated by Prof. Dr. C. E. A. WICHMANN).

(Communicated in the meeting of April 23, 1915).

To explain the phenomenon of volcanic eruptions and the mode of their origin, it has long been considered necessary to assume that large quantities of sea-water were suddenly brought in contact with incandescent and liquid magma, by means of deep-reaching fissures or crevasses in the crust of the earth.

The fact that the gaseous volcanic emanations showed some similarity with the constituent elements of sea water and the proximity of the seat of volcanic activity to marine areas, led to our looking for a causal connection between these phenomena.

The theory built up on it is now acknowledged untenable, both as some volcanic areas proved to be situated at considerable distance from the sea and because it was admitted impossible for sea water to penetrate to the magma along a fissure, only to be violently expelled again along another, a more difficult passage.

A. Daubrée (1) experimentally tried to establish the possibility of the necessary explosive energy, being furnished by the contact of water, reaching magma by capillary attraction, through the sedimentary strata; this assumption equally proved untenable however.

In short we may say that since, the solution of the problem has been sought in connection with the action of radioactive elements of the interior of the earth, with cosmic influences (solar and lunar attraction, maxima and minima of sun spots, etc.) or else in connection with mountainfolding. At the same time it was considered admissable to accept that both, the eruptive power and the presence of vapours and gases, are primordial elements of the magma (2).

Lately A. Brun (3) denied the existence of water-vapour in large quantities in volcanic emanations, an assertion which has been refuted by the results of L. Day and E. S. Shepherd's researches (4).

When now we examine the way in which volcanic regions are distributed over the earth, we notice that their situation coincides in general with the steep flanks of the G. A.[1]) which are, according to the doctrine of isostatic movements of the earth's crust, *the faulted and fissured regions of our globe.*

In the author's opinion it would not seem improbable, that a causal connection exists between the faulted condition of these regions and the occurrence of volcanism at those very places.

The products of erosion of the G. A. transported to the G. S. are deposited in *sea-water.*

Those sediments consequently consist of solid elements mixed with sea-water.

In the G.S. the liquid constituents of the upper layers surpass the solid material (Deep-sea ooze).

As sedimentation progresses, the proportion of solid material in the mixture increases, through entassement.

Ultimately the water contents of the sedimentary deposit will not exceed the capacity of the total of capillary- (pore-)spaces, left between the adjacent particles of solid material, of which the sediment is built up.[2])

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[1]) In what follows the initials G. A. and G. S. will be used respectively for the words Geo-anticlinal and Geo-synclinal.

[2]) The question whether larger cavities must be considered existable at very

To arrive at an appreciation of the quantity of sea water, which thus could possibly be contained in sedimentary strata, we have first to examine what the pore space in sedimentary strata can amount to.

If the constituting elements were perfectly spherical, the amount of pore space would depend only on the way of their being piled up, and would vary between the values of 25,95 to 47,64 volume percentage (5) (6) (7).

As the constituting elements are not perfectly spherical however, the pore space of sediments has to be determined empirically; it was found to vary between the values of 16 to 70 volume percentages[1]. And it is a remarkable fact that pore space-capacity of sedimentary strata increases with the diminution of their constituting elements.

The above holds for deposits situated relatively near to the surface; the question is now whether we may accept a similar conclusion for deposits situated at very great depths beneath the surface?

The overwhelming amounts of oil, water and gas met with in sedimentary strata at depths of 1000 meters and more, already seem to point towards such conclusion not being unlikely.

But we have more direct indications to go by in the ascertained pore space of Dakota sandstone (Cenomanian) and the Potsdam sandstone (Paleozoic).

The researches of F. H. King showed that, under their hydrostatic levels, the Dakota sandstone 15 to 38 and the considerably older Potsdam-sandstone contains 10 to 38 volume percentages of water[2]) (5).

The first mentioned deposit extends over an area of over 900,000 km²., the latter over an area of more than 350,000 km²., both with an average thickness of about 300 meters.

The former is covered in the Denver District by more recent deposits having a total thickness of 2000 m., the latter by a series

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great depths, is left undiscussed here; should we accept the possibility of it, the proportion of occluded water might be greater still.

[1]) loc. cit. (7) p. 127 and (5).

[2]) It is true that Newell found that a marble only contained 0,62⁰/₀ of water. But as a marble is not a sedimentary deposit but a modification of it, this percentage (as little as that of eruptive rocks) may not be taken as a basis for an appreciation of the amount of water which can be stored up in the pore-space of sedimentary strata, laid down in the G.S. The only conclusion we might perhaps be allowed to draw from it is, that as the percentage is yet considerable relatively, in spite of the intense metamorphism the deposit underwent since its deposition the original contents must have been much greater.

of more recent deposits, the total thickness of which amounts, for the paleozoic only, to over 12.000 m. in the Apallachian.

Here then we have an instance of well developed, similarly constituted sediments, deposited over vast areas, differing considerably in age and covered under layers of sediments, whose thickness amounts to 2000 m. and 12.000 m. and more.

Yet their pore-space was and is, very nearly identic, *and moreover coincides with that of similar sediments which both are recent and situated close to the surface.* (5).

On the ground of these facts, the conclusion does not seem unwarranted, that the pore space now proved to exist in these sandstones, was also present in them when they were still lying in the G.S. covered up by a powerful mass of more than 2000 m. and 12000 m. thickness.

It would not be difficult to increase the instances given above.

If it seems legitimate, on the ground of the above detailed facts to conclude that pore space in sedimentary rocks is existable at depths of more than 12.000 m., the recently published results of F. D. ADAMS's researches and L. F. KING's calculations proved that we may yet expect them to exist at far greater depths, *even when those pore spaces were not filled up by some liquid or gas imprisoned in them.*

Were these pore spaces filled with a liquid or gas, we might expect them to be still extant at depths where the temperature is so high, that under its influence the sediments would liquefy.

The question is now whether we may take it as probable, that the water originally occluded in these sedimentary deposits, will not have been expelled from there (by the tension of the vapour-converted water of underlying strata), long before those sediments could have reached the zone of liquefaction.

For should the water (vapour) still fill the pore-spaces, a sufficiently sound basis for explaining the origin and mechanism of volcanism were to be found, in the quantity of occluded water (vapour) and the high tensions acquired by it, under the influence of excessive high temperatures reigning in the magmatic zone.

The sedimentary rock would gradually pass into a plastic and liquid condition, during its downward course in the G. S.

And as the steep flank of the G. A. adjacent to the G. S. constitute a faulted and fissured region, the possibility might not be considered excluded that part of those vapour-tensions will discharge themselves into those fissures, thus creating the volcanic phenomenon at the surface of the earth.

Another possibility which we might conceive, would be that under the influence of these tensions the covering sedimentary masses in the G. S. were upheaved.

That might ultimately lead to the formation of overthrust planes (nappes de charriages), through a lateral bulging out of the raised up masses.

At last a local rupture through the enveloping strata might give birth to volcanic eruptions, which then might be sub-marine.

We might conceive the mechanism of volcanism in this way.

When by the action due to isostatic influences, a fissure or fault be engendered in the region of the steep flank of the G. A., or when in the raised up part of the G. S. a rupture should result from the high tensions prevailing there, the vapour tensions existing in the vicinity of such faults or fissures would discharge themselves entirely or partly in such fissure or fault.

Part of the plastic (or liquid) rock would be carried along, as water overcharged with carbon-dioxide is carried along by sudden and sufficient relief of pressure.

The subsidence of sedimentary deposits ever continuing, through accumulation of the products of erosion in the G. S., water (vapour-) charged sediments would ever and anon be conducted into the regions of excessive high temperatures; this might account for the periodicity of volcanism [1]).

Thus the appearance of volcanism might be expected in those regions of the earth, situated outside the G.S., which by some cause or other, are moving in centripetal direction or have lately done so.

Should on this basis a solution be offered for a certain amount of questions regarding the mechanism and origin of volcanism, the question still remains whether it may be considered plausible that the sea water imprisoned in the pore spaces of sedimentary strata, may be there still when these sediments have reached depths where liquefying temperatures are reigning.

The vapour tensions, it might be argued, there prevailing, must have expelled all the water once occluded in the pore space of these sediments, long before such deposits could have reached the vicinity of the regions of those high temperatures.

It is known however that the frictional resistance of liquids in capillary channels is considerable, being for a given flow, per unit

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[1]) I might be allowed to draw the attention to the fact that the absence of water in liquid state on the moon, and the absence of erosion, sedimentation and isostatic movements as a consequence of it, may perhaps stand in causal relation to the absence of periodicity of lunar volcanism, in contrast with terrestrial volcanism.

of time, in direct ratio to the length and in inverse ratio to the fourth power of the radius of the channel.

How considerable this resistance is in relatively porous rock, as e.g. the grès bigarré, is shown by A. Daubrée, in a note on his experiments about capillary attraction.

Daubrée draws attention to the fact that a thin disc of sandstone 2cm. thick, which completely shuts off a basin partly filled with water, is able to prevent water-vapour to escape (through the body of the rock) *even when the vapour has acquired a tension of several atmospheres.*

When now we take into consideration that the ratio of the diameters of capillary channels in sands and those in clays may be as from 1000 to 1, we shall be able to form an idea of the excessive resistances prevailling in finegrained sediments. (In inverse ratio to the fourth power of the radius).

Where moreover, the researches in folded areas have shown that the magnitudes of such fine-grained sedimentary (argiliceous-, impermeable-) strata may amount to hundreds and even thousands of meters in thickness, covering the total extent of the G.S., it does not seem unwarranted to pose the possibility of such impermeable strata preventing the water (vapour) occupying the capillary channels of the sedimentary deposits, from being expelled therefrom by the influence of the high temperatures and tensions engendered in those strata, on their way down to the zone of liquefaction.

This contribution purposes to point out a direction in which it might be considered possible to look for a satisfactory solution of the problem of the origin and the mechanism of volcanism.

(In the paper now in course of preparation, in collaboration with others, and which we hope to be able to publish in the Journal of Geology (Chicago, U.S.A.) before long, we intend to calculate the values of vapour-tensions at temperatures of 1000°—1200° C. in connection with the quantity of water supposed to be occluded in the sedimentary strata and their respective volumes; further to approximate the frictional resistance in sedimentary strata built up from clay and (or) sand, in order to approximate how thick a body of clay or sand should be, so that the frictional resistance (in its capillary channels) be sufficient to prevent the water occluded in the underlying sedimentary masses, to be expelled therefrom).

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Astronomy. — "*Observation of the moon during the Eclipse of the sun on Aug.* 21 1914 *and of the Transit of Mercury on Nov.* 7 1914, *made in the Leiden Observatory.* By J. Woltjer Jr. (Communicated by Prof. E. F. van de Sande Bakhuyzen).

(Communicated in the meeting of April 23, 1915).

1. Solar-eclipse of August 21, 1914.

During the eclipse of Aug. 21 1914, sun and moon passed over the meridian. At the suggestion of Professor E. F. van de Sande Bakhuyzen I have observed the declination of the south-limb of the moon with the transit-circle. The results of this observation including details concerning the method of reduction will be given here.

In order to obtain as large a number of pointings as possible Professor Bakhuyzen kindly undertook the reading of the microscopes (including those for the observation of the nadir).

The observed declination depends on the observation of the nadir. As two of the pointings had naturally to be made far outside the meridian, it was necessary to give special attention to the inclination and curvature of the horizontal wires. In 1911 an investigation on these points had been made; for this purpose a collimator provided with a level had been mounted on the south-pier; by means of one of the foot-screws the middle of the two horizontal wires of the collimator was pointed on various points of the horizontal wires of the meridian-telescope; by reading the level each time the inclination of the optical axis of the collimator becomes known and thus that of the line from the middle of the objective to the special point of the horizontal wire on which has been pointed.

The pointings were made on five different points of each wire, viz. on the centre and on two points on either side, one about halfway between the middle and the extreme vertical wire, and another just beyond the latter. In this manner the following corrections were deduced, to be applied to the declinations deduced from pointings at these points:

Clamp West	wire a:	$-0''.12$	$+0''.15$	$0''.00$	$-0''.11$	$-0''.33$
	wire b:	$-0''.67$	$0''.00$	$0''.00$	$+0''.04$	$-0''.08$

The points are given in order, starting from the side of the clamp.

The first and third pointing on the south-limb of the moon were made on wire a, the second on wire b. The following corrections to be applied to the zenith-distance were computed: $+0''.17$ $-0''.02$ $+0''41$.

On the ground of a number of nadir-determinations $6''.43$ was found as representing half the distance of the two horizontal wires. The refraction was calculated from tables in manuscript which are used in the observatory; these are based on BESSEL's constant and RADAU's theory. From observations made at the observatory it appears that this refraction has to be diminished by 0.2 %, and this correction has therefore been applied.

For the mean latitude of Leiden I have taken as the most probable value $52°9'19''.80$. The correction for the motion of the pole was deduced from the paper by ALBRECHT (A. N. 4749) for a moment 1.2 of a year prior to the eclipse; in this manner account was taken of the 14-monthly motion, but an error is introduced in the annual term. This error, however, seemed unimportant and in this way I found $\Delta\varphi = +0''.09$ 1) and therefore for the instantanious latitude $52°9'19''.89$; this value 2) was used in the reductions.

In order to pass from the observed declination of the limb to that of the centre of the moon I have taken into account the irregularities of the limb, which were very distinctly visible as the dark disc of the moon was projected on the bright disc of the sun. Using the profile given by HAYN (A. N. 4724) I have made a drawing of the part of the limb which was visible in the telescope and by the aid of notes, taken down during the observation, about the manner in which the pointings had been made, the corrections were estimated which had to be applied to the declinations as reduced with a mean radius of the moon; these corrections came to $-0''.70$, $-1''.90$,

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1) Dr. ZWIERS from a preliminary discussion of the latest results for the motion of the pole, in continuation of his paper in these Proceedings for 1911, finds $\Delta\varphi = +0''.14$ (however not including the z-term).

2) From the preliminary results of ALBRECHT (A. N. 4802) for the variation of latitude in the year 1914 I find $\Delta\varphi = +0''.20$ (*added June 1915*).

1″.90. For the mean radius the value $R = 932''.58$ was taken, which is the value adopted by Newcomb in his last great work on the motion of the moon, as it seemed to me that the radius to be used in occultations must be the same as the mean radius of the very sharp profile of the moon which projects itself on the bright disc of the sun.

In the computation of the parallax I have assumed $\frac{1}{298.2}$ for the ellipticity of the earth, both for the calculation of the reduction to geocentric latitude and of the radius-vector of the earth at the place of observation, and for deducing the constant of the sine-parallax. I therefore assumed for the constant 3422″.47 (Newcomb, Astr. Pap. IX 1 p. 44) and a correction of $+0''.40$ was applied to the N. A. value. The observations were made in the position of the instrument: Clamp-West and Circle A. was read; for the reduction of the declination so found to the mean of the two circles and the four positions of the instrument (objective and ocular-end can be interchanged and the instrument can be reversed) according to the investigations made in the observatory a correction of $+0''.11$ must be applied to the declination. Moreover for the reduction to Auwers's system a correction of $-0''.16$ has to be applied, for that to Newcomb's system one of $-0''.04$.

The observations and their reduction are given in the following table; the first column indicates whether or not a reversing prism was used; the second column contains the hour-angle, at which the observation was made; the third the mean of the four microscopes for the moon; the fourth the same for the nadir; the fifth the sum of the corrections for division-errors, run, reduction to the meridian, flexure of the instrument, irregularities of the limb, distance, inclination and curvature of the wires, the sixth the correction for refraction; the seventh the zenith-distance obtained in that manner and the eighth the geocentric declination of the centre of the moon.

	t	Limb	Nadir	Corr.	Refr.	Zenith-dist. limb	Declination centre
without pr.	−74 s	140° 17′ 57″28	0° 7′ 41″56	−8″02	47″15	39° 50′ 39″45	+13° 12′ 35″52
with pr.	+14	17′ 21″48	„	+4″42	47″16	51 2″82	12′ 12″45
without pr.	+91	17′ 14″50	„	−9″80	47″17	51 24″03	11′ 51″51

By reducing the first and the third declination to the moment of the second one we finally obtain: $\delta = +13°\ 12'\ 12''39$
12.45
11.80

The last pointing was made very near the end of the field and has therefore a smaller weight than the others. Taking the mean of the three with weights 1, 1, ½ we find: $\delta = +13^\circ 12' 12''30$; reducing to the mean of the two circles and the four positions of the instrument we get: $\delta = +13^\circ 12' 12''41$; finally we find for the declination

reduced to AUWERS's system: $\delta = +13^\circ\ 12'\ 12''25$
,, ,, NEWCOMB's ,, : $\delta = +13^\circ\ 12'\ 12''37$
Time of observ. $23^h 45^m 9^s 4$ M.T. Greenw.

A comparison with the Nautical Almanac gives:

Observ.— Calcul.: AUWERS's system: — 3″.58
NEWCOMB's ,, : — 3″.46.

II. TRANSIT OF MERCURY ON NOVEMBER 7 1914.

Using the great refractor of the observatory (aperture 266 mm.) I tried to observe the moments of inner and outer contact. At the first two contacts the sky was clouded over, so that only the last two could be observed. The power used was 170. As the moment of inner contact I took the breaking of the thread of light.

The times observed are

last inner contact: $2^h\ 6^m\ 24^s.8$ M.T. Greenwich
,, outer ,, : 2 8 43 ,, ,,

A comparison with the Nautical Almanac gives as the difference calculation minus observation:

last inner contact $+16^s.7$
,, outer ,, $+11^s$.

Leiden, April 1915.

Anatomy. — "*On the structure of the muscular abdominal wall of Primates.*" By W. A. MIJSBERG (Communicated by Prof. Dr. L. BOLK).

(Communicated in the meeting of April 23, 1915).

In the publications relating to the myology of Primates, the muscles of the abdomen are usually discussed very superficially, and where that discussion is a more elaborate one, that greater elaboration is as a rule restricted to an excessively accurate description of the origins of these muscles. Less attention however is paid to the way in which these muscles contribute to the formation of the sheath of the M. rectus; no publication is even known to me, in which something is communicated about the comparative anatomy of the rectal sheath of Primates. This subject however deserves greater attention, as from a few stray communications it appears, that the structure of the sheath of the different species of Primates can show rather considerable differences.

I shall communicate here shortly the results of an investigation into the comparative anatomy of the sheath of the rectus muscle made by me in the Anatomical Laboratory of Amsterdam. In this communication I shall leave Prosimiae entirely out of consideration, and consequently restrict myself to Simiae (Platyrrhini and Katarrhini) and Hominidae.

On the Membrana abdominis intermedia.

As the first result of my investigation I can communicate, that with all monkeys examined by me, both Katarrhini and Platyrrhini, a fourth element participates in the formation of the sheath of the M. rectus, besides the three flat muscles of the abdomen. Between the M. obliquus externus abdominis and the M. obliquus internus abdominis a fascial membrane is namely found. This membrane is solid, admits of a good free preparation, consequently it distinguishes itself obviously from the flimsy connective tissue, which is found in man between the flat muscles of the abdomen. In the literature this membrane is not mentioned; I shall designate it as *Membrana abdominis intermedia*. The anatomical lines of demarcation of this membrane can distinctly be indicated. In the caudal part the origin is immediately connected with that of the M. obliq. int.: the membrana interm. is attached to the fascia lumbodorsalis, crista iliaca, spina iliaca anterior and follows also in a caudal direction the origo of the M. obliq. int., so that — with a powerful development of the membrane — its last fibres are attached to the ramus superior ossis pubis. Sometimes however it cannot be followed as far as the origins indicated here; in these cases it is closely connected with the M. obliq. int., because it originates in the perimysium externum of the latter at some distance from the origo of that muscle. In the cranial part the origin of the membrane cannot be indicated so exactly: it is namely continued between the M. obliq. ext. and the thoracal wall, and looses itself in the flimsy connective tissue that is found here. An origin from ribs can consequently not be ascertained.

In a median direction the membrane passes into the sheath of the M. rectus in the forming of which it takes part with the three flat muscles of the abdomen.

What is now the signification that must be attributed to this membrane occurring so constantly in monkeys?

One might be inclined to regard the membrane as a condensation of the intermuscular connective tissue; for likewise in man one often sees that from the flimsy connective tissue between the abdominal muscles fascial membranes can develop to increase the solidity of the abdominal wall. There are however objections that tell against this view: in the first place it cannot be explained in this way, why in many Simiae such a membrane does exist between the M. obliq. ext. and the M. obliq. int., but no vestige of fascial tissue between M. obliq. int. and M. transv. is to be found; secondly it cannot be comprehended in this way, why the membrane possesses such distinct anatomical lines of demarcation; thirdly the great independence that this membrane possesses tells against this view. With most Platyrrhini e. g. the membrane runs in the cranial part behind the M. rectus, in the caudal part in front of it; it changes consequently its course with regard to this muscle and moreover independently of the abdominal muscles between which it is situated.

From these objections appears distinctly, that the membrane may by no means be regarded as a simple local condensation of intermuscular connective tissue. Most admissible it is to consider it as a rudiment of a muscle that has existed on this spot with lower vertebrates. With this hypothesis all the properties of the membrane — as its sharp anatomical lines of demarcation, its independence — can easily be explained. The correctness of this view is moreover proved by a discovery with Siamang. With a Siamanga syndactylus I found namely muscular fibres running in the membrane; these muscular fibres form a bundle of 8 mm. wide and 4.5 cm. long, which bundle is situated between the point of the last rib and the crista iliaca. The fibres do however not originate in the rib, but about $^3/_4$ cm. caudally from the point of the last rib the muscular fibres appear in the membrane. The fibres run almost vertically downward, their direction corresponds with that of the fibres of the M. obliq. ext. The fibres are inserted into the crista iliaca, a little behind the spina iliaca anterior. The muscle possesses moreover still a smaller head, arising from the fascia lumbodorsalis.

As now, in the direction of the ventral medianline, the membr. interm. is directly connected with this muscle, and as moreover the origin of the muscular fibres is not situated at the last rib, but the fibres appear in the membrane at a little distance caudally from the rib, it is clear that this muscle with Siamang is the last remaining part of a muscle which, with phylogenetically older forms, was situated on the spot of the membrane. Indeed we know, that with Urodele Amphibia and with Reptilia the abdominal wall is composed of more muscles than with Primates. The ontogeny and phylogeny of the abdominal muscles of lower Vertebrates (Pisces, Amphibia, Reptilia) has been accurately explained to us by the investigations of MAURER[1]). It is especially the structure of the muscular abdominal wall of the Urodele Amphibia that is of great interest for us; the abdominal muscles of Pisces still show very simple conditions, whilst the conditions of the abdominal muscles of Anure Amphibia and Reptilia can very well be deduced from those of Urodeles.

Urodele Amphibia possess four collateral abdominal muscles. Most superficially are situated two muscles, the fibres of which have an obliquely descending direction: a M. obliq. ext. superficialis and a M. obliq. ext. profundus. The direction of the fibres of these muscles differs little; that of the deep muscle is somewhat less oblique. Under the Musculi obliq. ext. one finds a M. obliq. int. with an obliquely ascending direction of the fibres, and abdominally from it lies the M. transversus, the fibres of which run in a transversal direction. MAURER distinguishes these muscles in primary and secondary ones. The primary muscles: M. obliq. int., M. obliq. ext. prof. and M. rectus profundus occur with the larva; the secondary ones: M. obliq. ext. superfic., M. transv. and M. rectus superficialis come into existence at the end of the larva-life by delamination of the younger cells at the surface of the primary muscles. From the development it is obvious, that the M. obliq. int. and the M. obliq. ext. prof. are dorsally connected with each other in the myotome and can never extend beyond the line of demarcation between the ventral and the dorsal musculature, the lateral line; ventrally both muscles are connected in the M. rectus profundus. The direction of their fibres changes here gradually from an oblique one into the longitudinal one of the M. rectus prof. The M. obliq. ext. superf. and the M. transv. however can extend dorsally from the lateral line, and from the beginning they possess an aponeurosis which runs before, resp. behind, the system of the Musculi recti to the linea alba.

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[1]) F. MAURER, Der Aufbau und die Entwicklung der ventralen Rumpfmuskulatur bei den urodelen Amphibien und deren Beziehung zu den gleichen Muskeln der Selachier und Teleostier. Morph. Jahrb. 18 Bd. 1892.

F. MAURER. Die ventrale Rumpfmuskulatur der anuren Amphibien. Morph. Jahrb. 22 Bd. 1894.

F. MAURER. Die ventrale Rumpfmuskulatur einiger Reptilien, eine vergleichend-anatomische Untersuchung. Festschrift zum 70 Geburtstage von CARL GEGENBAUR, 1896.

Which are now the homologies between the abdominal muscles of Primates and those of lower Vertebrates? That the M. transv. and the M. obliq. int. of man are homologous with the homonymous muscles of Urodela is obvious, on account of the corresponding direction of the fibres and the corresponding direction of the intercostal nerve between the two muscles. There are however different views concerning the M. obliq. ext. GEGENBAUR reckons this muscle together with the Musculi intercostales externi to the layer of the M. obliq. ext. prof. of Urodeles; in this case the M. obliq. ext. superf. of Urodeles could be found back in the Musculi serrati postici of man. According to EISLER [1]) the M. obliq. ext. and the Musculi serrati postici belong to the layer of the M. obliq. ext. superficialis; the M. obliq. ext. prof. of Urodeles is to be found back in the Musculi intercostales externi and the "tiefe Zacken des M. obliq. ext. abdominis". By these EISLER understands small bundles of muscles, which, as he communicates, occur frequently under the cranial origins of the M. obliq. ext. of man. They originate likewise from the ribs, are separated by some connective tissue from the M. obliq. ext. lying superficially from them, have an almost transversal direction and lose themselves at last in the anterior lamella of the sheath of the M. rectus.

The anatomy of the ventral trunkmusculature of man however cannot give us certainty with regard to the origin of the M. obliq. ext. As, however, with other Primates between this muscle and the M. obliq. int. a membrane occurs that can be conceived as the remaining part of an abdominal muscle, the situation becomes clearer. Superficially from the M. obliq. int. we find first a muscle reduced to a membrane and then a well developed muscle entirely independent of each other; it is thus without more obvious, that the more superficial one of these two layers must be homologous with the M. obliq. ext. superfic., the deeper one with the M. obliq. ext. prof. of Urodeles. Consequently the M. obliq. ext. of Primates is homologous with the M. obliq. ext. superfic., whilst the Membrana abdominis intermedia is the homologon of the Musculus obliq. ext. profundus of Urodeles.

The direction of the fibres of the M. obliq. ext. prof. of Urodeles differs little from that of the M. obliq. ext. superfic. The abdominal muscle, which with ancestral forms of Primates was found in the place of the Membrana intermedia, will also in all probability, with, regard to the direction of its fibres, have corresponded with the M. obliq. ext. (superficialis!) of Primates.

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[1]) P. EISLER. Die Muskeln des Stammes. Jena 1912.

In accordance with this is the fact, that the fibres of the "M. obliq. ext. prof." — for this name should be applied to the muscle — found by me with Siamang show a direction that is almost parallel with that of the fibres of the M. obliq. ext.

Further I will still remark in this connection, that according to Testut [1]) and Le Double [2]) several investigators have described by different names, and especially by that of "M rectus lateralis" as variations muscles of man, situated between the Musculi obliq. externus and internus and corresponding in the direction of their fibres with the M. obliq. ext. In the most typical cases this "M. rectus lateralis" originates from the 9th to the 11th rib, runs then almost vertically downwards and is inserted into the crista iliaca. It is obvious that we have to do here with the remaining part of the M. obliq. ext. prof., occurring as atavism, which muscle normally has been entirely reduced in man, whilst not even a membrane has remained. The variation has been described by the name of M. rectus lateralis. This name, though with regard to the direction of the fibres very correct, is however not preferable, as it could give rise to the entirely wrong notion, that this muscle is connected in some way or other with the M. rectus abdominis. In fact the two have nothing to do with each other. Consequently we had better call this variation M. obliq. ext. profundus, a name to which, as comparative anatomy teaches us, it has an indisputable right.

In conclusion be remarked that, in accordance with Eisler, I think it likely, that the deep origins of the M. obliq. ext. (vide before) described by him, can also be considered as remaining parts of the M. obliq. ext. prof.

It still remains to trace the relation the Membr. abdominis intermedia bears to the M. rectus: the membrane namely, as I communicated already takes part in the formation of the sheath of the M. rectus. With the description of the structure of the sheath of the different monkeys the relation of the membrane to the M. rectus will consequently likewise be discussed.

On the structure of the sheath of the M. rectus of Primates.

The relations the four elements, that compose the rectal sheath, bear to the M. rectus with the different monkeys will be briefly

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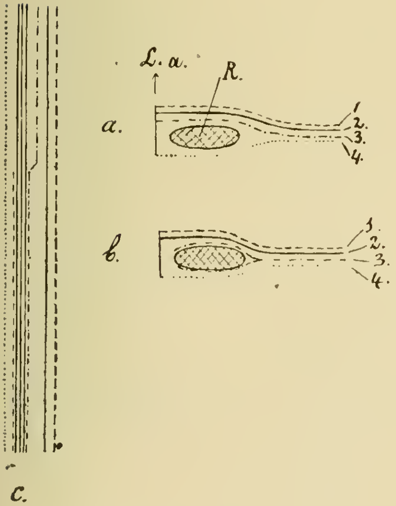
[1]) L. Testut. Les anomalies musculaires chez l'homme, expliquées par l'anatomie comparée, leur importance en anthropologie. Paris. 1884.

[2]) A. F. Le Double. Traité des variations du système musculair de l'homme et leur signification au point de vue de l'anthropologie zoologique. Paris. 1897.

described with the help of text-figures, representing diagrammatic transversal sections through the sheath. In all sections the M. obliq. ext. is represented by a dotted line, the Membrana abdominis intermedia by a point-dash-line, the M. obliq. int. by an uninterrupted line, and the M. transversus by a dash-line.

The structure of the rectal sheath of Primates shows considerable differences. It is however possible to unite all those cases under one point of view; it will appear that in this way a more primitive condition and relations that have removed from the original condition, can be distinguished. The succession in which the rectal sheath of the different Primates will be described is such, that I shall begin with a condition of which afterwards it will appear, that it is the most original one, and conclude with the description of the structure of the sheath of such monkeys, which have farthest removed from the primitive condition.

Fig. 1*a* represents a transversal section through the sheath of the M. rectus of *Ateles paniscus*, close under the caudal edge of the



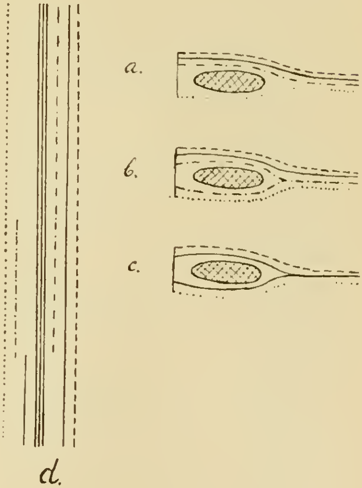


Fig. 1. Ateles paniscus.

Fig. 2. Ateles hypoxanthus.

L. a. = Linea alba.
R. = Musc. rectus abdominis.
1. = M. transversus abdominis.
2. = M. obliquus internus abdom.
3. = Membrana abdominis intermedia.
4. = M. obliquus externus abdom.

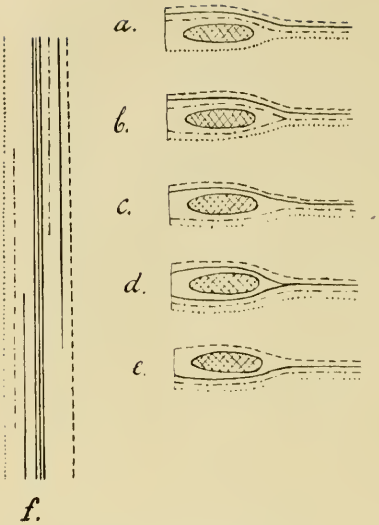


Fig. 3. Cebus capucinus.
(Scheme of Platyrrhini).

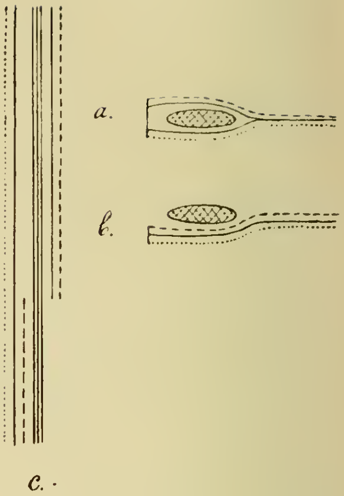


Fig. 4. Homo.

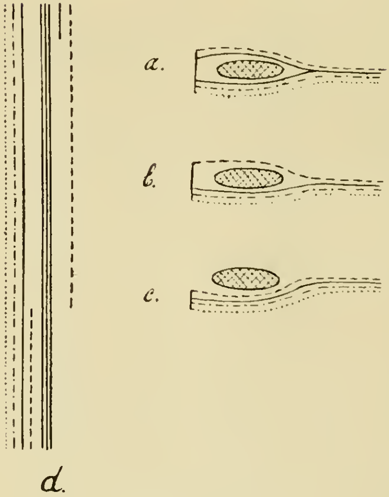


Fig. 5. Cercopithecus cynosurus.

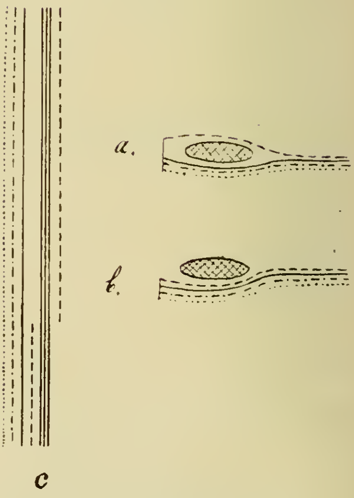


Fig. 6. Semnopithecus entellus.
(Scheme of Katarrhini).

sternum. The M. obliq. ext. (4) passes in front of the M. rectus, the Membr. interm. (3), the M. obliq. int. (2) and the M. transv. (1) form the posterior lamella of the sheath. These relations exist however only in the cranial $^3/_8$ part of the sheath; in the caudal part the M. obliq. ext. remains before the M. rectus, the M. obliq. int. and the M. transv. behind it, but the Membr. interm. passes at the lateral edge of the M. rectus into the perimysium externum of this muscle, (fig. 1*b*). These relations continue to exist till the symphysis. (Compare the sagittal section, fig. 1*c*).

With an *Ateles hypoxanthus* examined by me the relation of the M. obl. int. and Membr. intermedia to the M. rectus was different from that with *Ateles paniscus*. The M. obliq. ext. passes entirely before, the M. transv. entirely behind the M. rectus; the relations the Membr. interm. and the M. obliq. int. bear to the M. rectus are however not the same in all the parts of their course; in the cranial part both run behind the M. rectus (fig. 2*a*). About 6 cm. caudally from the inferior edge of the sternum (the total distance sternum-symphysis amounts to 12 cm.) the membrane splits into two layers one of which is passing before, the other behind the M. rectus. The M. obliq. int. continues to send its aponeurosis into the posterior lamella of the sheath (fig. 2*b*). $2^1/_2$ cm. cranially from the symphysis the two layers of the membrane terminate almost simultaneously; at the same time the M. obliq. int. changes its relation to the M. rectus: from here its aponeurosis divides itself into two layers, which include the M. rectus (vide fig. 2*c*). Fig. 2*d* gives an illustration of these different anatomical relations.

The third fig. relates to the rectal sheath of *Cebus Capucinus*. The M. obliq. ext. passes entirely before, the M. transv. entirely behind the M. rectus. The Membr. interm. passes in the cranial part, just like the M. obliq. int., behind the M. rectus (fig. 3*a*); in a caudal direction it splits into two layers, enclosing the M. rectus, the M. obliq. int. does provisionally not change its relation to the M. rectus (fig. 3*b*). Then the dorsal layer of the membrane disappears and thereupon the membrane passes entirely into the anterior lamella of the sheath (fig. 3*c*). A little farther caudally the aponeurosis of the M. obliq. int. splits into two layers (fig. 3*d*); then the deep layer disappears, so that in the caudal part the posterior lamella of the rectal sheath consists only of the aponeurosis of the M. transversus, whilst the other three elements pass in front of the M. rectus (fig. 3*e* and 3*f*).

With the condition of the rectal sheath found with *Cebus capucinus*, corresponds the structure of the sheath of all other

Platyrrhini (Mycetes niger, Chrysothrix sciurea and Hapale).

In fig. 4 are represented sections through the sheath of the M. rectus of *Man*. The M. obliq. ext. passes entirely in front of the M. rectus, the Membr. interm. fails. Cranially from the linea Douglasii the M. obliq. int. possesses two layers, and the M. transv. extends behind the M. rectus (fig. 4*a*), caudally from the linea semicircularis the aponeuroses of the three flat muscles of the abdomen are situated on the anterior surface of the M. rectus (fig. 4*b* and 4*c*).

The 5th figure relates to the sheath of a *Cercopithecus cynosurus*. As appears from the sections, the M. obliq. ext. and the membr. interm. pass entirely in front of the M. rectus, the M. obliq. int. which runs also before the M. rectus, possesses moreover in its most cranial part for a short distance a layer which passes behind the M. rectus (fig. 5*a*); soon however this layer ceases (fig. 5*b*). The M. transversus, which in the cranial part extends behind the M. rectus, sends in the caudal third part its aponeurosis likewise before the M. rectus (fig. 5*c* and 5*d*).

Figure 6 relates to the vagina M. recti of *Semnopithecus entellus*. The M. obliq. ext., the Membr. interm. and the M. obliq. int. pass entirely in front of the M. rectus. The M. transv. however runs in the cranial $^3/_4$ part of the sheath behind the M. rectus (fig. 6*a*), in the caudal 4th part its aponeurosis takes part in the forming of the anterior lamella of the sheath (fig. 6*b* and 6*c*). A condition of the vagina M. recti as represented in fig. 6, can be admitted as normal for *Katarrhini*; I found it with Cercopithecus patas, Macacus cynomolgus, Colobus gueresa, Semnopithecus entellus, Cynocephalus hamadryas, Siamanga syndactylus, Orang utan.

From this short description it appears that monkeys show great differences with regard to the composition of their rectal sheath, differences of such importance, that it seems in the beginning difficult to see a connection between all the conditions that present themselves. It will consequently be our task to try and find such a connection founded on the evidences given above. With this purpose we shall trace of each of the four elements that take part in the forming of the sheath separately how the relation is it bears to the M. rectus with the different Primates.

With Platyrrhini the *M. transversus* passes entirely into the posterior wall of the sheath, with Katarrhini and with man this condition exists only in the cranial part; in the caudal third or fourth parts the M. transv. takes part in the forming of the anterior wall of the sheath; with a Macacus rhesus I dissected, the aponeurosis possessed at this passage for a short distance two layers, with the other Katarrhini and with man the M. transv. suddenly, with an acute line, modifies its course behind the M. rectus into a course in front of the latter.

The condition of the M. transversus, as it shows itself with Katarrhini and with man, is certainly not a primary one. The anatomy of the sheath of the M. rectus of Amphibia and Reptilia teaches us that there the M. transv. runs entirely behind the M. rectus, and the ontogeny of the abdominal musculature of Urodeles shows us that this condition is the primary one. As now moreover with all Platyrrhini the M. transv. passes behind the M. rectus, there can no longer exist any doubt; decidedly the relation which with Katarrhini and with man the M. transversus bears to the M. rectus is a secondary one. With ancestral forms of monkeys of the old world and of man the M. transversus ran behind the M. rectus, as it does still with Platyrrhini. In the phylogenetical development of these groups of Primates an influence has been at work, in consequence of which the M. rectus pierces in the caudal part the M. transv., so that the latter muscle in the caudal part is found on the anterior surface of the M. rectus.

With most Katarrhini the M. transv. modifies its relation to the M. rectus suddenly, in an acute line; with Macacus rhesus the aponeurosis of the M. transv. possessed at the modification of its direction for a short distance two layers, i.e. the M. rectus does not pierce the M. transversus here abruptly, at right angles, but gradually, so that the M. rectus is situated for a short distance in the mass of the M. transversus.

The relation of the *M. obliquus internus* to the M. rectus shows with the different monkeys also great differences. With Katarrhini the M. obliq. int. runs entirely before the M. rectus; with Ateles paniscus on the contrary entirely behind that muscle. With all Platyrrhini, with the exception of Ateles paniscus, with man and also with a Cercopithecus cynosurus I examined, we find conditions in which the relation of the internus aponeurosis to the M. rectus is quite different in the cranial part from that in the caudal one. With the majority of Platyrrhini we find that the internus apeunorosis runs in the cranial part behind the M. rectus, and in the caudal part before the M. rectus; consequently the M. rectus pierces the M. obliq. int.; usually the piercing takes place gradually at an acute angle, so that the internus aponeurosis possesses for a short distance two layers. With Ateles hypoxanthus the aponeurosis runs in the cranial part behind the M. rectus and includes in the caudal part this muscle with two layers; with man and with Cercopithecus cynosurus on the contrary the M. obliq. int. shows in the cranial part two layers, and passes caudally entirely into the anterior wall of the Vagina M. recti.

In the relation the M. obliq. int. bears to the M. rectus consequently three types can be distinguished: the M. obliq. int. runs either entirely behind the M. rectus, or passes entirely into the anterior lamella of the sheath, or behaves differently, with regard to the M. rectus, in the cranial part than in the caudal part; now the question rises which of these conditions is the original one. It is self-evident, that the condition of the M. obliq. int. in which the relation to the M. rectus in the cranial part is so quite different from that in the caudal part will not have existed with the ancestral forms of Primates. With these doubtless the relation of the M. obliq. int. to the M. rectus will have answered to one of the two other types; consequently the M. obliq. int. has originally taken part either in the forming of the anterior or in that of the posterior lamella of the sheath of the M. rectus.

As we are compelled to admit with regard to the M. transversus, that this muscle was pierced in the course of the phylogeny by the M. rectus, it is a priori very likely that the piercing of the M. obliq. int. will depend upon the same cause that also brings about the modification in the course of the M. transv. From this simple consideration results the conclusion that originally the M. obliq. int. passed presumably behind the M. rectus.

Comparative anatomy can likewise support our view, that originally with Primates the M. obliq. int. is situated behind the M. rectus. If namely we consider the relation of this muscle to the M. rectus with different Vertebrates (Maurer) we find that with Urodeles the M. obliq. int. passes continuously into the M. rectus, with Anures this muscle exists only in the larva, with Reptiles, however, we find, that, where a M. obliq. int. exists as such, it has disengaged itself from the system of the Musculi recti and possesses an aponeurosis, that runs behind the M. rectus abdominis.

The *Membrana abdominis intermedia* with all Katarrhini takes part in the forming of the anterior lamella of the sheath; this cannot be otherwise, as both the M. obliq. ext. and the M. obliq. int. pass in front of the M. rectus. In case, however, as with Platyrrhini, the M. obliq. int. in the cranial part lies behind the M. rectus, the membrane also lies in the cranial part behind it. In the caudal part we find nowhere the membrane behind the M. rectus: with Ateles paniscus it is connected at the lateral edge with the perimysium externum of this muscle, with the other Platyrrhini it runs in the caudal part in front of the M. rectus.

Again the question rises what the original relation of the membrane to the M. rectus was. As in secondary situations of the Musculi obliq. int. and transversus the membrane is found in front of the M. rectus, and in the primary condition on the contrary, the membrane, — in the cranial part at least — passes behind the M. rectus, we may suppose, that, most likely, the Membr. abdominis intermedia was originally situated behind the M. rectus. This view is strengthened by considerations of the same nature as those, which we communicated regarding the M. obliq. int.; only the comparative anatomical argument cannot be applied here.

With all examined Primates the *M. obliquus externus* passes in front of the M. rectus.

The four elements that compose the sheath of the M. rectus will have taken part in the forming of the sheath, as ancestral forms of the now living Simiae and of man possessed, in such a way that the M. obliq. ext. passed in front of the M. rectus, whilst the three other elements formed the posterior lamella of the sheath.

In the phylogenetical development, however, an influence appeared, which brought about a variation in this structure, in consequence of which the M. rectus began to show an inclination to pierce the three elements lying behind it. This piercing begins in the caudal part. The first modification that occurs, consists in the fact, that the Membr. intermedia changes the relation it bears to the M. rectus and is found to be situated in the caudal part in front of the M. rectus. Whilst the piercing-process in the membrane is continuing, the M. obliq. int. in the caudal part begins to modify its direction with regard to the M. rectus.

When then the caudal part of the M. rectus has taken its place between the Musculi obliq. and transv., the piercing-process can begin to extend itself also over the M. transversus. The modification of direction of the latter is always restricted to the caudal part, the piercing of the Membr. interm. and of the M. obliq. int. by the M. rectus can however become a complete one, i. e. the piercing can go so far, that in the end both elements are situated entirely in front of the M. rectus.

In the phylogenetical development which has taken place in the different genera of Primates, the factor, that modified the topography of the flat abdominal muscles with regard to the M. rectus, made itself felt in varying degrees, so that the Primates that live at the present moment, find themselves in all sorts of phases of transformation.

The original condition of Membr. interm., M. obliq. int. and M. transv. has least changed with Ateles paniscus. With this monkey the M. transv. and the M. obliq. int. still show their original relation to the M. rectus; the Membr. interm. lies in the cranial part also behind the M. rectus, passes then, however, into the perimysium externum of that muscle. This relation must be regarded as a condition, in which the M. rectus is situated in the mass of the membrane, in other words: there exists here a beginning piercing of the membrane by the M. rectus. With the other Platyrrhini the piercing process has gone further than with Ateles paniscus, and the membrane lies then in the caudal part before the M. rectus. At the same time the piercing-process has with them extended over the M. obliq. int.; the M. transversus, however, passes still entirely behind the M. rectus.

The monkeys of the old world have removed farthest from the original condition of the structure of their sheath: with them the piercing of the Membr. interm. and of the M. obliq. int. is complete, whilst the M. transv. in the caudal part also modifies its direction with regard to the M. rectus. The structure of the sheath of the M. rectus of man forms the connecting link between those of Platyrrhini and Katarrhini. This vagina is less original than that of Platyrrhini, as in man the piercing-process extends also over the M. transversus, but because the piercing of the M. obliq. int. by the M. rectus is not yet complete, the sheath of man is at the same time more original than that of Katarrhini.

The linea semicircularis Douglasii is the line along which the transversus aponeurosis modifies its direction with regard to the M. rectus; it is formed by the last fibres of the M. transversus, which proceed behind the M. rectus towards the linea alba (with man the last fibres of the posterior layer of the aponeurosis of the M. obliq. int. take moreover part in the formation of the linea). The possession of a linea Douglasii does consequently mean, that the piercing-process that takes place in the sheath of the M. rectus, has advanced so much, that also the M. transversus is pierced in the caudal part by the M. rectus. By this explanation a new light is thrown on the dark question about the signification of the linea, a question, that, notwithstanding the different hypotheses that have been suggested, in order to explain this phenomenon in the posterior lamella of the rectal sheath, has not yet found a satisfactory solution. We need by no means be astonished at this fact, as, indeed, all investigators, who have hitherto occupied themselves with this question, have regarded the formation of the linea Douglasii as an independent process, because they were not acquainted with the considerations communicated above, from which appears that the formation of the linea is but part of a more comprehensive process, which takes place in the rectal sheath.

Among the different theories that have been suggested about the signification of the linea Douglasii, that of GEGENBAUR has become most generally known. His hypothesis, in which the views of RETZIUS and HENLE are united, makes the Vesica urinaria and the Vasa epigastrica inferiora responsible for the occurrence of the linea Douglasii.

Objections have been made against this theory and against those of DOUGLAS and of SOLGER, from which objections we must conclude that these hypotheses are incorrect. Only the theory of EISLER[1]), which is supported by the results of ontogeny and comparative anatomy, stands unattacked at the present moment. EISLER seeks the cause of the formation of the linea in the protuberation of the anterior abdominal wall, indicated as processus vaginalis, because this processus compels the fibres of the Musculi obliq. int. and transversus, which run cranially from the processus behind the M. rectus to give way ventralwards there, where the processus is, and to remove before the M. rectus.

It is obvious that the hypothesis of EISLER cannot be correct, for it tries likewise only to find a cause for the piercing of the M. transversus by the M. rectus; like all other theories previously suggested, it regards the formation of the linea Douglasii as an independent process, whilst it must only be regarded as the last phase of the piercing process that takes place in the rectal sheath.

It is consequently completely irrational to indicate for the formation of the linea Douglasii a cause that does not explain at the same time the other modifications occurring in the construction of the sheath. The question about the cause of the linea semicircularis must be replaced by the question about the inclination of the M. rectus to pierce the three elements, that originally formed the posterior lamella of the sheath of the M. rectus. Further investigations will perhaps give an answer to this question; for the present moment only the fact of the piercing can be ascertained.

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[1]) In P. EISLER. "Ueber die nächste Ursache der Linea semicircularis Douglasii Verhandl. der Anat. Gesellschaft 1898" one finds described all the theories about the cause of the linea, indicated here.

Physiology. — "*On the heart-rhythm.*" III. By Dr. S. de Boer.
(Communicated by Prof. J. K. A. Wertheim Salomonson).

(Communicated in the meeting of April 23, 1915.)

On the components of the a-v-interval.

In the estimation of the disturbances of the rhythmic functions of the heart the *a-v*-interval plays a comparatively important part. It is consequently of great interest to know exactly by what factors the duration of this interval is determined. When determining this interval, we measure the time that elapses between the beginning of the auricle-systole and the beginning of the next following systole of the ventricle. What we determine in this way is consequently not only the time of transmission of the stimulus from the place of entrance into the auricle till the time of entrance into the ventricle; for it is obvious that, in our determination, we have not left out of account the time that the stimulus has required to exert influence upon the ventricle, i.e. the time of the latent stimulation. If now we make our estimation by means of mechanical curves, then the latter amount is rather important, but with electrograms this latent time exists likewise.

It is now my intention to represent this with some curves.

In Fig. I we see two rows of curves of a suspended frog's heart; the rhythm of auricle and ventricle is halved. A stimulator is applied to the basis ventriculi by which we administer at the end of the diastole an extra-stimulus (the closing strokes at which the signal goes down are prevented, the opening strokes — motion of the signal upwards — reach the ventricle). The first stimulus of the upper row of curves falls in the refractory period. The second opening stroke, which takes place later in the heart-period occasions an extra-systole with a rather long latent period. After this extra-systole follows the auricle-systole of the normal rhythm, the *a-v*-interval between this auricle-systole, and the then following systole of the ventricle is almost twice as long as the *a-v*-interval of the normal rhythm. **It is obvious, that the cause thereof is to be found in the decreased irritability of the ventricle-musculature by the shortening of the preceding pause, the stimulus coming from the auricle requires more time to exert influence upon the ventricle.**

In the second row of this figure we see a repetition of this phenomenon with the same result for a stimulus occurring a little earlier. We see here, at the same time, that the latent time after an extra-stimulus is the longer in proportion as the stimulus takes place earlier in the heart-period. This figure illustrates likewise distinctly how the extent of the systole depends upon the metabolic

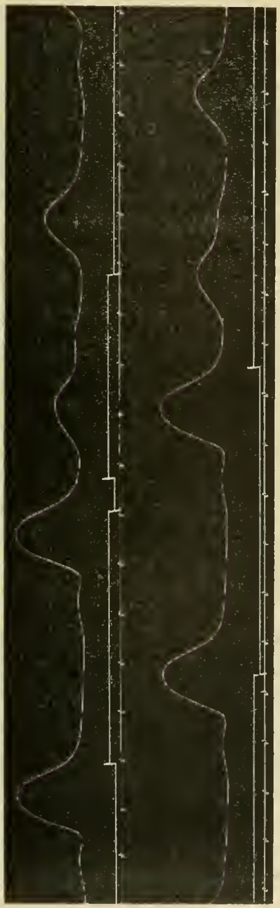

Fig. 1.

Two rows of curves of a frog's heart poisoned with veratrine after halving of auricle- and ventricle rhythm. The first opening induction-stroke on the basisventriculi (motion of the signal upward) takes place in the refractory period The 2nd opening-stimulus, which takes place later in the heart-period, gives an extra-systole. The then following auricle systole of the normal rhythm is followed with a *lengthened a v-interval* by a ventricle-systole. In the 2nd row repetition of this experiment with the same result. The closing-stimula (motion of the signal downward) are prevented. Time 1 sec.

condition of the heart-musculature. I found this fact everywhere confirmed in my frog's hearts poisoned with veratrine.

By a second observation of my frog's hearts poisoned with veratrine, it is shown, that the duration of the *a-v*-interval in unchanged metabolic condition of the ventricle-muscle can depend upon the condition of the transmission-systems from the point of beginning in the auricle to that of the ventricle. If namely first the ventricle-rhythm has been halved and afterwards the rhythm of the auricle, then I saw after the latter halving the *a-v*-interval considerably reduced.

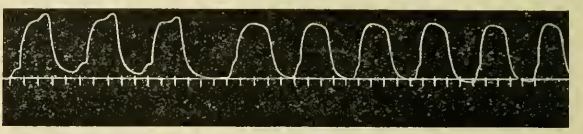

Fig. 2.

Halving of the ventricle-rhythm during the first 3 systoles, whilst the rhythm of the auricle is still normal. Thereupon the rhythm of the auricle halves likewise. The *a-v*-interval is then considerably shortened.

As an example we cite as follows: In Fig. 2 we see a row of curves of a suspended frog's heart, represented 40 min. after the injection of 10 drops of acetas veratrini into the abdominal cavity. During the first three systoles the rhythm of the ventricle is halved, whilst the auricle-rhythm is still undisturbed. After this the following auricle-systole falls out, so that on each then succeeding ventricle-systole an auricle-systole appears. It is remarkable how considerably the *a-v*-interval is now shortened. Apart from the influence of the hiatus, that during some succeeding systoles can improve the metabolic condition of the heart-muscle, the condition of the ventricle-musculature remains unaltered, for the ventricle continues to pulsate in the same rhythm. The condition however of the track of the transmission of stimula from the point of beginning in the auricle to that in the ventricle has changed.

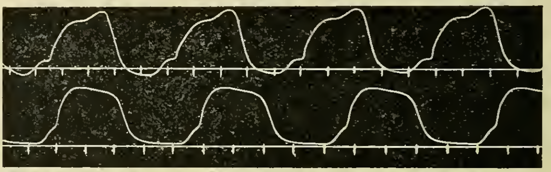

Fig. 3.

The lower row of curves was represented 5 minutes after the row of curves of fig. 2 with greater rapidity of the drum. The *a-v*-interval is still considerably shortened. The upper row of curves was represented 10 min. before that of fig. 2. Time 1 sec.

Formerly the stimulus was twice transmitted during one ventricle-systole along this track, now only once; formerly on each ventricle-systole two auricle-systoles occurred, now only one. [1])

That the hiatus, caused by the falling out of one auricle-systole is indeed not the cause of the shortening of the *a-v*-interval is proved by the further progress of the curves. Thus we see in the lower row of curves of Fig. 3, which is represented 5 minutes after that of the former figure, the *a-v*-interval still constantly shortened. The upper-row of curves of Fig. 3 was registered 10 min. before that of Fig. 2. We must pay attention to the fact that, when noting down the curves of Fig. 3, the rotations of the drum were quicker, and for the lower row again quicker than for the upper row; consequently the curves are drawn out more in width.

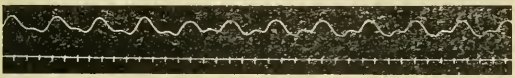

Fig. 4.

During the first 4 systoles halving of the ventricle-rhythm. Thereupon the rhythm of the auricle halves likewise. The first auricle-systole that falls out ought to have stood on the 5th ventricle systole. This is the cause that there occurs no hiatus. The *a-v*-interval after it is shortened. The curves show the falling out of every 2nd auricle-systole as the tops of the ventricle-curves become rounder.

We see in Fig. 4 another example. Half an hour after the injection of 8 drops of 1 °/₀ acetas veratrini the ventricle-rhythm of this frog's heart was halved, half an hour later when a few times variations of the ventricle-rhythm had taken place, the rhythm of the auricle halves. The first auricle-systole falls out on the top of the fifth ventricle-systole of the figure. The acute ventricle-top becomes by the falling out of the auricle-systole, that stood on its top, obtuse and rounded off (by looking at the heart I have also observed that afterwards on each auricle- one ventricle-systole occurred). Because the first auricle-systole, which falls out, ought to have come on the top of the ventricle-curve no hiatus occurs now. The shortening of the *a-v*-interval is also here obvious. By exact measurement we see, that after the halving of the auricle-rhythm

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[1]) The stage of the latent irritation of the auricle will certainly be shortened, but we may safely admit, that this has no influence on the *a-v*-interval, only the *si-a*-interval is shortened by it.

the *a-v*-interval is not suddenly reduced to the definitive extent, but becomes smaller from systole to systole; thus before this halving the *a-v*-interval amounts to $1^1/_4$ sec., for the first systole after the halving of the auricle-rhythm $1^1/_8$, for the second $1^1/_{10}$ till for the fifth, sixth and seventh this amount is 1 sec.; $1^1/_2$ min. later (vide Fig. 5 lower row) this amount is likewise still 1 sec. The upper-row of curves of Fig. 5 has been represented 15 min. before the lower. Here we see a variation of rhythm of the ventricle.

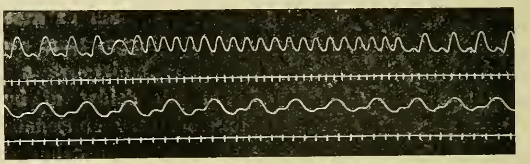

Fig. 5.

The lower row of curves has been represented $1^1/_2$ minutes after the curves of fig. 4. The *a-v*-interval is still shortened. The upper row has been represented 15 minutes before the lower. We see hereupon a variation of rhythm of the ventricle.

When estimating the variations of the *a-v*-interval we must consequently always ask, which amount of it must be attributed to the transmission of stimuli, and which amount is caused by the possibility of exerting influence upon the ventricle-musculature. So the shortening of the *a-v*-interval after the halving of the ventricle-rhythm must be attributed to the improved possibility of exerting influence upon the ventricle-musculature. If the rhythm of the auricle halves at the same time as that of the ventricle, then both factors contribute to the shortening of the *a-v*-interval.

For the extra-systole after irritation of the auricle both factors contribute to lengthen the *a-v*-interval, for the then succeeding post-compensatory systole to shorten the *a-v*-interval. For the post-compensatory systole after extra-irritation of the ventricle the *a-v*-interval is again shortened by the possibility of exerting influence more rapidly upon the ventricle-musculature.

We shall however continue to speak of the power of transmission of the connecting-systems, and estimate this in accordance with the *a-v* or *P-R*-interval, but the above evidence must guide us when drawing our conclusions.

Along a quite different way I showed that the ventricle-systoles have a latent stage for the irritation coming from the auricle, of a duration that changes in accordance with the metabolic situation of the ventricle-musculature. I found in fact that the duration of the R-V-interval (this name I gave to the interval between the beginning of the R-oscillation of the ventricle-electogram and the beginning of the ventricle-suspensioncurve belonging to it) increases considerably after poisoning with veratrine; when then the ventricle-rhythm halves this R-V-interval decreases again, and increases afterwards again when the poisoning-process continues. [1])

Mathematics. — "*A particular bilinear congruence of rational twisted quintics*". By Prof. J. DE VRIES.

(Communicated in the meeting of April 23, 1915).

1. In a communication in these Proceedings of March 27th last, (volume XVII, p. 1250) I considered a congruence of rational twisted quintics, ϱ^5, which is determined by a net of cubic surfaces the base of which consists of a twisted cubic, a straight line and three fundamental points. We arrive at a $[\varrho^5]$ differing from this by starting from a net of cubic ruled surfaces R^3 having a straight line q as nodal line. Two arbitrary surfaces of that net have another ϱ^5 in common, which is rational, because it has q as a quadrisecant. An arbitrarily chosen third surface intersects ϱ^5 eight times on q, consequently seven times outside q; hence all base-curves ϱ^5 of the pencils (R^3) comprised in the net have seven fundamental points F_k in common.

The congruence $[\varrho^5]$ *consists therefore of the curves* ϱ^5, *which intersect the straight line* q *four times and pass through seven points* F.

2. The hyperboloid R_1^2, containing the straight line q and the six points $F_k (k = 2$ to $7)$, has with an R^3 of the net another *rational curve* ϱ_1^4 in common of which q is a trisecant. This ϱ_1^4 is a component part of a degenerate curve of the congruence; the second component part is the straight line r_1, which connects F_1 with the point R_1, where ϱ_1^4 moreover intersects the plane $(F_1 q)$. To each ray of the plane pencil (r_1) belongs on the other hand a

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[1] Erelong an elaborate communication about this subject will appear in "The Journal of Physiology." Compare fig. 2, 3, 4 and 5 of communication I: "On the heart-rhythm" by Dr. S. DE BOER. Koninkl. Akademie van Wetenschappen at Amsterdam. Verslag van de gewone vergadering der Wis- en Natuurk. Afdeeling van 30 Januari 1915. Deel XXII, p. 1026 and 1027. Proceedings of the meeting of Saturday February 27 1915. Vol XVII p. 1075.

rational ϱ_1^4, with which it is connected into a degenerate ϱ^5. For through any point of a straight line r_1 pass ∞^1 ruled surfaces R^2, which have r_1 in common; so they pass all moreover through a rational ϱ^4, of which q is a trisecant. All pencils (R^2) which arise when r_1 is made to revolve round F_1 have in common the degenerate ruled surface composed of the plane $(F_1 q)$ and R_1^2. These two figures have in common, besides q, a straight line p_1, which is apparently the locus of the point $R_1 \equiv (r_1, \varrho_1^4)$.

Through the five points $F_k\,(k = 3$ to $7)$ a twisted cubic $\varrho^3_{1,2}$ may be laid intersecting q twice. If R_1 and R_2 are its points of intersection with the planes $(F_1 q)$ and $(F_2 q)$, the straight lines $r_1 \equiv F_1 R_1$ and $r_2 \equiv F_2 R_2$ form with $\varrho^3_{1,2}$ a degenerate ϱ^5. Apparently $\varrho^3_{1.2}$ forms with q the intersection of the hyperboloids R_1^2 and R_2^2.

The congruence therefore contains seven systems of degenerate curves (ϱ^4_k, r_k) *and* 21 *degenerate figures* $(\varrho^3_{kl}, r_k, r_l)$.

3. Any curve ϱ^5 intersecting the *singular quadrisecant* q in a point S belongs to the base of a pencil of which all the surfaces touch each other in S. In order to determine the locus of those curves, I consider two arbitrary pencils of the net $[R^2]$. If to each ruled surface of the first pencil the two ruled surfaces of the second pencil are associated, which touch the first ruled surface in S, the pencils are in a correspondence (2,2). To the figure of order 12, which they produce, the common ruled surface belongs twice. The curves ϱ^5 passing through S form therefore a surface Σ^6. This surface must be a *monoid* as an arbitrary straight line drawn through S is chord of *one* curve ϱ^5, consequently intersects Σ^6 outside S in *one* point only. From the consideration of a plane section it ensues as a matter of course that q is a *quadruple straight line* of the monoid.

Through the *quintuple point* S pass the *seven straight lines* $F_k S$. An arbitrary ϱ^5 of the congruence intersects Σ^6 only on q and in the points F; from this it ensues at once that the monoid has *seven nodes* F_k.

If Σ^6 is projected from S on a plane φ, the system ∞^1 of the curves in which the monoid is intersected by a pencil of planes finds its representation in a pencil of curves φ^6, passing through the images F'_k of the points F_k. One of these curves has apparently a node in F_k'; the remaining curves will therefore have in F_k' the tangent in common. Σ^6 has in that case the same tangent plane in all the points of SF_k: the monoid has *seven torsal straight lines* SF_k.

The curves ϱ^5 lying on Σ^6 are represented by a pencil of rational curves φ^4 passing through the seven points F_k and thrice through the intersection Q of q. To that pencil belong seven surfaces each consisting of a straight line QF_k and a nodal φ^3 passing through the remaining points F. Such a figure is the image of a degenerate ϱ^5, of which the ϱ^4 passes through S; while the straight line r is produced by the intersection of the plane $(F_k q)$.

4. The surface Λ formed by the curves ϱ^5, which intersect a straight line l, has q as a *sextuple straight line*; for in its intersections with a monoid Σ^6 the line l meets six curves ϱ^5 passing through the vertex S of the monoid.

The section of Λ with the plane $(F_1 q)$ consists of the sextuple straight line q and three straight lines r_1; of these, one is intersected by l, the other two are indicated by the two curves $\varrho_1{}^4$, which rest on l (§ 2). The surface Λ is therefore of *order nine;* it has *seven triple points* F_k, and contains 21 *straight lines* r.

The order of Λ may also be determined as follows. As in § 3 I consider two pencils (R^3). If each two ruled surfaces intersecting on l are associated to each other, a correspondence (3,3) arises. The figure produced by it is of order 18 and consists of three times the ruled surface which the pencils have in common and the surface Λ; this surface is consequently of order nine.

A plane λ passing through l intersects Λ^9 along a curve λ^8. The curve ϱ^5, which has l as a chord (hence is *nodal curve* of Λ^9) passes through two of the intersections of l and λ^8; in each of the remaining six intersections λ is touched by a ϱ^5. The locus of the points in which a plane φ is touched by curves ϱ^5 is therefore a *curve of order six*, φ^6, with *quintuple point* $S_0 = (q, \varphi)$.

With an arbitrary surface Λ^9 this curve has, outside S_0, $6 \times 9 - 5 \times 6 = 24$ points in common. The curves touching a plane φ form therefore a *surface of order* 24, Φ^{24}.

A monoid Σ^6 has with φ^6, outside S_0, moreover $6 \times 6 - 5 \times 4 = 16$ points in common; on φ^6 lie therefore the points of contact of 16 curves ϱ^5 passing through the vertex of Σ^6, in other words Φ^{24} has q as *sixteenfold straight line.*

An arbitrary ϱ^5 therefore intersects Φ^{24} 64 times on q; as the remaining 56 intersections are united in the points F, Φ^{24} has *seven octuple points* F.

The hyperboloid R_1^2 has, outside S_0, seven points in common with $\boldsymbol{\varphi}^6$; in those points φ is touched by as many rational curves ϱ^1. The corresponding straight lines r_1 lie on Φ^{24}. The section of this surface with $(F_1 q)$ consists of q and 8 straight lines r_1. The eighth of those straight lines belongs to a degenerate ϱ^5, which touches q improperly.

The plane q has in common with Φ^{24}, besides two times the curve of contact φ, another curve q^{12}, which has a sextuple point in S_0. Outside S_0 the curves q^6 and q^{12} have moreover $6 \times 12 - 5 \times 6 = 42$ points in common; from this it ensues that *each plane is osculated by* 21 *curves* ϱ^5.

The curve ψ^6 along which the plane ψ is touched by Ψ^{24}, has in common with Φ^{24}, outside the intersection of q, moreover $6 \times 24 - 5 \times 16 = 64$ points. *Two arbitrary planes are therefore touched by* 64 *curves* ϱ^5.

5. Any straight line t, containing three points of a ϱ^5, is a *singular trisecant.* For through t passes *one* R^8; the remaining ruled surfaces of the net intersect it therefore in the triplets of an involution so that it is trisecant for ∞^1 curves ϱ^5. From this it ensues that the singular trisecants form a *congruence.* As each ϱ^5 is intersected in each of its points by three trisecants, *the congruence* $[t]$ *is of order three.*

The fundamental points F are *singular points* of $[t]$; for each of those points bears ∞^1 singular trisecants. The cone $\mathfrak{T}$, which they form, has in common with the cone $\mathfrak{K}^4$, which projects an arbitrary ϱ^5 out of F, three straight lines t, which are nodal edges of $\mathfrak{K}^4$, and further the straight lines to the remaining six points F. From this it ensues that $\mathfrak{T}$ is a cubic cone. The points F are consequently *singular points of the third order for the congruence of rays* $[t]$.

The trisecants of ϱ^5 form a ruled surface $\mathfrak{R}^8$, on which ϱ^5 is a triple curve [1]).

The axial ruled surface $\mathfrak{A}$ formed by the straight lines t, resting on a straight line a has therefore with a ϱ^5 in common the 24 points, in which ϱ^5 is intersected by the eight trisecants resting on a. Outside these points they have only in common the seven points F, which, however, are threefold on $\mathfrak{A}$. We conclude from this that $\mathfrak{A}$ must be a ruled surface of order nine. As a is a triple straight line on it, a plane passing through a possesses moreover six straight lines t. *The congruence of rays* $[t]$ *is therefore of class six.*

In connection with this the plane $F_1F_2F_3$ contains, besides the

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[1]) The points of support of the trisecants form the pairs of an involutorial correspondence (6). The involution I_5, which the planes passing through a straight line l produce on ϱ^5, has apparently 24 pairs in common with (6); consequently eight trisecants rest on l.

three straight lines F_1F_2, F_2F_3, F_3F_1, three trisecants, consecutively passing through F_1, F_2, F_3.

The three straight lines t, meeting in an arbitrary point P, are nodal lines on the surface Π^6, containing the points of support of the chords drawn through P of the curves of the $[\varrho^5]$. With the cone which projects the ϱ^5 passing through P, Π^6 has, besides this ϱ^5, only straight lines passing through P in common; they are the three trisecants out of P, which are nodal lines for both surfaces, and the seven singular bisecants PF_k. From the consideration of the points which Π^6 has in common with an arbitrary ϱ^5 follows that this surface has nodes in the seven fundamental points.

For a point S of the singular quadrisecant Π^6 passes into the monoid Σ^6.

Mathematics. — "*Bilinear congruences of elliptic and hyperelliptic twisted quintics.*" By Prof. Jan de Vries.

(Communicated in the meeting of April 23, 1915).

1. We consider a net of cubic surfaces Φ^3 of which all figures have a *rational quartic*, σ^4, in common. Two arbitrary Φ^3 have moreover an elliptic quintic ϱ^5 in common, resting on σ^4 in *ten* points. A third surface of the net therefore intersects ϱ^5, outside σ^4, in *five* points F_k; they form with σ^4 the base of the net. As a Φ^3 passing through 13 points of σ^4 wholly contains this curve, only four of the points F_k may be taken arbitrarily for the determination of the net. The base-curves ϱ^5 of the pencils of the net form a *bilinear congruence, with singular curve σ^4 and five fundamental points F_k.*

The singular curve σ^4 may be replaced by the figure composed of a σ^3 with one of its secants, or by the figure composed of two conics, which have *one* point in common, or by the figure consisting of a conic and two straight lines intersecting it.

2. The curves ϱ^5, which intersect σ^4 in the *singular points S*, form a cubic surface Σ^3, with node S, which belongs to the net; S is therefore a *singular point of order three.* The monoids Σ^3 belonging to two points S have σ^4 and a curve ϱ^5 in common; through two points of σ^4 passes therefore in general *one* curve ϱ^5. The groups of 10 points which σ^4 has in common with the curves of the congruence form therefore an involution of the second rank.

On σ^4 lie consequently 36 pairs of points, each bearing ∞^1 curves ϱ^5; in other words, the net contains 36 dimonoids, of which the two nodes are lying on σ^4. The congruence further contains 24 curves ϱ^5, which osculate the singular curve σ^4.

The curves ϱ^6 lying on the monoid Σ^3, are, by central projection out of S, represented by a pencil of plane curves φ^4, with two double base-points and eight single base-points; to it belong the images of the five fundamental points. The remaining three are the intersections of *three singular bisecants* b; through each point of such a straight line passes a ϱ^5 of Σ^3. The two nodes are the intersections of *two singular trisecants* t; each straight line t is moreover intersected in two points by each ϱ^5 of the monoid; for two ϱ^5 the line t is a tangent. The three straight lines b, and the two straight lines t lie of course on Σ^3; the sixth straight line passing through S is a *trisecant* d of σ^4. It is component part of a *degenerate* ϱ^5; for all Φ^3 passing through an arbitrary point of d contain this straight line and have moreover another *elliptic curve* ϱ^4 in common.

3. The locus of the straight lines d is the *hyperboloid* Δ^2, which may be laid through σ^4. The latter has with a monoid Σ^3 the singular curve σ^4 and two trisecants d in common. Consequently Σ^3 contains a straight line d *not* passing through S; the curve ϱ^4 coupled to this straight line must contain the point S. It is represented by a curve φ^3, containing the intersections of the straight lines t, b and the images of the points F, while the line connecting the intersections of the two singular trisecants is the image of the straight line d belonging to this ϱ^4.

The locus of the curves ϱ^4 has in common with Σ^3 the curves σ^4 and two curves ϱ^4; so it is a *surface of order four*, Δ^4. With Δ^2 the surface Δ^4 has in common the curve σ^4; the remaining section is a rational curve δ^4, being the locus of the point $D \equiv (d, \varrho^4)$. As the trisecants of δ^4 form the second system of straight lines of $\angle^2$, δ^4 and σ^4 have ten points in common. This is confirmed by the observation that the pairs d, ϱ^4 determine on σ^4 a correspondence (7, 3), which has the said ten points as coincidences.

4. The locus of the pairs of points which the curves ϱ^5 have in common with their chords drawn through a point P is a surface Π^6, with a quadruple point P. The tangents in P form the cone $\mathfrak{K}^4$, which projects the curve ϱ^5 laid through P; the two trisecants t of this curve are nodal edges of that cone and at the same time nodal lines of Π^6. The cone, which projects σ^4 out of P has in common with $\mathfrak{K}^4$ the 10 edges containing the points of intersection of σ^4 and ϱ^5; the remaining 6 common edges q are singular bisecants. For q is chord of the curve ϱ^5 passing through P, and moreover of a ϱ^5 intersecting it on σ^4, but in that case it must be chord of ∞^1 curves ϱ^5. The surface Φ^3, which may be laid through q, σ^4 and ϱ^5 does belong to the net; the other surfaces of this net consequently intersect this net in the pairs of a quadratic involution; in other words, q is a singular bisecant.

The six straight lines q lie apparently on H^6; this surface also contains the five straight lines $f_k = PF_k$, which, as the above mentioned straight lines b, are *particular* (parabolic) *singular bisecants*; through each point f passes a ϱ^5, which has its second point of support in F, so that the involution of the points of support is parabolic. The section of H^6 and $\mathfrak{K}^4$ apparently consists of a ϱ^5, two straight lines t (which are nodal lines for both surfaces) five straight lines f and six straight lines q.

For a point S of the singular curve σ^4 the surface H^6 consists of two parts: the *monoid* Σ^3 and a *cubic cone* formed by the singular bisecants q, which intersect σ^4 in S. As a plane contains four points S, consequently 4×3 straight lines q, the singular bisecants form a congruence of rays (6, 12), belonging to the complex of secants of σ^4, which congruence of rays possesses in σ^4 a singular curve of order three.

5. The singular trisecants t form, as has been proved, a congruence of rays of *order two*. The latter has the five fundamental points F as *singular points*, for each of those points bears ∞^1 straight lines t, which form a cone $\mathfrak{T}$. With the cone $\mathfrak{F}^4$, which projects an arbitrary ϱ^5 out of F, $\mathfrak{T}$ has the four straight lines to the remaining points in common and further the two straight lines t, passing through F. As these straight lines are nodal edges of $\mathfrak{F}^4$, $\mathfrak{T}$ must be a quadric cone. The congruence $[t]$ has therefore *five singular points of order two.*

The trisecants t of an elliptic ϱ^5 form 1) a ruled surface $\mathfrak{R}^6$, with nodal curve ϱ^6. The axial ruled surface $\mathfrak{A}$ formed by the straight lines t which intersect a given straight line a, has in common with an arbitrary ϱ^5 in the first place 5×3 points, in which ϱ^6 is intersected by the five straight lines t resting on a. Moreover they have in common the five points F, which, however, are nodes of $\mathfrak{A}$. Consequently $\mathfrak{A}$ is a ruled surface of order five. As a is nodal line

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1) Vid. e.g. my paper in volume II (p. 374) of these Proceedings.

of $\mathfrak{A}^6$, a plane passing through a contains three straight lines more hence the *singular trisecants* form *a congruence* (2, 3).

6. A straight line l intersects three curves ϱ^5 of a monoid Σ^3; consequently σ^4 is a *triple curve* on the surface Λ formed by the ϱ^5, intersecting l. As two surfaces Λ^c, outside σ^4, have but x curves ϱ^5 in common, we have $x^2 = 5x + 36$, hence $x = 9$. An arbitrary curve ϱ^5 intersects Λ^9 on σ^4 in 10×3 points, consequently fifteen times in F_k; so Λ^9 has *five triple points* F_k. On Λ^9 lie (§ 3) *six* straight lines and *six* elliptic curves ϱ^4; the ϱ^5, for which l is a chord, is a *nodal curve.*

In a plane λ passing through l, the congruence $[\varrho^5]$ determines a quintuple-involution possessing four singular points S of order three. It transforms a straight line l into a curve λ^8 with four triple points, and has a *curve of coincidence* of order six, γ^6, with four nodes S. With an arbitrary surface Λ^9 the curve γ^6, has outside S_k, $9 \times 6 - 4 \times 3 \times 2 = 30$ points in common. The curves ϱ^5, touching a plane q, consequently form a surface Φ^{30}; on it σ^4 is a *decuple curve* (Σ^3 intersects γ^6, outside S_k, in $3 \times 6 - 4 \times 2$ points) while F_k are *decuple points* (an arbitrary ϱ^5 intersects Φ^{30}, outside σ^4, in $5 \times 30 - 10 \times 10$ points).

Φ^{30} has in common with q another curve φ^{18}, possessing four sextuple points S; it touches q^n in 20 points; q is therefore *osculated* by *thirty curves* ϱ^5.

Two surfaces Φ^{30} have, outside σ^4, 100 curves ϱ^5 in common, *two planes* are therefore *touched* by 100 curves ϱ^5.

7. When all the surfaces Φ^3 of a net have an *elliptic twisted curve* σ^4 in common, the variable base-curves ϱ^5 of the pencils comprised in the net form a *bilinear congruence of hyperelliptic curves.* Each ϱ^5 rests in *eight* points on σ^4 and has with an arbitrary surface Φ^3 moreover *seven fundamental points* F_k in common. As the net is completely determined by σ^4 and five points F, the points F cannot be taken arbitrarily.

The *singular curve* σ^4 may be replaced by the figure composed of a curve σ^3 and one of its chords, or by two conics having two points in common.[1])

8. The *monoid* Σ^3, which has the *singular point* S as node

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[1]) In both cases a Φ^3, containing 12 points of the base-figure, will contain it entirely. This elucidates the fact that Φ^3 needs only to be laid through 12 points of the elliptic σ^4 in order to contain it entirely.

and belongs to the net $[\Phi^3]$, again contains all the ϱ^5 intersecting the singular curve σ^4 in S. In representing Σ^3 on a plane φ the system of those curves passes into a pencil of hyperelliptic curves φ^4, with a double base-point and 12 simple base-points. The first is the intersection of a singular trisecant t, consequently of a straight line passing through S, which is moreover twice intersected by all the ϱ^5 lying on Σ^3.

To the simple base-points belong the central projections of the 7 fundamental points. The remaining five are *singular bisecants* b, consequently straight lines, which have a second point in common with any ϱ^5 passing through S. With the trisecant already mentioned they form the six straight lines of Σ^3 passing through S. The straight lines b, are, as well as the straight lines f passing through the fundamental points, *parabolic bisecants*.

9. In the same way as above (§ 4) it is proved that an arbitrary point bears *eight singular bisecants* q, i.e. straight lines, which are intersected by $[\Phi^3]$ in the pairs of an involution; they belong to the complex of secants of σ^4. The straight lines q passing through a point S of σ^4 again form a *cubic cone*, so that $[q]$ is a congruence of rays (8, 12).

The singular trisecants t form a congruence of *order one*, which has the points F as singular points. The singular cone $\mathfrak{T}$ belonging to F is a quadric cone as it has in common with the cone ζ^4, which projects an arbitrary ϱ^5 out of F, six straight lines FF' and a trisecant t, which is nodal edge of ζ^4. As the trisecants of ϱ^5 form a ruled surface $\mathfrak{R}^2$, the axial ruled surface $\mathfrak{A}$, belonging to a straight line a, has in common with a ϱ^5 the six points of support of two trisecants and the seven nodes F, consequently is of order four. But in that case $[t]$ is of *class three*, consequently the congruence of the bisecants of a *cubic* τ^3, passing through the seven points F.

As in § 6 we find that two arbitrary straight lines are intersected by *nine* curves ϱ^5, that two arbitrary planes are touched by *a hundred* curves, that there are *thirty* curves osculating a given plane.

Here too, the fundamental points are triple on Δ^9, decuple on Φ^3.

Mathematics. — "*Remark on inner limiting sets*". By Prof. L. E. J. Brouwer.

(Communicated in the meeting of April 23, 1915).

The notion of *inner limiting set* i. e. the set of all the points common to a series of sets of regions, was prepared by Borel [1]), and fully developed by Young [2]). The two principal theorems about this class of sets are the following:

1. *An inner limiting set containing a component dense in itself, has the continuous potency.*

2. *A countable set containing no component dense in itself, is an inner limiting set.*

The former theorem has been proved by Young, first for the linear domain, then for the space of n dimensions [3]). The latter theorem has been proved for the first time by Hobson [4]). It is true that this theorem can be considered as a corollary of the following theorem ennunciated somewhat before by Young [5]):

3. *If Q be an arbitrary set of points, an inner limiting set exists containing besides Q only limiting points of the ultimate coherence* [6]) *of Q*;

but this theorem was deduced by Young [5]) from the property: "*Each of the successive adherences* [7]) *of a set of points consists entirely of points which are limiting points of every preceding adherence*", and the proof given by Young for this property is erroneous [8]), so that undoubtedly the priority for the proof of theorem 2 belongs to Hobson.

We can, however, arrive at theorem 2 in a much simpler way

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[1]) Leçons sur la théorie des fonctions, p. 44.

[2]) Leipziger Ber. 1903, p. 288; Proc. London M. S. (2) 3, p. 372.

[3]) Leipziger Ber. 1903, p. 289—292; Proc. London M. S. (2) 3, p. 372—374. These proofs are referred to not quite exactly by Schoenflies, Bericht über die Mengenlehre II, p. 81 and Entwickelung der Mengenlehre I, p. 356.

[4]) Proc. London M. S. (2) 2, p. 316—323.

[5]) Proc. London M. S. (2) 1, p. 262—266.

[6]) Young, Quarterly Journ of Math., vol. 35, p. 113.

[7]) Cantor, Acta Mathematica 7, p. 110.

[8]) Quarterly Journ. of Math., vol. 35, p. 115. The error is contained in the sentence (line 8—6 from the bottom): "Thus P, being a limiting point of every one of the derived coherences, is a limiting point of F". A correct proof of the property in question was communicated to me about two years ago by G. Chisholm Young.

than HOBSON and YOUNG did, by means of the following[1]) proof of theorem 3, which is valid for the space of n dimensions:

For each positive integer ν we describe round each point q of Q as centre with a radius smaller than ε_ν ($lim\, \varepsilon_\nu = 0$) a sphere which, if q is a point of the adherence $Qc^{\beta}a$, excludes all points of the derived set of Qc^{β}. In this way for each positive integer ν a set of regions J_ν containing Q is determined.

The inner limiting set $\mathfrak{D}(J_\nu)$ then possesses the property required. For, if p be a limiting point of Q not belonging to Q and not being a limiting point of the ultimate coherence of Q, a transfinite number τ_p exists with the property that p is not a limiting point of Qc^{τ_p}, but for any $\alpha < \tau_p$ is a limiting point of Qc^{α}. Then on one hand p is excluded by every sphere described round a point of $\sum\limits_{\alpha<\tau_p} Qc^{\alpha}a$, on the other hand a positive integer σ_p exists so that p is excluded by every sphere described for a $\nu > \sigma_p$ round a point of Qc^{τ_p}. Hence p lies outside every J_ν for which $\nu > \sigma_p$, so that p cannot belong to $\mathfrak{D}(J_\nu)$. Thus the theorem has been established.

Chemistry. — "*Investigations on* PASTEUR'S *Principle of the Relation between Molecular and Physical Dissymmetry.*" II. By Prof. Dr. F. M. JAEGER. (Communicated by Prof. H. HAGA).

(Communicated in the meeting of April 23, 1915).

§ 1. In the following are reviewed the results of the crystallographical investigations upon which the conclusions explained in the previous paper[2]) are founded.

I. *Racemic Luteo-Triethylenediamine-Cobaltibromide.*
Formula: $\{Co\,(Aein)_3\}\,Br_3 + 3\,H_2O$.

This compound was prepared by two methods: 1. Starting from *praseo-diethylenediamine-dichloro-cobaltichloride*: $\{Co\,(Aein)_2\,Cl_2\}\,Cl$, by heating with ethylenediamine and precipitating with a concentrated solution of sodiumbromide; 2. By heating *purpureo-pentamine-*

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[1]) This proof was communicated about two years ago to SCHOENFLIES, who on p. 356 of his Entwickelung der Mengenlehre I, applies it to prove the following special case of theorem 2: "*Every component of a countable closed set is an inner limiting set*". Comp. HOBSON, l. c. p. 320: "*Every reducible set is an inner limiting set*".

[2]) Vid These Proceedings, March 1915.

chlorocobaltichloride: $\left\{Co\begin{matrix}(NH_3)_5\\ Cl\end{matrix}\right\}Cl_2$, with three molecules of triethylenediamine for a considerable time, and precipitating the compound with sodiumbromide.

A. The salt prepared by the method indicated sub 1 is deposited from the yellow-brown solutions as hexagonal plates of red-brown or orange colour, or in the shape of hexagonal, short prisms. (fig .1*a* and 1*b*).

Pseudo-ditrigonal-scalenoëdrical, but probably really *monoclinic*

$$a : c = 1 : 0.6794.$$

The compound is almost perfectly isomorphous with the corresponding chloride; however the cleavage differs in the two salts.

Observed Forms: $c = \{0001\}$, most prominent and giving good images; $m = \{10\bar{1}0\}$, often very well developed, shows however in most cases broken faces, giving multiple reflections; $r = \{10\bar{1}1\}$, sometimes small, but occasionally rather large; $r' = \{10\bar{1}\bar{1}\}$, often absent, several times very narrow, and in rare cases as well developed as r; perhaps $s = \{42\bar{6}3\}$, occasionally visible as an extremely narrow blunting.

Angular Values:	*Measured*:	*Calculated*:
$r : c = (10\bar{1}1) : (0001) =$	*38° 7′	—
$r : m = (10\bar{1}1) : (10\bar{1}0) =$	51 50	51°53′
$m : m = (10\bar{1}0) : (01\bar{1}0) =$	60 2	60 0
$c : s = (0001) : (42\bar{6}3) =$	*ca.* 54°	54 9
$r : r = (10\bar{1}1) : (\bar{1}101) =$	—	64 38

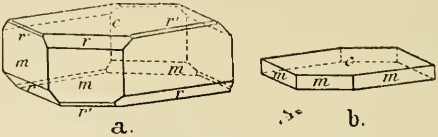

Fig. 1.
Racemic Triethylenediamine-Cobaltibromide.

A perfect cleavage occurs parallel to {0001}. Plates perpendicular to the *c*-axis are however completely dark in no situation between crossed nicols, if the light is polarized parallel. Occasionally they appear to be composed of lamellae parallel to {0001}, like the well-known mica-piles of Reusch and Mallard, as might also be proved perhaps by the often observed anomalies of the angular values.

The crystals are optically-uniaxial; the birefringence is of a negative character. They do not show a rotatory polarisation; their dichroism is clearly visible: on $\{10\overline{1}0\}$ for vibrations parallel to the c-axis orange-red, for those perpendicular to the former orange-yellow. The specific weight of the crystals was determined at 25° C. pycnometrically: $d_{4^\circ}^{25^\circ} = 1.845$; the molecular volume[1]) is thus: 577.8, and the topical axes $\chi : \omega = 10,9400 : 7,4328$.

B. The substance prepared from *purpureo-dichloro*-salt crystallised from its aqueous solution in the shape of hexagonal plates, which will commonly show not only c and m, but also r and r'. The optical behaviour and the angular values agree completely with those of the previously described salt. Further, we obtained the same modifications in separating the bromo-tartrate into its optically active forms as in the first case; also the d-bromo-tartrate was here identical with that obtained from the first salt. There cannot be any doubt, but that the two bromides are quite identical; the specific gravity of the last crystals also, being found at: 1.142 at 25° C., is in agreement with this supposition.

With the kind assistance of my colleague Haga a beautiful Röntgenogram of these hexagonal plates was made. The stereographic projection of it is reproduced on Plate I, in *A*. It appears now, that there is no ditrigonal symmetry at all: the photo reveals only a single plane of symmetry, as if a mere monoclinic-domatic symmetry were present. For the present no other explanation can be given here, than the supposition of the crystal being only a pseudotrigonal complex of perhaps monoclinic lamellae; in every case the very perfect approximation of that complex to a real ditrigonal crystal is a quite remarkable fact; it remains yet very strange however, why only a single plane of symmetry will appear in this image.

II. Dextrogyratory Luteo-Triethylenediamine-Cobaltibromide.

Formula: $\{Co\,(Aein)_3\}\,Br_3 + 2\,H_2O$.

The compound was obtained by the transformation of the racemic salt in aqueous solution into the corresponding *d-bromo-d-tartrate* by means of silver-d-tartrate and afterwards fractionated crystallisation. The *d-bromo-d-tartrate* which is deposited first and whose beautiful crystals are also described in the following, is then treated with HBr to convert it into the dextrogyratory bromide; the same happened with the *l-bromo-d-tartrate*, which can be obtained only in the form of a colloidal mass. The rotation of the two salts in aqueous solutions appeared to be really equal but of opposite direction.

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[1]) In the following calculations we adopted $2M$ instead of M as the molecular weight of the racemic compounds. This latter one is undoubtedly also present still in the aqueous solutions of the salts.

Big crystals, occasionally a cc.m. in volume; they are brownish red, in most cases thick prisms with beautifully developed, lustrous faces. Commonly they are flattened parallel to two opposite faces of *m*; also the dodecahedrical crystals were observed, which are described in the case of the laevogyratory antipode.

Ditetragonal-bipyramidal.

$a : c = 1 : 0.8399.$

Observed Forms: $m = \{110\}$, in most cases predominant, sometimes giving multiple images; $o = \{101\}$, with great, lustrous faces, allowing very accurate measurements; $\omega = \{201\}$, well developed, but often absent. (fig. 2*a* and 2*b*).

Angular Values:	*Measured*:	*Calculated*:
$o : o = (101) : (011) =$	*54° 8½	—
$m : o = (101) : (110) =$	62 56	
$m : m = (110) : (1\bar{1}0) =$	90 1	90 0
$o : \omega = (101) : (201) =$	18 59	19 12
$\omega : m = (201) : (110) =$	52 36	52 35

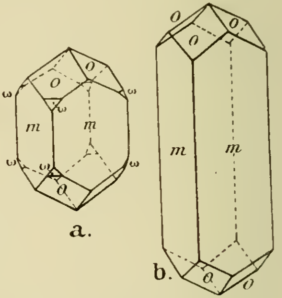


Fig. 2.
Dextrogyratory Triethylenediamine-Cobaltibromide.

A distinct cleavage could not be stated.

On {110} the extinction is normal; the crystals are not appreciably dichroitic. They are uniaxial, with negative birefringence. They show a strong rotatory polarisation: a plate perpendicular to the optical axis appeared to be strongly dextrogyratory: about 25° or 30° for the transmitted orange-red light, and a thickness of 1 m.m. If a similarly directed plate of the laevogyratory salt is combined with it, one sees the spirals of *Airy* very distinctly like four dark beams, radiating from the centrum of the image into direction of motion of the hands of a clock, if the dextrogyratory plate is the upper-one of the two.

The specific weight of the crystrals was at 25° C.: $d_{4^\circ} = 1.971$; the molecular volume is thus: 261.29, and the topical parameters are:

$\chi : \psi : \omega = 6{,}7759 : 6{,}7759 : 5{,}6910.$

By means of a diluted solution of potassiumchlorate, finally corrosionfigures on {110} could be obtained, having the shape of kites or long hexagons; they appeared symmetrical with respect to a horizontal and to a vertical plane. From this and the holohedrical development of the crystals, it must be concluded that they can *not* be considered to have tetragonal-trapezohedrical symmetry, but that they must be described as of ditetragonal-bipyramidal symmetry.

On the rotation in solution and its dispersion, the data of the previous paper can be consulted.

The Röntgenogram obtained of a plate perpendicular to the *c*-axis was too imperfect, to make a good reproduction possible. Thus on Plate *I* in *B* we have given its stereographical projection; it appears to possess all the symmetry-elements of a ditetragonal-bipyramidal crystal, and *inter alia* the four vertical symmetry-planes and the quaternary axis can be easily distinguished. In reality the photo for the laevogyratory salt, notwithstanding its imperfection, appeared to be *identical* with that of the dextrogyratory salt. In all cases studied up till now, *we have found the* Röntgen*ograms of the dextro- and laevogyratory crystals always identical,* just as the theory of the phenomenon postulates: so in the cases of *quartz, cinnabar,* etc. However we found in these investigations some quite remarkable facts, which are already partially described in these Proceedings (March 1915), and which can lead to a perhaps justifiable doubt about the correctness of the suppositions accepted hitherto about the explanation of the symmetry-properties of the Röntgenograms, notwithstanding the above-mentioned agreement of facts and theory in the case of the optically active crystals.

In any case it appeared *not* to be possible to prove in this way the presence of enantiomorphous forms.

All experiments made with the purpose of obtaining limiting crystalfaces, which could demonstrate the hemihedrical character of the crystals, either by crystallisation from neutral or alkaline or acid solutions, either by addition of other salts to the aqueous solutions, — were without any other result, than that of *always* giving holohedrical crystal-forms. In connection with the above-mentioned experience, we have *no* reason to suppose the occurrence of hemihedrical crystals in this case.

The optical rotation of the crystals must thus be ascribed wholly to the optically active molecules themselves, which here build up the holohedrical molecular configuration of the crystals. In the same way, as e.g. sodiumchlorate is a salt, whose *in*active molecules are arranged in a hemihedrical space-lattice, which causes the rotatory power of the crystals, — in the same way we must suppose the reverse case to be present here, where a holohedrical molecular structure will thus be built up by optically active molecules.

III. In connection with the foregoing description of the dextrogyratory antipode, the crystal forms of the corresponding *bromo-* and *chlorotartrates,* from which the active compound could be prepared, may here be described in detail also.

The *dd′-luteo-triethylenediamine-cobaltichlorotartrate,* as well as the corresponding *dd′-luteo-triethylenediamine-cobaltibromotartrate,* crystallise from the solutions of the racemic chloride, resp. bromide, after being mixed with silver-*d*-tartrate-solutions, in the shape of hard, very beautiful, translucid and commonly big crystals. If eliminated from the original solution, this last will solidify, after having been again concentrated and some more of the above-mentioned crystals having been separated, into a brownish-red jelly, which for the greater part represents the *dl′-bromotartrate*, and which after treatment with HBr, will give the laevogyratory antipode, besides some of the racemic compound. After a considerable time the jelly of the *dl′*-bromotartrate often gradually transforms into a cryptocrystalline mass.

a. dd′-Luteo-Triethylenediamine-Cobaltichlorotartrate.

$$\text{Formula: } \{Co\,(Aein)_3\} \begin{matrix} Cl \\ (C_4O_6H_4) \end{matrix}$$

Big lustrous, brownish-yellow crystals (fig. 3), which commonly have the aspect of oblique parallelopipeda.

Triclinic-pedial.

$a : b : c = 0.6211 : 1 : 0.6521$

$A = 103° 42^1/_2{}'$ $\alpha = 102° 20'$

$B = 102° 46'$ $\beta = 101° 16'$

$C = 98° 1^1/_2{}'$ $\gamma = 95° 16^2/_3{}'$

Observed Forms: $a = \{100\}$ and $a' = \{\bar{1}00\}$, large and lustrous; $b = \{010\}$, $b' = \{0\bar{1}0\}$, $c = \{001\}$ and $c' = \{00\bar{1}\}$, equally large and well reflecting; $r = \{101\}$, well developed; $q = \{011\}$, about as large as r; $m = \{2\bar{3}0\}$, only very narrow, and often totally absent. The angular values oscillate, as in the case of the bromotartrate, not unappreciably: deviations of 0°30′ to 1° are not seldom found with different individuals. A distinct cleavage was not found.

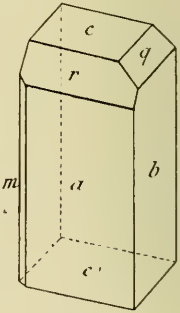
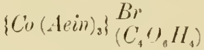


Fig. 3.
dd′-Triethylenediamine-Cobaltichlorotartrate.

Angular Values:	*Observed:*	*Calculated:*
$a : b = (100) : (010) =$	*81° $58\frac{1}{2}$	—
$b : c = (010) : (001) =$	*76 $17\frac{1}{2}$	—
$a : c = (100) : (001) =$	*77 14	—
$a : r = (100) : (101) =$	*38 11	—
$q : c = (011) : (001) =$	*28 26	—
$q : b = (011) : (010) =$	47 $50\frac{1}{2}$	47° $50\frac{1}{2}'$
$r : c = (101) : (001) =$	39 3	39 3
$a : m = (100) : (2\bar{3}0) =$	46 $59\frac{1}{2}$	46 49

A distinct dichroism was not observed. On all faces the extinction was oblique, but the extinction-angle on the prism-faces was only small with respect to the direction of the *c*-axis, — which is in agreement with the evident approximation to monoclinic symmetry, this last one can be easily seen, if the forms *a* and *b* are taken as $\{1\bar{1}0\}$, resp. $\{110\}$, while *c* remains $\{001\}$.

b. dd′-Luteo-Triethylenediamine-Cobaltibromotartrate.

Formula: 

$$\{Co\,(Aein)_3\}\begin{matrix}Br\\(C_4O_6H_4)\end{matrix}$$

Big, very lustrous, perfectly transparent crystals (fig. 4), which are wholly analogous to those of the corresponding chlorotartrate. The angular values oscillate here still a little more than in the preceding case; but undoubtedly the crystals are completely isomorphous with the above-mentioned ones.

Triclinic-pedial.

$a : b : c = 0.6208 : 1 : 0.6528.$

$\alpha = 102°\ 50\frac{2}{3}'$ $\qquad A = 104°\ 8'$

$\beta = 100°\ 35'$ $\qquad B = 102°\ 7'$

$\gamma = 95°\ 14'$ $\qquad C = 97°\ 55'$

Observed forms: $b = \{010\}$ and $b' = \{0\bar{1}0\}$ large and lustrous; $a = \{100\}$ and $a' = \{\bar{1}00\}$, $c = \{001\}$ and $c' = \{00\bar{1}\}$, all about equally well developed and giving good images; $r = \{101\}$, well developed and lustrous; $r' = \{\bar{1}0\bar{1}\}$ commonly absent; $o = \{\bar{1}13\}$ small, but allowing exact measurements; $o' = \{03\bar{2}\}$ narrow and somewhat dull. The angular values oscillate with different individuals not unappreciably, with differences of about 1°.

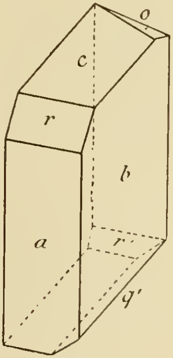


Fig. 4.
dd′-Triethylenediamine-Cobaltibromotartrate.

Angular Values:	*Measured:*	*Calculated:*
$a : b = (100) : (010) =$	*82° 5	—
$b : c = (010) : (001) =$	*75 52	--
$a : c = (100) : (001) =$	*77 53	—
$o : b = (\bar{1}13) : (010) =$	*66 56	—
$c : r = (001) : (101) =$	*39 37	—
$a : r = (100) : (101) =$	38 23	38° 16′
$o : c = (\bar{1}13) : (001) =$	21 39	21 7
$o : a = (\bar{1}13) : (100) =$	84 46	84 42
$c' : q = (00\bar{1}) : (03\bar{2}) =$	50 38	50 49½

No distinct cleavage could be stated.

On all faces the extinction-angles are other than rectangles; the crystals have a sherry-like colour, and are not distinctly dichroitic.

IV. *Laevogyratory Luteo-Triethylenediamine-Cobaltibromide.*

Formula: $\{Co\,(Aeu)_3\}\,Br_3 + 2H_2O$.

Big, brownish-red, commonly rhombic dodecahedrically shaped, very lustrous crystals, which make very accurate measurements possible.

Ditetragonal-bipyramidal.

$a : c = 1 : 0.8399.$

Observed Forms: $m = \{110\}$, usually as largely developed as o, giving the crystals thereby the aspect of rhombicdodecahedrons (fig. 5); sometimes however m is strongly predominant either with all its faces or with two parallel ones only, in such a way that the crystals get a column-shaped or tabular aspect. Further: $o = \{101\}$, big and lustrous; rarely: $\omega = \{201\}$, small but very easily measurable. The faces of $\{110\}$ sometimes give multiple images.

Angular Values:	*Observed:*	*Calculated:*
$o : o = (101) : (011) =$	*54° 6′	—
$o : m = (101) : (110) =$	62 55	62° 57′
$o : o = (101) : (\bar{1}01) =$	80 7	80 3⅓
$\omega : o = (201) : (101) =$	19 8	19 12⅓
$\omega : m = (201) : (110) =$	52 30	52 35

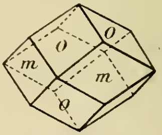
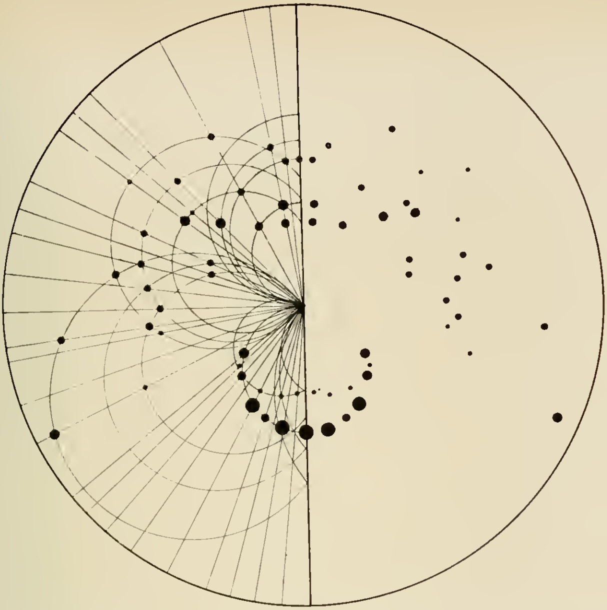


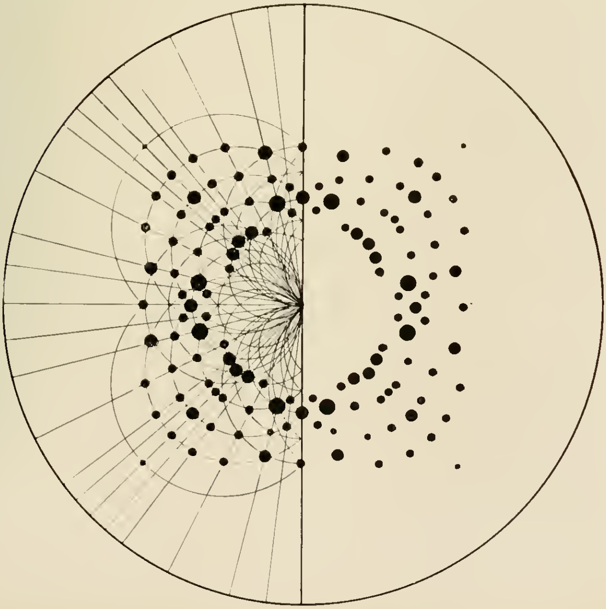
Fig. 5.
Laevogyratory Luteo-Triethylenediamine-Cobaltibromide.

No distinct cleavage was found.

Prof. Dr. F. M. JAEGER, „Investigations on Pasteur's Principle of the Relation between Molecular and Physical Dissymmetry." II.



A. Stereographical Projection of the Röntgenogram of the pseudo-ditrigonal racemic $[Co(Aein)_3]Br_3 + 3H_2O$; plate perpendicular to the *c*-axis.



B. Stereographical Projection of the Röntgenogram of dextrogyratory- and laevogyratory $[Co\ Aein)_3] + 2H\ O$; plate perpendicular to the *c*-axis.

With respect to the symmetry of the crystals the same can be said as in the case of the dextrogyratory compound. Corrosion-experiments on the faces {101} and {110} by means of water, mixtures of water and alcohol, etc. in most case gave irregularly defined corrosion-figures, which had the character of elevations.

The crystals are uniaxial with negative birefringence; like those of the dextrogyratory component they show a strong circular polarisation in the direction of the optical axis, which for a plate of about 1 mm. thickness appeared to be equal and directed oppositely to that of the dextrogyratory crystals.

On superposition of a dextro- and laevogyratory crystal, the latter being the upper, the Airy-spirals are nicely seen, with their direction of rotation just opposite to that mentioned in the description of the dextrogyratory crystals.

The specific gravity of the crystals was pycnometrically determined and found to be $d\frac{25^\circ}{4^\circ} = 1.972$; the molecular volume thus is: 261.19, and the topical parameters are : $\chi : \psi : \omega = 6.7589 : 5.6767$.

V. Racemic Luteo-Triethylenediamine-Cobaltinitrate.

Formula : $\{Co\,(Aein)_3\}\,(NO_3)_3$

This compound was prepared by treatment of the racemic bromide in aqueous solution with a warm solution of the quantity of silver-nitrate calculated. The solution separated from the precipitated silver-bromide was sufficiently concentrated on the waterbath; at roomtemperature dark red or brownish red, big, hemimorphic crystals will be separated.

In general the parameters and angular values appear to be the same as previously published (Z. f. Kryst. **39**. 548. (1904). The figure reproduced there however must now be changed, because the hemimorphy is now clearly demonstrated; further a wrong value of the angle $o:q$ was introduced in the description, evidently by an accidental interchange of the symbols {021} and {120}.[1] For the purpose of comparison of the calculated parameters with those of the optically active forms, we have, contrary to the common usage the polar binary axis as the a-axis.

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[1] These incorrect data are also reproduced in Groth's Chemische Krystallographie, II. 140. (1908); they must be corrected there by the numbers given here.

Rhombic-pyramidal.

$a : b : c = 0.8079 : 1 : 1{,}1279.$

Observed forms: $o = \{112\}$, large and lustrous; $a = \{100\}$, smaller, but also giving beautiful images; $m = \{\bar{1}20\}$, almost equally well developed as o, sometimes even with yet larger faces; $p = \{120\}$, appreciably smaller than m, but very lustrous; $b = \{010\}$ narrow; $c = \{001\}$ commonly absent, but if present well developed and giving good images; $\omega = \{\bar{1}12\}$, with very small but lustrous faces; $a' = \{\bar{1}00\}$ almost in every case absent, but sometimes present as a very narrow blunting of the intersection $(120) : (\bar{1}20)$. The crystals possess commonly a very peculiar irregularly-tetrahedrical habit, with prominent faces of o and m.

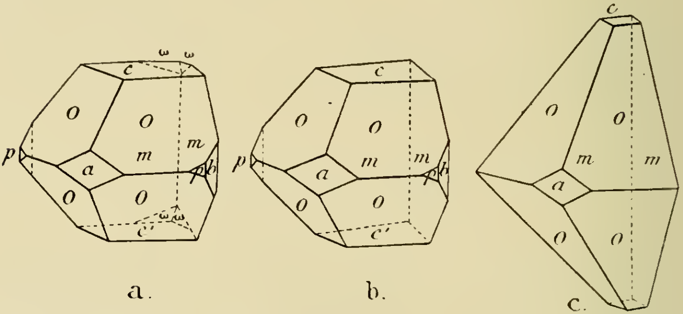


Fig. 6.
Racemic Triethylenediamine-Cobaltinitrate.

Angular Values:	*Observed*:	*Calculated*:
$a : o = (100) : (112) =$	*58° 42'	—
$o : o = (112) : (1\bar{1}2) =$	*49 38	—
$o : o = (112) : (11\bar{2}) =$	96 11	96° 12'
$o : m = (1\bar{1}2) : (\bar{1}\bar{2}0) =$	85 18	85 13
$o : p = (112) : (120) =$	50 53	50 56
$b : m = (010) : (\bar{1}20) =$	31 53	31 45
$a : p = (100) : (120) =$	58 10	58 15
$p : p = (120) : (1\bar{2}0) =$	116 20	116 30
$m : m = (\bar{1}20) : (\bar{1}\bar{2}0) =$	116 17	116 30
$c : \omega = (001) : (112) =$	41 54	41 54
$\omega : \omega = (\bar{1}\bar{1}2) : (\bar{1}12) =$	49 36	49 38

A distinct cleavage was not found.

On {100} and {001} diagonal extinction.

The specific gravity of the crystals was determined at 25° C. pycnometrically to be: $d\frac{25°}{4°} = 1.709$; the molecular volume is thus 497.64.

Topical parameters: $\chi : \psi : \omega = 6{,}6037 : 8{,}1740 : 9.2194$.

The compound does not change the direction of the plane of polarisation of the incident light.

VI. Laevogyratory Luteo-Triethylenediamine-Cobalti-nitrate.

Formula: $\{Co\,(Aein)_3\}\,(NO_3)_3$.

The compound was prepared from the bromide by means of silvernitrate in small excess and at lower temperature; after separating from the silverbromide, the solution obtained was concentrated on the waterbath. From this solution, which thus contained a slight excess of silvernitrate, big, dark-red crystals were obtained, which gave splendid images, and made very accurate measurements possible.

The crystals, which have the habit of thick, trapezohedrically or pentagonally bounded plates, are usually developed parallel to opposite faces of the prism. They are extraordinarily rich in faces, and geometrically very well built; commonly the faces of the forms 011}, {021}, {211} and {010}, are only partially present, a fact, which in connection with the peculiar distortion of the crystals, often impedes appreciably the exact crystallographical analyses of them.

Rhombic-bisphenoidic.

$a : b : c = 0.8647 : 1 : 0{,}5983.$

Observed Forms: $a = \{100\}$, well developed and giving beautiful images; $m = \{110\}$; larger than a, giving good reflections; $r = \{101\}$, somewhat smaller than m, but in most cases equally well developed; $o = \{111\}$, giving good images and relatively large; $s = \{2\bar{1}1\}$ narrower, but reflecting well; $q = \{011\}$ and $p = \{021\}$, usually with only half the number of their faces present, but developed rather largely; $b = \{010\}$, narrower than a and reflecting well.

Angular Values:	*Observed:*		*Calculated:*	
$a : m = (100) : (110) =$	*40°	51′	—	
$a : o = (100) : (111) =$	*59	18	—	
$o : m = (111) : (110) =$	47	28	47°	33′
$m : m = (110) : (1\bar{1}0) =$	98	18	98	18
$r : m = (101) : (1\bar{1}0) =$	64	30½	64	30½
$o : o = (111) : (\bar{1}1\bar{1}) =$	84	58	84	54
$b : s = (0\bar{1}0) : (2\bar{1}1) =$	70	41	70	41
$r : q = (\bar{1}01) : (0\bar{1}1) =$	45	16	45	7
$r : o = (101) : (111) =$	26	22	26	12
$o : b = (\bar{1}1\bar{1}) : (010) =$	63	43	63	48
$b : m = (010) : (110) =$	49	4	49	9
$a : r = (100) : (101) =$	55	15	55	19
$m : q = (110) : (011) =$	70	21	70	23
$m : p = (110) : (02\bar{1}) =$	59	43	59	52½
$p : o = (02\bar{1}) : (\bar{1}1\bar{1}) =$	35	43	35	43
$o : m = (\bar{1}1\bar{1}) : (\bar{1}\bar{1}0) =$	84	33	84	24½
$r : s = (10\bar{1}) : (21\bar{1}) =$	27	13	27	9½
$m : s = (\bar{1}10) : (21\bar{1}) =$	37	17	37	21
$r : p = (10\bar{1}) : (02\bar{1}) =$	58	20	58	10½
$q : p = (011) : (021) =$	19	14	19	13
$a : s = (100) : (21\bar{1}) =$	40	4	40	6½
$q : s = (01\bar{1}) : (21\bar{1}) =$	49	56	49	53½
$q : o = (01\bar{1}) : (11\bar{1}) =$	30	48	30	42
$o : s = (11\bar{1}) : (21\bar{1}) =$	19	15	19	11½
$b : q = (010) : (01\bar{1}) =$	59	4	59	6½
$b : p = (010) : (021) =$	39	58	39	53

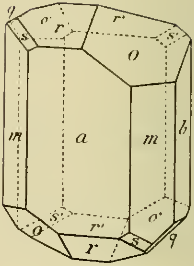


Fig. 7.
Laevagyratory Triethylenediamine-Cobaltinitrate.

A distinct cleavage was not observed.

On {100} and {010}, also on {101} and {110} everywhere a normal extinction was found. The crystals are not appreciably dichroitic.

The specific gravity of the crystals at 25° C was: $d_{4^\circ}^{25^\circ} = 1.729$: the molecular volume is thus: 245.91. Topical parameters:

$$\chi : \psi : \omega = 6.7486 : 7.8046 : 4.6695.$$

VII. Dextrogyratory Luteo-Triethylenediamine-Cobaltinitrate,

Formula: $\{Co\,(Aein)_3\}\,(NO_3)_3$.

This compound was prepared in perfectly analogous way to the left-handed isomeride. From its aqueous solutions it crystallises as dark red, very large crystals with rectangular outlines. They are also very beautifully developed and give sharp images; the habit as well as the limiting planes are quite analogous to those of the laevogyratory compouent, but the crystals were in general not so strangely distorted, and they had somewhat smaller dimensions. They are the complete mirror-images of the crystals previously described.

Rhombic--bisphenoidic.

$a : b : c = 0.8652 : 1 : 0.6009.$

Observed Forms: $a = \{100\}$ and $m = \{110\}$, both reflecting very well; m is somewhat more largely developed than a, and the crystals usually appear flattened parallel to two opposite faces of $\{1\bar{1}0\}$. Further-on: $r = \{101\}$, well developed, and like $o = \{1\bar{1}1\}$, giving very sharp images; $s = \{211\}$, small and showing in most cases only two faces; $q = \{011\}$, very small; $p = \{120\}$ and $b = \{010\}$, extremely narrow and reflecting badly, often absent (fig. 8).

Angular Values:	*Observed*:	*Calculated*:
$a : m = (100) : (110) =$	*40° 52′	—
$o : m = (1\bar{1}1) : (1\bar{1}0) =$	*47 26	—
$a : o = (100) : (1\bar{1}1) =$	59 18	59° 14′
$r : m = (101) : (110) =$	64 31	64 26½
$a : r = (100) : (101) =$	55 14	55 13
$o : r = (1\bar{1}1) : (101) =$	26 32	26 25
$m : m = (110) : (1\bar{1}0) =$	98 14	98 12
$r : r = (101) : (\bar{1}01) =$	69 31	69 34
$b : s = (010) : (211) =$	70 37	70 39½
$o : o = (1\bar{1}1) : (\bar{1}11) =$	85 8	85 5
$m : q = (1\bar{1}0) : (0\bar{1}1) =$	70 16	70 13½
$r : q = (10\bar{1}) : (01\bar{1}) =$	45 20	45 7
$m : p = (110) : (\bar{1}20) =$	18 55	19 6½
$b : p = (010) : (120) =$	30 0	30 1½
$b : m = (010) : (110) =$	49 4	49 8
$b : o = (0\bar{1}0) : (1\bar{1}1) =$	63 40	63 44

Topical parameters: $\chi : \psi : \omega = 6{,}7467 : 7{,}: 7979 : 4{,}6856.$

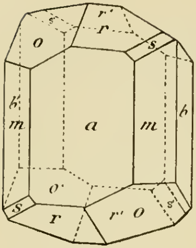


Fig. 8.
Dextrogyratory Triethylenediamine-Cobaltinitrate

A distinct cleavage was not observed.

On {100}, {110} and {101} the extinction is normal; the crystals are not distinctly dichroitic. The plane of the optical axes is {001}; probably the *b*-axis is first bisectrix. The apparent axial angle is great, the dispersion has no exceptional value; round the *a*-axis it is $\varrho > v$, with a negative character of the birefringence.

The specific weight of the crystals at 25° C. was determined at $d\,\frac{25^\circ}{4^\circ} = 1{,}725$; the molecular volume consequently is 246,51.

VIII. Racemic Luteo-Triethylenediamine-Cobalti-iodide.

Formula: $\{Co\,(Aein)_3\}\,J_3 + 1\;H_2O$

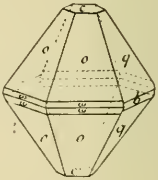


Fig. 9.
Racemic
Triethylenediamine-
Cobalti-iodide.

The compound was prepared from the corresponding bromide by double decomposition with a solution of potassium-iodide; the precipitate was washed and recrystallised from warm water. On slow evaporation of the saturated solution, the small crystals can grow to fairly big individuals.

Splendid, dark-red to red-brown, very lustrous and clear crystals of octahedrical habit. The angular values of the different individuals may differ about 20′; every crystal as a whole however is geometrically very well built.

Rhombic-bipyramidal.

$a : b : c = 0{,}8700 : 1 : 1.7399.$

The crystals may be considered as pseudo-tetragonal, if the *b*-axis is chosen as the pseudo-quaternary axis.

Observed Forms: $o = \{112\}$, and $q = \{021\}$, about equally well developed; the faces of q are sometimes a little smaller than those of o, but both give very sharp images. Furthermore $c = \{001\}$, much smaller but giving good reflections; $w = \{111\}$, very narrow and somewhat dull, but quite measurable; $b = \{010\}$, extremely narrow and reflecting badly; $x = \{101\}$, rare and almost imperceptible.

Angular values:	*Observed:*	*Calculated:*
$o : o = (112) : (1\bar{1}2) =$	*63° 12′	—
$c : q = (001) : (021) =$	*73 58	—
$c : o = (001) : (112) =$	53 3	52° 58′
$o : w = (112) : (111) =$	16 11	162 2
$w : w = (111) : (11\bar{1}) =$	41 35	41 20
$q : q = (021) : (0\bar{2}1) =$	32 4	32 4
$q : b = (021) : (010) =$	16 2	16 2
$o : q = (112) : (021) =$	48 1	47 56
$c : x = (001) : (101) =$	*circa* 45 —	44 59½
$x : x = (101) : (10\bar{1}) =$	89 52	90 1

A distinct cleavage could not be observed.

On {001} diagonal extinction; the crystals are not perceptibly dichroitic. The plane of the optical axis is {010}; the c-axis is first bisectrix. The apparent optical angle is very small.

The specific gravity of the crystals at 25° C. was pycnometrically determined $d_4^{25°} = 2.270$; the molecular volume is thus: 562.10.

Topical parameters: $\chi : \psi : \omega = 6.2532 : 7.1877 : 12.5070$.

IX. Dextrogyratory Luteo-Triethylenediamine-Cobalti-iodide.

Formula: $\{Co(Aein)_3\} J_3 + 1 H_2O$.

This compound was prepared by the precipitation of a solution of the dextrogyratory bromide with a concentrated solution of potassium-iodide; the precipitate was washed out and recrystallised from warm water. Analysis showed, that the compound, just like the racemic one, crystallizes with 1 molecule of water.

Long, dark-red, in transmitted light, blood-red needles, with lustrous faces. All faces of the prism-zone, with the exception of those of the forms {100} and {010}, are vertically striated; the vertical zone furthermore shows many vicinal forms, which make it often difficult, to find the exact angular values. (fig. 10).

Rhombic-bipyramidal.

$a : b : c = 0{,}8276 : 1 : 0{,}7386.$

Observed Forms: $m = \{340\}$, the largest of all prism-faces, giving like all prismatic faces, multiple reflections and diffraction-images; $b = \{010\}$, and $a = \{100\}$, somewhat narrower, but giving sharp reflections; $p = \{120\}$ and $s = \{3.16.0\}$, both narrower than a, with s in most cases again smaller than p; $q = \{011\}$, well developed, but with rather appreciably oscillating angular values; $r = \{102\}$, giving very sharp reflections and easily measurable; ; $t = \{104\}$ and $\sigma = \{101\}$, small but distinctly reflecting; $w = \{071\}$, very small and dull.

The habit of the crystals is elongated parallel to the c-axis.

A distinct cleavage was not observed.

On all faces of the vertical zone a normal extinction is found; no appreciable dichroism. The plane of the optical axes is $\{001\}$, with the b-axis as first bisectrix. The apparent axial angle is very small; the dispersion is strong: $\rho < v$. The birefringence is positive.

The specific gravity of the crystals at 25° C. was: $d_{4^\circ}^{25^\circ} = 2.289$; the molecular-volume is thus: 278,72.

Topical parameters: $\chi : \psi : \omega = 6{,}3699 : 7{,}6968 : 5{,}6849$.

Angular Forms:		*Observed:*	*Calculated:*
$a : r$ =	(100) : (102) =	*65° 57′	—
$p : q$ =	(120) : (011) =	*59 26	—
$r : q$ =	$(\bar{1}02)$: (011) =	42 48	42° 44′
$r : p$ =	$(\bar{1}02)$: $(\bar{1}\bar{2}0)$ =	77 41	77 50
$a : m$ =	(100) : (340) =	47 50	47 49
$m : p$ =	(340) : (120) =	11 4	11 $2\frac{2}{3}$
$p : s$ =	(120) : (3.16.0) =	18 20	18 $22\frac{1}{3}$
$s : b$ =	(3.16.0) : (010) =	12 46	12 46
$r : r$ =	(102) : $(\bar{1}02)$ =	48 12	48 6
$m : q$ =	(340) : (011) =	63 40	63 53
$q : q$ =	(011) : $(0\bar{1}1)$ =	72 52	72 54
$b : q$ =	(010) : (011) =	53 34	53 33
$r : t$ =	(101) : $(\bar{1}04)$ =	11 38	11 $28\frac{1}{3}$
$t : t$ =	(104) : $(\bar{1}04)$ =	25 15	25 $7\frac{1}{3}$
$r : \sigma$ =	(102) : (101) =	17 48	17 42
$\sigma : a$ =	(101) : (100) =	48 25	48 15
$b : w$ =	(010) : (071) =	10 59	10 $56\frac{3}{4}$

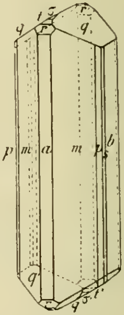


Fig. 10.

Dextrogyratory Triethylenediamine-Cobalti-iodide.

On $\{100\}$ we obtained with mixtures of alcohol and water very long, acute, hexagonal corrosion-figures and irregularly bordered rectangular elevations arranged in long rows. On the other hand we obtained on the faces of the prism triangular and trapezium-shaped corrosion-figures, *which proved beyond doubt the presence of a horizontal symmetry-plane, parallel to* $(//\{001\})$.

The Röntgenogram of a plate parallel to $//\{001\}$ was very irregular and rudimentary, very probably however at least one single symmetry-plane might be present.

X. *Laevogyratory Luteo-Triethylenediamine-Cobalti-iodide.*

Formula: $\{Co\,(Aein)_3\}\,J_3 + 1\ H_2O$.

This antipode was prepared in a quite analogous way to that indicated in the case of the dextrogyratory component, and recrystallised from warm water. The crystals also contain, according to analysis, 1 molecule of water of crystallisation. They may grow to considerable size: one individual had a volume of more than 0.5 ccm.

Flat, dark-red to blood-red crystals, with lustrous faces, which give multiple reflections however, especially in the prism-zone.

Observed Forms: $p = \{120\}$, large, but giving multiple images: $q = \{011\}$, also largely developed, and better reflecting than p; $b = \{010\}$, very lustrous and well reflecting; $r = \{102\}$, small, but very lustrous and well measurable; $m = \{340\}$, very narrow: $\sigma = \{101\}$, very small, and often absent; $a = \{100\}$, extremely narrow.

The habit is somewhat elongated with respect to the c-axis. (fig. 11).

Rhombic-bipyramidal.

$$a : b : c = 0.8256 : 1 : 0.7395.$$

Angular Values:	*Observed*:		*Calculated*:	
$b : p = (010) : (120) =$	*31°	12′	—	
$q : q = (011) : (0\bar{1}1) =$	*72	58	—	
$b : q = (010) : (011) =$	53	31	53°	31′
$a : p = (100) : (120) =$	58	43	58	48
$r : r = (102) : (\bar{1}02) =$	48	10	48	$15\frac{1}{3}$
$r : \sigma = (102) : (101) =$	17	52	17	$43\frac{1}{3}$
$p : q = (120) : (011) =$	59	22	59	26
$m : p = (340) : (120) =$	11	10	10	57

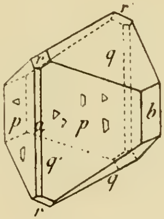


Fig. 11.
Laevogyratory
Triethylenediamine-
Cobalti-iodide.

No distinct cleavage was observed; one parallel to $\{001\}$ may perhaps be supposed.

The optical orientation is the same as in the case of the dextrogyratory compound.

The specific gravity of the crystals at 25° C is: $d\frac{25^\circ}{4^\circ} = 2.288$: the molecular volume is thus: 278.84.

Topical parameter: $\chi : \psi : \omega = 6.3580 : 7{,}7010 : 5.6950$.

With cold water we obtained on {010} elongated, commonly irregularly shaped corrosion-figures. They seem to be symmetrical with respect to {100}, but perfect certainty could not be procured, notwithstanding many attempts made for this purpose.

XI. *Racemic Luteo-Triethylenediamine-Cobalti-rhodanide.*

Formula: $\{Co(Aein)_3\}(CNS)_3$.

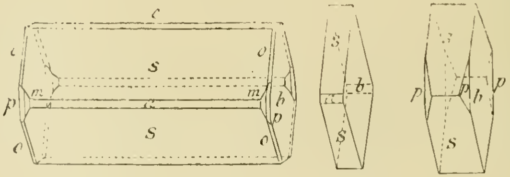
The compound was prepared by double composition of the racemic bromide with a concentrated solution of potassiumrhodanide, washing the yellow precipitate, and recrystallising from hot water. The crystals grow to rather large individuals in the solution, saturated at room-temperature and have a flat, spindle-like shape. According to analysis, they are *anhydrous.*

Red-yellow or yellow-brown, flat, spindle-shaped, acute, often distorted crystals, which are easily measurable.

Rhombic-bipyramidal.

$a : b : c = 0.8405 : 1 : 0.8130.$

Observed Forms: $s = \{201\}$, prominent and reflecting well, but sometimes giving multiple images; $b = \{010\}$ and $p = \{120\}$, giving extremely sharp reflections, and thus exactly measurable; $m = \{110\}$, lustrous, somewhat smaller than p; $o = \{211\}$ and $x = \{321\}$, as narrow bluntings. The crystals are elongated parallel to the b-axis, in several cases also parallel the a-xis; in the last mentioned case the habit of the small crystals is the acute, spindle-like one already described. (fig. 12 a, b and c).



a b. c

Fig. 12.

Racemic Triethylenediamine-Cobalti-rhodanide.

Angular Values:	*Observed:*	*Calculated:*
$s : c = (201) : (001) =$	*62° 40′	—
$b : p = (010) : (120) =$	*30 45	—
$s : a = (201) : (100) =$	27 20	27° 20′
$p : a = (120) : (100) =$	59 15	59 15
$p : m = (120) : (110) =$	19 5	19 $12\frac{1}{3}$
$p : s = (120) : (201) =$	62 52	62 59
$p : x = (120) : (321) =$	33 55	33 57
$x : s = (321) : (201) =$	29 16	29 2
$b : o = (010) : (211 =$	69 19	69 32
$o : s = (211) : (201) =$	20 41	20 28

A distinct cleavage was not observed.

In the zone of the ortho-diagonal the extinction is everywhere normal; the crystals are not distinctly dichroitic. On {120} triangular corrosionfigures were obtained, which were in agreement with the symmetry mentioned.

The specific weight of the crystals was at 25° C. pycnometrically determined to be: $d_{4^\circ}^{25^\circ} = 1.511$; the molecular volume is: 547.24.

Topical parameters: $\chi : \psi : \omega = 7.8053 : 9.2864 : 7.5499$.

XII. Dextrogyratory Luteo-Triethylenediamine-Cobalti-rhodanide.

Formula: $\{Co(Aein)_3\}(CNS)_3$.

The active compounds were prepared from the dextro- or laevogyratory bromides in a quite analogous way, as indicated by the racemic rhodanide. Analysis proved that these optically active modifications crystallise *without* water of crystallisation.

Beautifully formed, orange to blood-red, splendidly reflecting, quadrangular thick plates or flattened, shortprismatic, small crystals, which make accurate measurements quite possible. They are extraordinarily rich in faces, and geometrically generally very well built. (fig. 13).

Rhombic-bipyramidal.

$a : b : c = 0.8494 : 1 : 0.8376$.

Observed Forms: $c = \{001\}$, in most cases predominant and always well developed; $q = \{011\}$, with large faces; $r = \{101\}$, also large, but narrower than q; $a = \{100\}$, well developed and giving excellent images, just like $b = \{010\}$, whose faces are somewhat narrower;

$s = \{201\}$ and $t = \{012\}$, well developed; there are commonly only two faces of the form t present.

Further: $o = \{121\}$, showing among all pyramids present the largest faces; $\omega = \{111\}$, somewhat smaller than o; $h = \{122\}$, very small, but giving distinct images; $m = \{110\}$ and $p = \{120\}$, very small and subsidiary, but measurable.

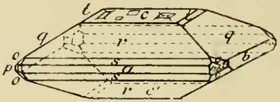


Fig. 13.

Dextrogyratory Triethylenediamine-Cobalti-rhodanide.

Angular Values:	*Observed*:		*Calculated*:	
$c : q = (001) : (011) =$	*39°	57	—	
$r : q = (101) : (011) =$	*56	56	—	
$r : s = (101) : (201) =$	18	23	18°	31′
$c : r = (001) : (101) =$	44	39	44	36
$s : a = (201) : (100) =$	26	58	26	53
$b : q = (010) : (011) =$	50	2	50	3
$s : q = (201) : (011) =$	69	39	69	42
$c : t = (001) : (012) =$	22	39	22	43½
$t : q = (012) : (011) =$	17	16	17	13½
$r : w = (\bar{1}0\bar{1}) : (\bar{1}1\bar{1}) =$	30	57	30	49
$w : o = (\bar{1}1\bar{1}) : (\bar{1}2\bar{1}) =$	19	9	19	12½
$o : b = (\bar{1}2\bar{1}) : (010) =$	40	3	39	58½
$c : h = (001) : (122) =$	44	4	44	11
$h : o = (1\bar{2}2) : (1\bar{2}\bar{1}) =$	73	0	73	2½
$c : o = (001) : (121) =$	62	51	62	46½
$o : o = (\bar{1}2\bar{1}) : (121) =$	80	6	79	57
$o : q = (\bar{1}2\bar{1}) : (011) =$	81	56	81	53½
$o : p = (121) : (120) =$	27	9	27	9
$a : m = (100) : (110) =$	40	15	40	21
$m : b = (110) : (010) =$	49	45	49	39
$a : w = (100) : (111) =$	52	44	52	55
$w : m = (111) : (110) =$	37	46	37	42
$w : c = (111) : (001) =$	52	24	52	18

A distinct cleavage was not observed.

On {001}, {011} and {101} everywhere normal extinction. The crystals are not appreciably dichroitic. The optical axial plane is {100}; the apparent axial angle is small, and the c-axis is first bisectrix.

The specific weight of the substance at 25° C was found to be: $d\,^{25°}_{4°} = 1.502$; the molecular volume is: 275.26.

Topical parameters: $\chi : \psi : \omega = 6.1893 : 7.2867 : 6.1034$.

With tepid water on {001} beautiful corrosion-figures were obtained after short treatment. They represented rectangular, pyramidal elevations, *which were distinctly symmetrical with respect to the planes* {100} *and* {010}. Consequently the crystals must be considered as having *bipyramidal* symmetry; with mixtures of alcohol and water rectangular, bilateral-symmetrical corrosion-figures were also obtained, which are in agreement with the holohedrical symmetry of the rhombic system.

XIII. Laevogyratory Luteo-Triethylenediamine-Cobalti-rhodanide.

Formula: $\{Co(Aein)_3\}(CNS)_3$.

Thick, short-prismatic, orange- or blood-red needles, which are very well built, and which give excellent images. Although the habit is different from that of the dextrogyratory compound, the crystalform is evidently quite the same.

Rhombic-bipyramidal.

$a : b : c = 0.8494 : 1 : 0.8375$.

Observed Forms: $b = \{010\}$, predominant and, like $a = \{100\}$, which is also well developed, giving excellent images; $c = \{001\}$, small but very lustrous; $s = \{201\}$ and $r = \{101\}$, rather large; $q = \{011\}$, somewhat larger yet, and like both foregoing forms, reflecting excellently; $m = \{110\}$, about as broad as r, and reflecting well; $p = \{120\}$, narrow and a little duller; $o = \{121\}$, well developed; $\omega = \{111\}$, with small faces between o and r. The habit is short-prismatic with respect to the c-axis, with predominance of {010} and {100}. (Fig. 14).

Angular Values:		*Observed:*	*Calculated:*
$c : q = (001) : (011) =$		*39° 54′	—
$r : q = (101) : (011) =$		*56 56	—
$q : b = (011) : (010) =$		50 6	50° 6′
$a : s = (100) : (201) =$		26 53	26 53
$s : r = (201) : (101) =$		18 35	18 31
$r : c = (101) : (001) =$		44 34	44 36
$a : m = (100) : (110) =$		40 22	40 21
$m : p = (110) : (120) =$		19 13	19 10
$p : b = (120) : (010) =$		30 35	30 29
$b : o = (010) : (121) =$		40 0	39 58½
$o : r = (121) : (101) =$		50 0	50 1½
$r : \omega = (101) : (111) =$	*circa*	20 —	20 35½
$\omega : o = (111) : (121) =$		30 1	29 26

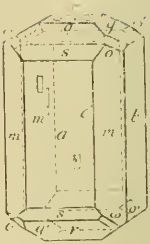


Fig. 14.
Laevogyratory
Triethylenediamine-
Cobalti-rhodanide.

A distinct cleavage could not be found.

The optical properties are the same as indicated in the previous case.

Ths specific gravity of the crystals was pycnometrically determined to be: $d\frac{25^\circ}{4^\circ} = 1.496$; the molecular volume is: 276.37.

Topical parameters $\chi : \psi : \omega = 6.1979 : 7.2968 : 6.1110$.

Of a plate parallel to {001} we obtained a Röntgenogram which notwithstanding its imperfectness, in every case showed the presence of at least one plane of symmetry.

XIV. *Racemic Luteo-Triethylenediamine-Cobalti-perchlorate*

Formula: $\{Co(Aein)_3\}(ClO_4)_3$.

The salt was prepared by double decomposition between the racemic bromide and silver-perchlorate.

It is rather difficult to obtain well developed crystals of this compound; commonly thin, rectangular, tabular crystals are obtained possessing round edges and giving considerably oscillating angular values; or they are complicated intergrowths of extremely thin plates arranged in rosettes. Between crossed nicols such intergrowths will in no situation show a complete extinction, but lamellar polarisation and high interference-colours, in some cases also a mosaic-like structure:

Finally we succeeded in making the necessary measurements with the rectangular, tabular crystals.

Rhombic-bipyramidal.

$a : b : c = 0.8569 : 1 : 2.7751$.

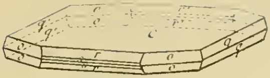


Fig. 15.
Racemic Triethylenediamine-Cobaltiperchlorate.

Observed Forms: $c = \{001\}$, large and lustrous, in most cases striated parallel to the intersection: $c : q$; $r = \{102\}$, $o = \{111\}$ and $q = \{011\}$, about equally largely developed; commonly q gives the better, r the feebler images. Finally again: $s = \{101\}$, narrow, but easily measurable. The habit is tabular parallel to $\{001\}$, with a slight elongation parallel to the b-axis.

Angular Values:	*Observed:*	*Calculated:*
$c : q = (001) : (011) =$	*70° 11′	—
$c : r = (001) : (102) =$	*58 20	—
$c : o = (001) : (111) =$	77 10	76° 49′
$c : s = (001) : (101) =$	72 56	72 $50\frac{1}{3}$
$s : s = (101) : (10\bar{1}) =$	34 8	34 $19\frac{1}{3}$
$r : r = (102) : (10\bar{2}) =$	63 35	63 20
$q : q = (011) : (01\bar{1}) =$	40 2	39 38
$r : s = (102) : (101) =$	14 38	14 36

On $\{001\}$ the extinction is perpendicular and parallel with respect to the intersections $c : r$ and $c : q$. The plane of the optical axes is $\{010\}$; the crystals are distinctly dichroitic, namely orange for vibrations parallel to the plane of the optical axes, orange-yellow for such as are perpendicular to it.

The specific weight of the crystals at 25°.1 C. was: $d_{4_0} = 1.878$; the molecular volume is thus: 572.72.

Topical parameters: $\chi : \psi : \omega = 5.3314 : 6.2217 : 17.2660$.

XV. *Dextrogyratory Luteo-Triethylenediamine-Cobalti-perchlorate.*

Formula: $\{Co\,(Aein)_3\}\,(ClO_4)_3$.

The compound was prepared by transformation of the d-bromide by means of a solution of silver-perchlorate. The salt crystallizes from its aqueous solution in the shape of flat, brownish-red, very lustrous crystals, which show rather strong oscillations of their angular values, especially in the vertical zone. (Fig. 16).

They are *rhombic bisphenoidic*.

$$a : b : c = 1.0572 : 1 : 0.6801.$$

Observed Forms: $b = \{010\}$, strongly predominant and rather sharply reflecting; $a = \{100\}$, very narrow or wholly absent, but with some crystals prominent; $m = \{110\}$, well developed, giving however multiple images; $r = \{101\}$ and $q = \{011\}$, giving very sharp reflections; $o = \{111\}$, in most cases broader and larger than $\omega = \{1\bar{1}1\}$; this last form reflects very well.

Angular Values:	*Observed*:	*Calculated*:
$b : q = (010) : (011) =$	*55° 47′	—
$b : o = (010) : (111) =$	*60 14	—
$q : q = (011) : (0\bar{1}1) =$	68 26	68° 26′
$o : r = (111) : (101) =$	29 46	29 46
$b : m = (010) : (110) =$	43 28	43 24½
$m : a = (110) : (100) =$	46 32	46 35½
$r : r = (101) : (\bar{1}01) =$	65 30	65 30
$m : q = (110) : (011) =$	65 48	65 53½
$q : r = (011) : (101) =$	46 4	45 56
$r : m = (101) : (110) =$	68 16	68 10½
$a : o = (100) : (111) =$	62 3	61 59½
$o : c = (111) : (001) =$	43 0	43 6½
$b : \omega = (010) : (1\bar{1}1) =$	60 16	60 14
$\omega : r = (1\bar{1}1) : (101) =$	29 50	29 46

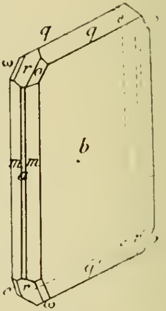


Fig. 16.
Dextrogyratory
Triethylenediamine-
Cobalti-perchlorate.

No distinct cleavage was observed.

The specific gravity of the crystals was pycnometrically determined at 25° C., and found to be $d\frac{25^\circ}{4^\circ} = 1.881$, the molecular volume is thus: 285.80, and the topical axes are: $\chi : \psi : \omega = 7.7731 : 7.3526 : 5.004$.

XVI. *Laevogyratory Triethylenediamine-Cobalti-perchlorate.*

Formula: $\{Co\,(Aein)_3\}\,(ClO_4)_3$.

This salt was prepared from the corresponding *l*-bromide by means of silver-perchlorate, and the concentrated solution afterwards slowly evaporated at 15° C.

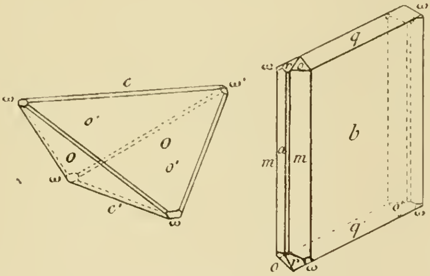
From an aqueous solution, still containing a trace of the silver-salt in excess, the salt crystallized in the form of beautiful, sphenoidic crystals (fig. 17*a*), which immediately showed the presence of hemihedrical symmetry. From the pure solutions in most cases the flat, rectangular crystals, reproduced in fig. 17*b* were obtained; they had a brownish-red or brownish-yellow colour, and show more constant angular values than the sphenoidic crystals, whose angles oscillate and which possess considerable geometrical anomalies.

Evidently these kinds of crystals are however quite identical.

Rhombic-bisphenoidic.

$$a : b : c = 1.0580 : 1 : 0.6806.$$

Observed Forms: $b = \{010\}$, highly predominant, and reflecting well; the faces are however often spoiled, and then give multiple reflections. Further $m = \{110\}$, giving good images and about as large as $c = \{011\}$, which form shows very lustrous faces; $r = \{101\}$, giving sharp images, and very well developed, about as large as $o = \{111\}$; $\omega = \{1\bar{1}1\}$ on the contrary small, and rather dull, although giving well defined images; $a = \{100\}$, very narrow and dull. In



a Fig. 17. *b*

Laevogyratory Triethylenediamine-Cobaltiperchlorate.

the crystals drawn in fig. 17*a*, the form $o = \{111\}$ is predominant; $\omega = \{1\bar{1}1\}$ small and narrow, $b = \{010\}$, narrow but reflecting well, like $a = \{100\}$, which form is developed about equally to it; $c = \{001\}$ in most cases absent, but rarely present with only one single curved and rudimentary face.

Angular Values:	*Observed:*		*Calculated:*	
$b : o = (010):(111) =$	*60	12′	—	
$b : m = (010):(110) =$	*43	23	—	
$b : q = (010):(011) =$	55	48	55°	46′
$a : m = (100):(110) =$	46	39	46	37
$q : q = (011):(0\bar{1}1) =$	68	28	68	$28\frac{1}{2}$
$\omega : b = (1\bar{1}1):(0\bar{1}0) =$	60	13	60	$12\frac{2}{3}$
$\omega : r = (1\bar{1}1):(101) =$	29	49	29	45
$r : a = (101):(\bar{1}00) =$	57	12	57	17
$r : r = (101):(101) =$	65	43	65	36
$a : o = (100):(111) =$	62	0	62	0
$c : o = (001):(111) =$	43	0	43	8
$o : \omega = (111):(11\bar{1}) =$	93	48	93	44
$\omega : o = (\bar{1}11):(111) =$	55	11	55	46
$o : \omega = (111):(1\bar{1}1) =$	59	50	59	32
$o : o = (111):(1\bar{1}\bar{1}) =$	86	13	86	16

No distinct cleavage could be observed.

Feebly dichroitic: on $\{010\}$ for vibrations parallel to the *a*-axis orange-yellow; for those perpendicular to these, yellow-orange.

The plane of the optical axis is $\{001\}$; the *a*-axis is probably first bisectrix.

The specific gravity of the crystals was pycnometrically determined to be: $d\,\frac{25^\circ}{4^\circ} = 1.888$; the molecular volume is thus: 284.74.

Topical parameters: $\chi : \psi : \omega = 7.7657 : 7.3399 : 4.9955$.

XVII. Racemic Triethylenediamine-Cobalti-nitrite.

Formula: $\{Co\,(Aein)_3\}\,(NO_2)_3$

Thin, orange-yellow, in thicker layers orange-brown, hexagonal plates, often showing mutilated faces, and intergrowths parallel $\{0001\}$, $m : m = (10\bar{1}0):(01\bar{1}0) = 60°$; $m : c = (10\bar{1}0):(0001) = 90°$.

The crystals are uniaxial and negative.

The optically active components are so highly soluble that it was impossible up to now, to obtain crystals suitable for measurements.

About the general conclusions, relating to the facts here described, vid. Publication I (March 1915) on this same subject.

Laboratory for Inorganic and Physical
Chemistry of the University.

Groningen, March 1915.

Chemistry. — "*Investigations on the Temperature-Coefficients of the free Molecular Surface-Energy of Liquids at Temperatures from* -80° *to* 1650° *C.*" **IX.** *The Surface-Energy of homologous Aliphatic Amines.* By Prof. F. M. Jaeger and Dr. Jul. Kahn. (Communicated by Prof. P. van Romburgh).

(Communicated in the meeting of April 23, 1915).

§ **1.** During the continuation of our studies regarding the influence of special substitutions in the molecules on the specific and molecular surface-energy of homologous compounds, our attention was drawn to the fact, that the free surface-energy and its temperature-coefficient in the case of organic derivatives of the trivalent nitrogen often show remarkably low values. We therefore determined to study systematically a greater number of the homologous series of the aliphatic amines in the way previously described. The results of these investigations are communicated in the following pages.

A single determination of the value of the free surface-energy of carefully purified and dried anhydrous *ammonia*: NH_3 taught us that with this mother-substance itself, even at lower temperatures, the value of χ is a relatively small one.

We found at -73° C. for the specific surface-tension of liquid ammonia: about **37** Erg pro cm². ¹), a value considerably different from the sparsely published data in literature regarding the surface-energy of this liquid. As we had at the moment no means of maintaining constant lower temperatures for a longer time, we could not for the present continue these experiments further; however we hope to be able to return to these researches later on.

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¹) The radius of the capillar tube was: 0.04595 c.m., the depth of immersion: 0.1 mm. The maximum pressure observed was: 1.210 mm. of mercury of 0° C.

The 23 compounds of this homologous series studied here are: *Methyl-*, *Dimethyl-*, and *Trimethylamine; Ethyl-*, *Diethyl-*, and *Triethylamine; norm. Propyl-*, *Dipropyl-*, and *Tripropylamine; Isopropylamine; Allylamine*; *norm. Butylamine*; *Isobutyl-*, *Diisobutyl-*, and *Triisobutylamine*; *tertiary Butylamine*; *norm. Amylamine*; *Isoamyl-*, and *Diisoamylamine*; *tertiary Amylamine*; *norm. Hexyl-*, and *Isohexylamine*; *norm. Heptylamine*; while for the purpose of comparison the measurements of *Formamide* are reproduced here also.

The pure amines were first dried by means of metallic sodium or potassiumhydroxide, then fractionated in vacuo over *KOH*; because of the inevitable bumping of the liquid, the thermometer-readings oscillated within limits of about 2°.

The specific gravity must be determinated with most of these substances by means of a volumeter, because of their volatility and their tendency to attract carbondioxide and water-vapour from the atmosphere. Especially in the case of the lower-boiling amines these experiments appeared to be highly cumbersome and demanded much time; however we think the obtained results to be exact within about 0.1°/₀, which must be quite sufficient for the use here made of them.

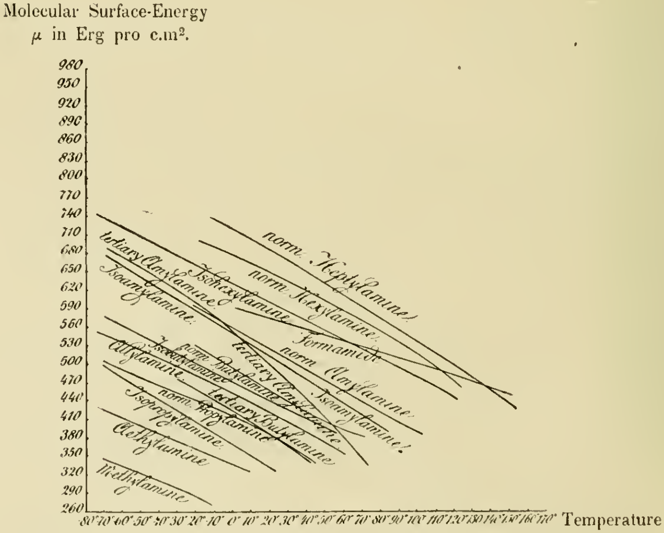

Fig. 1. Primary Amines.

§ 2.

I.

Monomethylamine: $CH_3 . NH_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
−70°	1.324	1764.8	29.2	0.759	346.7
−49	1.225	1633.2	26.5	0.736	321.2
−20	1.068	1423.9	23.0	0.705	286.9
−18	1.049	1399.8	22.7	0.702	283.9
−12	1.005	1340.1	21.7	0.696	272.9

Molecular weight: **31.05.**

Radius of the Capillary tube: 0.03343 cm.
Depth: 0.1 mm.

The dry amine boils under atmospheric pressure at −6° C. At −79° it is still a thin fluid mass, without any trace of beginning crystallisation. At the boilingpoint the value of χ can only slightly differ from: 20.9 Erg. pro cm².

The specific gravity was determined by means of a volumeter: at −79° C. it was: 0.7691; at 0° C. 0.6831. At t° it may be calculated from: $d_{4^\circ} = 0.6831 - 0.00109\, t$.

The temperature-coefficient of μ increases gradually at higher temperatures: between −70° and −20° C. it is: **1.20**; between −20° and −18° C. it is: **1.50**; and between −18° and −12°: **1.83** Erg. per degree.

II.

Dimethylamine: $(CH_3)_2 NH$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
−78°	0.842	1121.4	25.2	0.757	384.2
−50	0.745	995.5	22.5	0.730	351.4
−23	0.672	897.0	20.2	0.703	323.5
0	0.606	807.9	18.1	0.680	296.4
5	0.586	783.5	17.7	0.675	291.3

Molecular weight: **45.06.**

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The liquid boils at $+7.^\circ 5$; at −76° C. it is not yet solidified. At the boilingpoint χ has the value: 17.5 Erg. per cm². The specific weight at 0° C. was: 0.6804; at −79° C.: 0.758; at t° C.: it is: $d_{4^\circ} = 0.6804 - 0.0009886\, t$.

The temperature-coefficient of μ has a mean value of **1.10** Erg. per degree.

III.

Trimethylamine: $(CH_3)_3N$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—73°	0.827	1102.5	24.8	0.748	456.6
—52	0.737	983.7	22.2	0.725	417.4
—32	0.678	897.8	20.0	0.704	383.5
—19	0.627	834.8	18.6	0.691	361.0
— 4	0.583	777.2	17.3	0.675	341.1

Molecular weight: **59.10.**

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The liquid boils at about —3° C.; even at —75° C. it was still as thin as water, and no trace of crystallisation could be observed. The specific gravity at 0° C. was: 0.6709; at —79° C.: 0.7537; at t° C. is $d_{4^\circ} = 0.6709 - 0.001048\ t$. The temperature-coefficient of μ decreases slowly with rising temperature: between —73° and —52° C. it is: **1.89**; between —52° C. and —19° C.: **1.71**; and between —19° and —4° C.: **1.33** Erg. per degree.

IV.

Ethylamine: $(C_2H_5) . NH_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—74°	0.961	1281.2	29.1	0.785	433.1
—33	0.807	1078.1	24.6	0.741	380.5
—21.5	0.773	1030.6	23.4	0.729	365.9
0	0.709	945.2	21.4	0.708	341.1
9.9	0.676	901.2	20.4	0.698	328.4

Molecular weight: **45.07.**

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The amine boils at 20° C.; even at —76° it is liquid still. At the boiling-point χ is about: 19.9 Erg. pro cm². The specific weight at 0° C. was volumetrically determined to be: $d_{4^\circ} = 0.708$ at 0° C.; and 0.790 at —79° C. At t° C. it is: $d_{4^\circ} = 0.7085 - 0.001032\ t$.

The temperature-coefficient of μ is constant and **1.25** Erg. per degree.

V.

Diethylamine: $(C_2H_5)_2\,NH$

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
21°.5	0.765	1019.9	23.0	0.752	486.2
0	0.693	923.9	20.8	0.731	448.1
10	0.655	873.8	19.7	0.720	428.8
23.4	0.616	819.5	18.3	0.708	402.8
35	0.587	781.4	17.4	0.695	387.7
45	0.568	754.5	16.6	0.686	373.1

Molecular weight: **73.10.**

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The amine boils at 56° C. and crystallises at about —40° C. At the boilingpoint χ possesses the value: 16.2 Erg. pro cm². The specific gravity at 0° C. was: 0.7315; at 25° C.: 0.7045; at 50° C.: 0.677. At $t°$ in general: $d_{4°} = 0.7315 - 0.00107\,t - 0.000001\,t^2$.
The temperature coefficient of μ has a mean value of: **1.69** Erg. per degree.

VI.

Triethylamine: $(C_2H_5)_3\,N$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
—70°	0.929	1238.5	28.1	0.816	698.5
—20.5	0.740	985.5	22.1	0.769	571.5
0	0.658	887.0	20.0	0.749	526.4
25.6	0.596	794.6	17.8	0.725	478.8
41.2	0.572	753.1	16.7	0.710	455.5
55.7	0.505	681.1	15.8	0.695	437.1
70.4	0.478	637.3	14.1	0.681	395.4
84.3	0.453	603.9	13.3	0.667	378.2

Molecular weight: **101.13.**

Radius of the Capillary tube: 0.04676 cm.
Depth: 0.1 mm.

The liquid boils under 762 mm. at 87° or 89° C. Even at —72° the amine is still a thin liquid. The specific weight was determined volumetrically: at 0° C. it was: 0.7495; at 25° C.: 0.7255; at 50° C.: 0.701. At $t°$ C.: $d_{4°} = 0.7495 - 0.00095\,t - 0.0000004\,t^2$. At the boilingpoint χ has the value: 12.8 Erg.

The temperature-coëfficient of μ decreases gradually with increasing temperature: between —70° and —20° C. it is: **2.56**; between —20° C and 0° C.: **2.20**; between 0° and 26° C.: **1.86**; and between 26° and 84° C: **1.71** Erg. per degree Celsius.

VII.

normal Propylamine: $C_3H_7NH_2$.

Temperatuur in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm²	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
−71°	0.951	1267.9	29.3	0.817	508.6
−21	0.795	1059.9	24.5	0.763	445.1
0	0.725	966.6	22.3	0.741	412.8
15	0.665	889.6	20.7	0.724	389.4
25.6	0.639	851.9	19.7	0.714	374.1
42	0.585	779.8	18.0	0.696	347.7

Molecular weight: **59.08.**

Radius of the Capillary tube: 0.04676 cm.
Depth: 0.1 mm.

The liquid boils under a pressure of 760 mm. constantly at 47.°5 C.; at −72° C. it is still very thin. The density at 0° C. is: 0,741; at 25° C.: 0,714; at 40° C.: 0.698. At $t°$ in general: $d_{4°} = 0.741 - 0.001075\,t$. At the boilingpoint the value of χ is: 17.5 Erg.

The temperature-coefficient of μ is fairly constant and equal to: **1.54** Erg. per degree.

VIII.

Dipropylamine: $(C_3H_7)_2NH$.

Temperature in ° C	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
*−19°.5	0.816	1087.9	25.7	0.775	661.0
* 0	0.746	994.6	23.5	0.756	614.6
29.9	0.652	878.0	20.4	0.728	547.1
48.3	0.596	795.4	18.4	0.712	500.8
65	0.546	728.5	16.8	0.696	464.2
80.9	0.505	674.0	15.6	0.682	434.2
104.5	0.453	603.9	13.8	0.662	394.3

Molecular weight: **101.10.**

Radius of the Capillary tube: 0.04777 cm.; in the measurements indicated by *, the radius was: 0.04839 cm.
Depth: 0.1 mm.

Under a pressure of 762 mm. the liquid boils at 110.°5 C. Even at −78° C. it remained clear, but solidifies afterwards into a mass of white crystals, melting at −45° C. At the boilingpoint $\chi = 13.9$ Erg. pro cm². The specific weight at 0° C. was: 0.7565; at 25° C.: 0.733; at 50° C.: 0.710. At $t°$ C. it is: $d_{4°} = 0.7565 - 0.00095\,t + 0.0000004\,t^2$. The temperature-coefficient of μ decreases gradually with increasing temperature: it is **2.38** between −20° and 48° C; between 48° and 65° C.: **2.19**; between 65° and 81° C.: **1.89**; between 81° and 104° C.: **1.69** Erg.

IX.

Tripropylamine: $(C_3H_7)_3N$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—71°	0.977	1302.5	30.6	0.830	948.2
—20.5	0.816	1087.9	25.6	0.789	820.6
0	0.758	1010.4	23.6	0.773	766.9
25.6	0.693	923.9	21.5	0.753	710.9
40.5	0.647	862.6	20.1	0.741	671.8
55.5	0.607	810.5	18.8	0.729	635.2
80.2	0.545	726.6	16.8	0.709	578.3
92.2	0.513	684.4	15.8	0.699	549.0
116.1	0.460	613.5	14.1	0.680	499.0
*136	0.421	561.3	12.6	0.664	453.1
*149.5	0.385	513.9	11.5	0.653	418.2

Molecular weight: **143.18**.

Radius of the Capillary tube: 0.04792 cm.; in the observations indicated by *, the radius was: 0.04670 cm.
Depth: 0.1 mm.

The amine boils constantly at 157° C. and 765 mm. pressure. Even at —79° it remains liquid. The specific gravity was determined with the aid of a volumeter: at 0° C. it was 0.773; at 25° C.: 0.753; at 50° C.: 0.733. At t° generally: $d_{4^\circ} = 0.773 - 0.0008\,t$. At the boilingpoint χ was about: **10.9** Erg.

The temperature coefficient of μ is fairly constant; its mean value is: **2.41** Erg. per degree.

X.

Isopropylamine: $C_3H_7NH_2$.

Temperature in ° C.	Maximum Pressure H		Surface tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—79°	0.929	1238.5	28.1	0.781	502.7
—10.5	0.734	975.7	21.8	0.728	408.7
5	0.636	852.0	19.4	0.709	370.1
1	0.596	794.6	17.7	0.694	342.6
25.2	0.564	751.9	16.8	0.684	328.3

Molecular weight: **59.09**.

Radius of the Capillary tube: 0.04676 cm.
Depth: 0.1 mm.

The amine boils at 33 —35° C., under 760 mm. The specific gravity at 18° C. is: 0.691; the other values were calculated by adopting 0.001 as the mean temperature coefficient, which may not deviate much from the true value of it. At the boilingpoint χ has the value: 16.0 Erg.

The temperature-coefficient of μ is fairly constant, and in mean: **1.76** Erg. per degree Celsius.

XI.

Allylamine: $C_3H_5 . NH_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
−75°	1.547	2064.0	34.2	0.867	557.5
−15	1.265	1687.1	27.9	0.801	479.5
0	1.180	1573.4	26.0	0.785	452.9
9.7	1.122	1495.7	24.7	0.777	433.2
20	1.072	1429.8	23.6	0.763	418.9
29.5	1.031	1376.0	22.7	0.752	406.9
40	0.979	1304.2	21.5	0.741	389.2
50.5	0.935	1245.1	20.5	0.730	374.8

Molecular weight: **57.07.**

Radius of the Capillary tube: 0.03343 cm.
Depth: 0.1 mm.

Under a pressure of 751 mm. the substance boils at 53° C. At the boilingpoint χ has the value of 20.6 Erg. pro cm². The specific gravity at 0° C. was: 0.785; at 25° C.: 0.757; at 50° C.: 0.730. At $t°$ in general: $d_{4^\circ} = 0.785 - 0.0011\ t$.

The temperature-coefficient of μ oscillates round a mean value of: **1.40** Erg. per degree.

XII.

normal Butylamine: $C_4H_9NH_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
−21°	0.853	1137.6	26.1	0.785	536.2
0	0.779	1038.6	23.8	0.764	497.9
25.3	0.695	926.6	21.2	0.739	453.5
41	0.650	866.6	19.7	0.723	427.5
55	0.606	808.4	18.4	0.709	404.6
70.8	0.574	765.2	17.4	0.693	388.5

Molecular weight: **73.1.**

Radius of the Capillary tube: 0.04676 cm.
Depth: 0.1 mm.

Under a pressure of 760.5 mm., the boilingpoint was 76° — 78° C. The liquid crystallises in a bath of solid carbondioxide and alcool, and then melts at —46° C. At the boilingpoint χ has the value: 17.0 Erg. The specific weight at 0° C. is: 0.764; at 25° C.: 0.739; at 40° C.: 0.727. At $t°$ C.: $d_{4^\circ} = 0.764 - 0.001\ t$.

The temperature-coefficient of μ decreases gradually with increasing temperature: between —21° and 0° C. it is: **1.82**; between 0° and 25° C.: **1.75**; between 25° and 55° C.: **1.64**; and between 55° and 71° C.: **1.02** Erg. per degree.

XIII.

Isobutylamine: $C_4H_9NH_2$.

Temperature in ° C	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—70°	0.931	1243.5	28.9	0.812	580.5
—20.5	0.779	1038.5	24.0	0.771	499.0
0	0.730	973.2	22.4	0.750	474.4
25.3	0.666	887.9	20.4	0.724	442.3
41.8	0.626	831.2	18.8	0.706	414.5
55.8	0.574	761.0	17.7	0.692	395.5

Molecular weight: **73.10**.

Radius of the Capillary tube: 0.04676 cm.
Depth: 0.1 mm.

Under a pressure of 760.5 mm. the amine boils at 67°—68° C. At —70° it is still liquid and not viscous. At 0 C. the specific weight was: 0.750; at 25° C.: 0.724; at 50° C.: 0.698. At t° C. it can be calculated from the formula: $d_{4°} = 0.7505 - 0.00104\,t$.

The temperature-coefficient of μ oscillates somewhat round a mean value of: **1.44** Erg. per degree.

XIV.

Diïsobutylamine: $\{(CH_3)_2CH.CH_2\}_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—72°	0.994	1325.2	29.9	0.825	868.5
—22.5	0.838	1124.4	25.4	0.782	764.6
0	0.769	1026.4	23.2	0.763	709.9
10	0.731	974.9	21.9	0.754	675.5
23	0.691	924.0	20.7	0.743	644.8
35.2	0.660	879.9	19.7	0.733	619.2
45	0.634	842.8	18.8	0.724	595.8
56.7	0.605	802.6	17.8	0.714	569.3
63	0.583	775.2	17.2	0.709	552.7
* 80.9	0.515	686.6	15.9	0.693	518.8
* 104.5	0.459	611.9	14.1	0.673	469.1
* 125	0.408	544.3	12.5	0.656	423.1

Molecular weight: **129.16**.

Radius of the Capillary tube: 0.04595 cm.; with the measurements, indicated by *, the radius was: 0.04777 cm.
Depth: 0.1 mm.

Under a pressure of 760 mm. the amine boils constantly at 142° C. At —78° the liquid becomes very viscous, but does not crystallize. At the boilingpoint χ has the value: **11.3** Erg. pro cm². The density was volumetrically determined; it was found at 0° C.: 0.763; at 25° C.: 0.741; at 50° C.: 0.720. At t° therefore: $d_{4°} = 0.763 - 0.00086\,t$. The temperature-coefficient of μ is in general: **2.40** Erg. per degree.

XV.

Triisobutylamine: $(C_4H_9)_3N$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
−21°	1.026	1367.9	24.5	0.797	926.2
0	0.982	1309.1	23.4	0.782	895.9
20.5	0.932	1243.1	22.2	0.767	861.0
35.3	0.894	1191.9	21.3	0.757	833.4
50.5	0.862	1149.2	20.5	0.745	810.6
65.5	0.825	1100.1	19.6	0.733	783.5
75.5	0.798	1063.9	18.9	0.725	761.1
90.3	0.758	1010.6	18.0	0.713	732.9
99.8	0.726	968.1	17.2	0.704	706.3
115.1	0.684	911.9	16.2	0.692	672.9
124.5	0.652	869.2	15.4	0.683	645.3
139	0.612	814.0	14.4	0.672	610.0
155.8	0.563	751.0	13.3	0.654	573.6
170	0.519	693.0	12.2	0.640	533.9
185	0.471	627.0	11.0	0.626	488.5

Molecular weight: **185.26**.

Radius of the Capillary tube: 0.03636 cm.
Depth: 0.1 mm.

The amine boils under a pressure of 754 mm. constantly at 189° C. In a bath of solid carbondioxide and alcool it solidifies, and will melt afterwards at −24° C. At the boilingpoint the value of χ is: **10.6** Erg. The specific weight was determined by means of a volumeter: at 0° C. it was found: 0.782; at 25° C.: 0.764; at 50° C.: 0.745. At t° generally: $d_{4^\circ} = 0.782 - 0.0007\,t - 0.0000008\,t^2$. The temperature-coefficient of μ increases gradually with rise of temperature: between −21° and 0° it is: **1.44**; between 0° and 100°: **1.86**; between 100° and 185° C. its mean value is: **2.61** Erg. per degree Celsius.

XVI.

tertiary Butylamine: $(CH_3)_3 . C . NH_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
−30°	1.023	1364.0	22.5	0.747	477.8
−15	0.956	1274.5	21.0	0.732	452.0
0	0.884	1177.7	19.4	0.716	423.8
10	0.840	1120.2	18.4	0.706	405.7
20	0.797	1061.0	17.4	0.694	388.1
29.5	0.749	999.0	16.4	0.685	369.0
40.5	0.698	930.6	15.3	0.672	348.6

Molecular weight: **73.1**.

Radius of the Capillary tube: 0.03343 cm.
Depth: 0.1 mm.

The amine boils at 44° C. under a pressure of 757 mm. In a bath of solid carbondioxide and alcohol, it crystallizes readily at −54° C. At the boilingpoint χ has about the value: **14.9** Erg. pro cm². The density at 0° C. was: 0.716; at 25°: 0.689; at 40° C.: 0.672; in general at t° C.: $d_{4^\circ} = 0.716 - 0.001048\,t - 0.000001\,t^2$. The temperature-coefficient of μ is between −30° and 0° C. about **1.85**; afterwards: **1.25** Erg. per degree.

XVII.

normal Amylamine: $C_5H_{11}NH_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
—21°	0.861	1146.7	25.9	0.791	595.1
0	0.789	1054.7	24.1	0.770	563.5
25.5	0.730	973.2	21.9	0.746	523.2
41.2	0.669	895.3	20.4	0.731	494.0
55.5	0.641	858.1	19.2	0.718	470.5
70.9	0.601	800.7	17.9	0.705	444.1
85.0	0.568	762.1	17.0	0.692	427.0
99.8	0.526	701.1	15.6	0.681	396.0

Molecular weight: **87.11.**

Radius of the Capillary tube: 0.04676 cm.
Depth: 0.1 mm.

The liquid boils at 103°—104° C. under a pressure of 762 mm. At —79° it solidifies and crystallizes in needles, which melt at —38° C. The specific gravity was determined by means of a volumeter; at 0° C. it was found to be: 0.770; at 25° C.: 0.746; at 50° C.: 0.723. In general at t° C.: $d_{4^\circ} = 0.770 - 0.00098\,t + 0.0000008\,t^2$.

The temperature-coefficient of μ has a mean value of **1.68** Erg. per degree.

XVIII.

Isoamylamine: $C_5H_{11}NH_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
—69°	1.010	1346.5	30.9	0.840	682.1
—20.5	0.780	1042.0	25.9	0.791	595.1
0	0.779	1038.6	23.7	0.771	553.9
25.5	0.701	934.6	21.2	0.747	506.1
41.3	0.661	879.5	19.8	0.734	478.2
55.8	0.612	818.8	18.6	0.720	455.1
70.5	0.589	784.0	17.6	0.705	436.7
85.8	0.520	693.3	15.6	0.692	391.9

Molecular weight: **87.12.**

Radius of the Capillary tube: 0.04676 cm.
Depth: 0,1 mm.

Under a pressure of 761 mm. the amine boils at 95°—97°. At —72° C. it is still a thin liquid. The specific gravity at 0° C. was: 0.771; at 25° C.: 0.747; at 50° C: 0.724. At t° C. in general: $d_{4^\circ} = 0.771 - 0.00098\,t + 0.0000008\,t^2$.

The temperature-coefficient of μ oscillates somewhat round a mean value of **1.88** Erg. per degree.

XIX.

Diisoamylamine: $[(CH_3)_2CH . CH_2 . CH_2]_2NH.$

Temperature in ° C.	Maximum Pressure H		Surface tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
*—20°	0.838	1117.2	26.5	0.801	894.9
* 0	0.778	1037.4	24.6	0.784	842.7
29.9	0.698	930.6	21.7	0.760	759.0
48.8	0.647	862.6	20.1	0.746	711.7
65	0.612	816.4	19.0	0.732	681.3
80.8	0.578	770.3	17.9	0.721	648.4
104.5	0.518	690.8	16.0	0.705	588.3
124	0.475	633.3	14.6	0.691	544.0
151.5	0.413	550.6	12.6	0.675	476.9
178.5	0.354	471.9	10.8	0.659	415.4

Molecular weight: **157.19.**

Radius of the Capillary tube: 0.04777 c.m.; with the observations indicated by *, the radius was: 0.04839 c.m.
Depth: 0.1 m.m.

The liquid boils constantly at 188° C. and 760 m.m. In solid carbondioxide and alcohol the amine solidifies, and melts then at —44° C. At the boilingpoint χ has the value: **10.2** Erg. pro cm². The specific weight was volumetrically determined; it was 0.784 at 0° C.; 0.764 at 25° C.; 0.745 at 50° C. At t° C. in general: $d_{4^\circ} = 0.784 - 0.00084\,t + 0.0000008\,t^2$. The temperature-coefficient of μ has a mean value of: **2.37** Erg. pro degree.

XX.

tertiary Amylamine: $(CH_3)_2(C_2H_5)C . NH_2.$

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—70°	1.252	1669.1	27.6	0.830	695.9
—19	1.101	1466.5	24.2	0.786	605.0
0	1.018	1357.2	22.4	0.756	554.7
9.5	0.983	1310.5	21.6	0.747	530.3
20	0.935	1245.1	20.5	0.736	498.2
29.3	0.895	1199.3	19.7	0.727	474.9
40.5	0.854	1138.5	18.7	0.716	446.3
50.5	0.812	1082.9	17.8	0.707	421.5
60	0.758	1011.0	16.6	0.697	383.0
70	0.709	945.2	15.5	0.688	344.9

Molecular weight: **87.11.**

Radius of the Capillary tube: 0.03343 cm.
Depth: 0.1 mm.

Under a pressure of 757 mm. the amine boils at 76°.5 C. At —78° it is still a thin liquid, without any trace of crystallisation. At the boilingpoint χ has about the value: **15.0** Erg. The specific gravity was determined by means of a volumeter. At 0° C. it was: 0.756; at 25° C.: 0.731; at 50° C.: 0.707; at t° C. in general: $d_{4^\circ} = 0.756 - 0.00102\,t + 0.0000008\,t^2$.

The temperature-coefficient of μ is between —70° and 50° C. fairly constant; its mean value is: **2.54** Erg. Above 50° it increases to about: **3.9** Erg.

XXI.

normal Hexylamine: $C_6H_{13}.NH_2$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
−18°	1.171	1562.1	28.0	0.801	704.7
0	1.125	1499.8	26.9	0.785	686.2
20.4	1.058	1410.5	25.2	0.767	652.8
35.1	1.010	1347.6	24.1	0.754	631.5
50	0.956	1274.6	22.9	0.740	607.6
65	0.911	1215.6	21.7	0.725	583.7
74.8	0.884	1179.3	21.0	0.715	570.1
90.4	0.832	1109.2	19.8	0.700	545.2
99.8	0.795	1059.9	18.9	0.689	525.9
116	0.728	972.5	17.4	0.673	491.8
124.5	0.696	929.3	16.5	0.664	470.6

Molecular weight: **101.13.**

Radius of the Capillary tube: 0.03636 cm.
Depth: 0.1 mm.

The substance boils at 129°—130° C. under a pressure of 742 mm.; it solidifies in solid carbondioxide and alcohol and melts then at —19° C. At the boilingpoint χ has the value: 16.0 Erg. The specific gravity at 0° C. is: 0 7855; at 25° C.: 0.763; at 40° C.: 0.749. At t° C.: $d_{4°} = 0.7855 - 0.00088\,t - 0\,0000008\,t^2$.

The coefficient of μ is originally small: about **1.03** between —18° and 0° C.; between 0° and 75° C. it is almost constant, with **1.55** Erg. as a mean value; above 75° C. it increases gradually from **1.55** Erg. to **2.50** Erg. per degree.

XXII.

Isohexylamine: $(CH_3)_2\,CH\,.\,CH_2\,.\,CH_2\,.\,CH_2\,NH_2$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
—75°	1.397	1862.5	30.8	0.840	751.0
—20.8	1.203	1603.8	26.5	0.798	668.6
0	1.126	1501.6	24.8	0.780	635.3
10	1.096	1461.2	24.1	0.771	622.2
20	1.074	1430.2	23.3	0.762	606.3
29.8	1.021	1359.7	22.5	0.754	589.5
40.5	0.991	1321.2	21.8	0.744	576.3
60	0.924	1231.9	20.3	0.724	546.5
70	0.894	1191.9	19.6	0.716	532.1
80	0.861	1148.6	18.9	0.707	516.9
90	0.828	1103.9	18.1	0.698	499.3
100	0.795	1059.9	17.4	0.686	485.6
110.2	0.765	1019.9	16.7	0.676	470.6
121	0.726	969.1	15.9	0.665	453.0

Molecular weight: **101.13.**

Radius of the Capillary tube. 0.03343 cm.
Depth: 0.1 mM.

The amine boils at 123° C. under a pressure of 751 mm. Even at —79° it is still a thin liquid. At the boilingpoint the value of χ will be about: 15.8 Erg pro cm². The specific gravity was determined by the aid of a volumeter; at 0° C. it is: 0.780; at 25° C.: 0.758; at 50° C.: 0.735. At t° generally: $d_{4°} = 0.780 - 0.00086\,t - 0.0000008\,t^2$. The temperature-coefficient of μ oscillates round a mean value of: **1.51** Erg. per degree.

XXIII.

normal Heptylamine: $C_7H_{15}NH_2$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
−18.5°	0.902	1202.4	27.5	0.804	752.8
0	0.857	1142.5	26.1	0.787	724.7
25.3	0.793	1057.2	24.1	0.765	681.9
41.5	0.744	993.0	22.7	0.750	650.9
56	0.714	950.8	21.5	0.737	623.7
70.9	0.663	886.2	20.3	0.723	596.4
84.5	0.634	845.2	19.1	0.711	567.5
100	0.607	809.2	18.3	0.697	551.0
*115.2	0.541	724.1	17.0	0.684	518.3
*130.8	0.545	723.8	15.7	0.669	485.8
*145.5	0.507	673.2	14.4	0.657	451.0

Molecular weight: **115.15.**

Radius of the Capillary tube: 0.04676 cm.; in the measurements indicated by *, this radius was: 0.04529 cm.
Depth: 0.1 mm.

Under a pressure of 761 mm. the amine boils at 152°–154° C. The liquid can be undercooled, but finally solidifies in a bath of carbondioxide and alcohol into a colourless crystal-aggregation, melting at −18° C. Above 130° a slow decomposition is observable. At 0° C. the density is: $d_{4^\circ} = 0.7875$; at 25° C.: 0,7650; at 40° C.: 0.7515. At t° C. it can be calculated from the formula: $d_{4^\circ} = 0.7875 - 0.0009\, t$.

The temperature-coefficient of μ increases gradually at higher temperatures: between −18° and 0° C.: **1.52** Erg.; between 0° and 25° C.: **1.69**; between 25° and 71° C.: **1.87**; and between 71° and 145°: **1.98** Erg. per degree, as a mean value.

XXIV.

Formamide: $HCONH_2$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
*0°	1.875	2499.7	59.6	1.167	596
29.9	1.806	2407.3	56.6	1.136	566
48.1	1.755	2340.3	55.1	1.120	551
65	1.702	2269.2	53.4	1.107	534
80.7	1.661	2214.8	52.1	1.094	521
104.5	1.598	2131.0	50.1	1.080	501
123.2	1.551	2068.2	48.6	1.071	486
152	1.460	1946.8	45.7	1.058	456

Molecular weight: **45.03.**

Radius of the Capillary tube: 0.04777 cm.; in the observations indicated by *, the radius was: 0.04839 cm.
Depth: 0.1 mm.

Under a pressure of about 18 mm., the liquid boils at 114°. In a freezing mixture it solidifies into an aggregate of white crystals, which melts at −5° C. Above 145° C. a gradual decomposition under development of gas-bubbles, is observed; the χ-t-curve then rapidly falls towards the t-axis.

§ 3. The results obtained are reviewed in the Tables I—XXIV above, while the relations of the corresponding μ-t-curves can be seen from the fig. **1—3**.

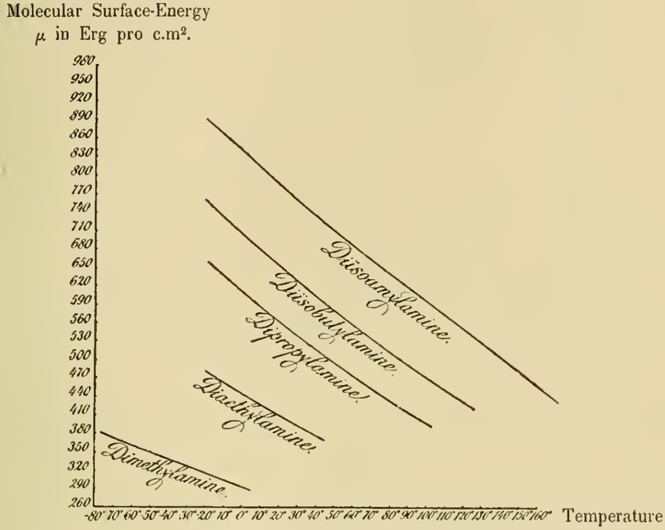

Fig. 2. Secondary Amines.

From these experiments it appears in the first instance, that the substitution of H-atoms in the ammonia-molecule by hydrocarbon-radicals, makes the surface-energy of the liquid compounds at the same temperatures increase regularly; and that, — peculiarities left out of question, — that increase goes in general parallel to the augmentation of the number of C- and H-atoms. That however, even with the same number of C- and H-atoms, the special configuration of the molecule plays an important rôle in this, can soon be seen: e. g. the μ-t-curves for $(C_3H_7)NH_2$ are not only situated above those for $(CH_3)_3N$, etc., but it is also quite clear from fig. **1—3** *that generally in the case of correspondingly built-up isomer amines, those with normal hydrocarbon-chains generally possess at any temperature a greater surface-tension than those with ramified hydrocarbon-chains*; *and that generally the surface-tension of such isomerides under the same conditions appears to be the lower, the more ramified the hydrocarbon-chains are* (e.g. *butyl-*, *isobutyl-*, and 3^{ary} *butyl-amines*; in the same way the corresp. *amylamines* between 10° and 70°; etc.)

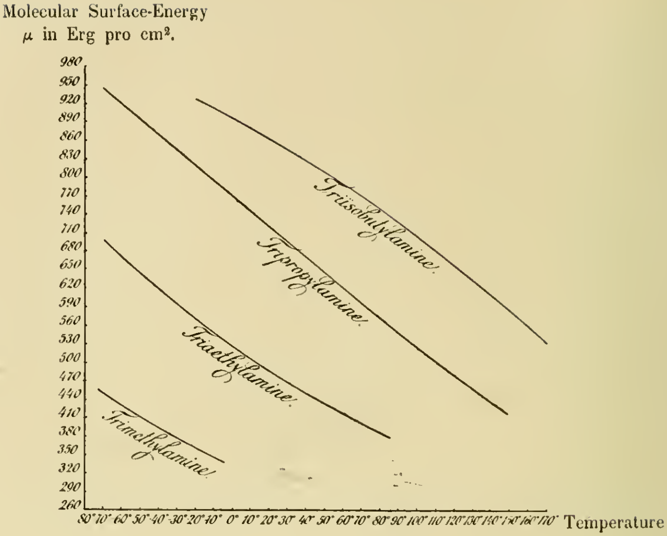

Fig. 3. Tertiary Amines.

On a comparison of the primary, secondary and tertiary amines of the same alkyl-radical, it appears that *the temperature-coefficients of* μ *are often analogous for* 1^{ary} *and* 3^{ary} *amines, but smaller than those for the* 2^{ary} *amines.*

However it becomes also clear, that a direct comparison of the μ-t-curves with the aim of studying the influence of the substitution by hydrocarbon-radicals in homologous compounds, may properly be made only in the case of amines of the same fundamental configuration; as e.g. by comparison of all primary, or all secondary, resp. tertiary amines, with each other. (fig. 1, 2 and 3). Really then the regular increase of the values of μ in these cases, if substitution occurs by more complicated hydrocarbon-radicals, comes to the fore in a most striking way.

With respect to the temperature-coefficients of μ it may be remarked that these generally appear rather *small*; the smallest values being present in the case of *primary* amines (1.2—1.8), while in the case of secondary amines these values are often somewhat greater (1.7—2.3), and just as with the tertiary amines, approach gradually to the values observed with other organic compounds. However, these rules are not without exceptions: e.g. in the case of *di*methylamine the value of $\frac{\partial \mu}{\partial t}$ appears beyond doubt to be *smaller* than with *monomethylamine*.

Finally the increase of the surface-energy by substitution of *H*-atoms also appears here, as formerly stated, to be appreciably greater if substitution occurs by *unsaturated*, than by saturated hydrocarbon-radicals: a comparison of the data for *allylamine* on the one side, and of *propyl-*, and *isopropylamine* on the other side, soon convinces of the truth of this.

Lastly we may draw attention here to the data regarding the *formamide*, which are also reproduced among those of the derivatives of trivalent nitrogen. Although this compound does not possess more than a single *C*-atom, the value of μ nevertheless appears here to be much greater than e.g. for $(CH_3)NH_2$, demonstrating the special influence of the strongly electronegative oxygen-atom, and more especially of the unsaturated carbonyl-radical, in a perfectly clear way.

Moreover this liquid, which in several respects shows some analogy with the strongly dissociating solvents, appears to possess a *very small* temperature-coefficient $\frac{\partial \mu}{\partial t}$: on an average about 0.89 Erg. per degree. It would be of interest to study the behaviour of inorganic salts if dissolved in this liquid, with respect to the electric current. In analogy to the case of water, one would be inclined to conclude in this case from the exceptionally small value of $\frac{\partial \mu}{\partial t}$, that the liquid formamide might be highly associated.

Laboratory for Inorganic and
Groningen, April 1915. *Physical Chemistry of the University.*

Chemistry. — "*The Allotropy of Sodium.*" I. By Prof. Ernst Cohen and Dr. S. Wolff.

(Communicated in the meeting of April 23, 1915).

1. Some time ago Ernst Cohen and G. de Bruin[1]) relying on the determinations by Ezer Griffiths[2]) of the true specific heat of sodium, proved that this metal shows allotropy and that the substance known hitherto as "sodium" is a metastable system in consequence of the simultaneous presence of α- and β-sodium.

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[1]) These Proc. **23**, 896 (1915).

[2]) Proc. Roy. Soc. London **89**, (A) 561 (1914).

Some preliminary determinations carried out by GRIFFITHS proved that the densities of the two modifications are different (at the same temperature) and that this difference is of the order of 1 : 7000. The modification formed by quenching cet. par. has the greater specific volume.

The investigations to be described below were carried out in order to fix the limits of stability of both modifications, viz. to investigate whether sodium is enantiotropic[1]) or monotropic.

2. Although the change of volume which accompanies the transformation of α-sodium into β-sodium is small according to GRIFFITHS' measurements, yet the use of the dilatometer is suitable, if certain precautions are taken, which enable us to carry out exact measurements with this instrument.

These precautions are:

a. A large dilatometer must be used; we employed an instrument of about 380 cc.

b. The bore of the capillary tube must be small (Bore of our tube 1.2 mm.).

c. The quantity of liquid put in, (rock oil) must be as small as possible.

d. The temperature at which the readings are taken must be constant within some thousandths of a degree.

3. Special care has to be taken in filling the dilatometer. This operation was carried out in the following manner: The metal (sodium in rods from KAHLBAUM-Berlin, comp. § 6 and 8) was melted under petroleum in a Jena-glass flask. The rock oil had been prepared in the way to be described in § 4, while the metal had been treated in a special manner (comp. § 5). The flask *O* (Fig. 1) is put into an oil bath *RR*, heated to 130°. Pieces of sodium are added until there are about 400 cc. of molten metal in *O*.[2])

The dilatometer after being filled with rock oil, is placed in the same bath. *O* and *G* are connected by means of a glass tube *PLH* the end of which (in *G*) is drawn out.

The neck of the dilatometer is connected with a tube *L* by means of rubber tubing *K*.

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[1]) In the paper mentioned above [These Proc. 23, 896 (1915)] the opinion was expressed that there exists a transition point between 0° and 90°.

[2]) Generally there are formed spheres of metal which do not coalesce unless the molten metal is cooled below the melting point and gently stirred at the same time.

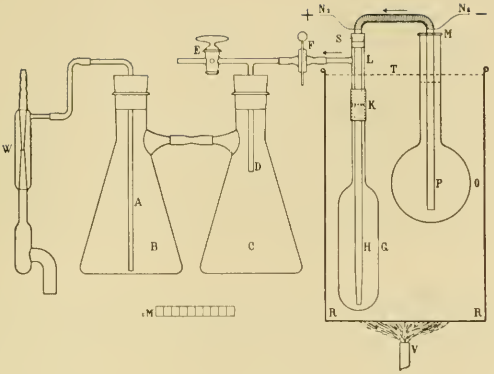

Fig. 1.

W represents a water pump, while *B* and *C* are filter flasks. *F* represents a clip, *S* a rubber stopper through which the tube *PLH* passes.

O is left open at *M*. A manganin wire N_1N_2 serves as a heater; 5 or 6 storage cells are used as a source of current, whilst a regulating resistance and an ammeter are put in the circuit.

The purpose of the wire N_1N_2 is to heat that part of *PLH* which is not heated by the oil bath, above the melting temperature of sodium in order to prevent the solidification of the molten metal when flowing from *O* to *G*. The wire is separated from the wall of the tube by means of asbestos paper. In order to prevent loss of heat the wire is also covered with asbestos paper. The oil bath is heated to 130° and when the metal has entirely melted the stopcock *E* is shut, the heating current started, and the pump *W* put in action As soon as the tube *M* is sufficiently heated the clip *F* is cautiously opened. The molten metal flows into the dilatometer and displaces the rock oil present which flows into the flask *C*.

As soon as the sodium reaches *F* (the dilatometer being then full of the metal) it solidifies, as the side tube is at room temperature. In this way suction stops automatically[1]). The stopper *S* is now removed while the tube *PLH* is taken out of the dilatometer. The level of the metal falls and the rock oil present protects the sodium from oxidation.

After the solidification of the metal which is accompanied by a

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[1]) If any molten metal should still pass over, it enters the flask *C* containing some rock oil which covers the metal.

decrease of volume of about 2.5 percent, the capillary tube is sealed at the bulb. After having been filled up with rock oil (by means of an air pump) the instrument is ready for use. It may be pointed out that only a few cc. of rock oil were used (comp. § 2. c.).

4. The petroleum used was prepared as follows: After having been heated for 24 hours at 100° in contact with sodium, it was distilled off from the metal. The part distilling below 175° was not used; the remaining liquid was kept in contact with sodium and used for the experiments.

5. In order to get the metal free from oxide the method described by v. Rossen Hoogendijk v. Bleiswijk[1]) may be followed. Small pieces of the metal are put into benzene to which small portions of amylalcohol are cautiously added. When the metal has become bright it is put into the rock oil prepared as described above.

6. We were not able to detect any impurity in 10 grams of the metal.

7. We used the (electric) thermostat described by Ernst Cohen and Helderman in their investigations on cadmium[2]), which enabled us to keep the temperature constant within some thousandths of a degree. The thermometers used were compared with two instruments checked by the Phys. Techn. Reichsanstalt at Charlottenburg-Berlin.

8. Before describing the measurements some remarks may be made concerning the melting point of the metal experimented with.

As is generally known, metals show, even if they are pure, a range of fusion. This can be determined here very exactly by dilatometric measurements as the process of melting is accompanied by a marked change of volume (about 2.5 per cent).

While the level of the meniscus remained constant at 97°.12 during 17 hours, there occurred a strong dilatation at 97°.22.

The beginning of solidification of the molten metal was determined in the following way: We put 25 cc. of sodium into a wide glass tube which contained some rock oil in order to prevent the metal from oxidation. A Beckmann thermometer (graduated to hundredths of a degree) and a glass stirrer pass through a cork in the neck of the tube. The whole was placed into an oil thermostat the temperature

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[1]) Zeitschr. f. anorg. Chemie 74, 152 (1912).

[2]) Zeitschr. f. physik. Chemie 87, 409 (1914).

of which was kept constant within some thousandths of a degree. Its temperature was 97°.10.

The tube and its contents is heated to 99° and put into the thermostat. When the temperature of the metal had become 97°.10 the stirrer was put in motion. The temperature rose to 97°.51 and remained constant for some time. The experiment was repeated, the molten metal being cooled 0°.7 lower than before. After stirring the temperature rose again to 97°.51.

The beginning of solidification consequently occurs at 97°.51, while the range of melting covers 0°.3 C.

9. As the changes of volume which play a rôle in these investigations are only small, and as the glass of the dilatometer was exposed in our experiments to sudden and strong changes of temperature (about 100°) we thought it important to prove that the glass used did not show thermal hysteresis. For this purpose we filled our dilatometer with rock oil and heated it for some hours in a thermostat at 95°.00. After having noted the place of the meniscus (358.0) we dipped the instrument into petroleum which had been cooled (by means of solid carbon dioxyde) to — 20° C. After half an hour we put it again into the thermostat at 95°.00. After two hours the level of oil was again 358.0. Twenty-four hours later it had not changed: consequently *thermal hysteresis had not occurred.*

10. The dilatometer was now filled in the way described above (comp. § 3) with molten sodium and some cc. of petroleum. After this it was cooled very slowly in the thermostat to 15° C., so that the metal might be transformed into the α-modification.

The following results were obtained (Comp. Table I).

TABLE I.

Temperature	Duration of the observations (hours)	Rise of the level (mm)
50°	$3\frac{1}{3}$	0
68.5	16	0
90.0	19	0
96.0	22	0

At 97°.3 the melting of the metal occurred which is accompanied by a very marked increase in volume.

11. In order to melt the metal entirely, the dilatometer was heated to 100° C.; the change of volume having ceased, the metal was chilled at 0° C.

The observations carried out with the chilled metal are given in Table II.

TABLE II.

Temperature	Duration of the observations (hours)	Rise of the level (mm.)
45°.2	22	0
70.0	31	0
90.0	48	0
96.02	24	— 1
96.02	72	— 3
96.02	144	— 6
96.02	240	—10

At 97°.22 C. fusion had already begun to take place.

12. The measurements given in the tables I and II in conjunction with those of Griffiths which show that the β-modification has cet. par. a greater specific volume than the α-modification, indicate that we have to deal with a case of monotropy.

13. That at 94° we have not passed beyond a transition point may be proved by showing that the transformation velocity does not increase at higher temperatures (which would be the case above a transition point) but that there exists a maximum of velocity. This may also occur with monotropic transformations (for instance in the case of β-dibromproprionic acid[1]) and if this is really the case, it indicates that the transition point which cannot be reached lies in the neighbourhood of the melting point.

14. The following experiments show that we really have to deal with such a case with sodium: the metal was melted in the dilatometer and chilled.

After this the transformation velocity (β-sodium → α-sodium) was determined at different temperatures. (Duration of observations 48 hours). The velocity was found to be:

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[1] O. Lehmann, Molekularphysik 1, 197. Leipzig 1888.

At 94°.4 3
95°.4 4
97°.1 2.

A maximum was thus found at 95°.4, viz. two degrees below the melting point.

15. The facts stated in § 14 exclude the existence of pseudo-monotropy, but we are able to go a step farther and, from what has already been stated as well as from the phenomena immediately to be described, can conclude that sodium is monotropic.

16. These phenomena are: The metal was cooled very slowly in order to transform it into the α-modification. After this the dilatometer was kept at 97°.22, a temperature at which melting began. (At 97°.12 melting does not take place). Table III gives the results:

TABLE III.

Temp. 97°.22 (= 5°.998 on BECKMANN's thermometer).

Temp. on BECKMANN's thermometer	Time (minutes)	Level in mm.
5°998	0	268
5.998	16	274
5.998	51	279
5.998	83	284½

The metal having been melted and chilled (the metal was now present in the β-modification) the dilatometer was brought back to 97°.22. Table IV gives the results:

TABLE IV.

Temp. 97°.22 (= 5°.998 on BECKMANN's thermometer).

Temp. on BECKMANN's therm.	Time (minutes)	Level in mm.
5°998	0	266 [1]
5.998	5	275
5.998	31	309
5.998	51	326
5.998	76	344

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[1] In order to use the same part of the capillary tube, the meniscus was brought to the same point of the scale as with the experiments mentioned in Table III.

17. From these tables it is evident that the velocity of melting at the same temperature is cet. par. greater with β-sodium than with α-sodium. Consequently the quantity of heat wanted to transform 1 gram of solid β-sodium into the molten state is less than that which must be added for that purpose to the same quantity of α-sodium. From this we may conclude that the transformation β-sodium → α-sodium is accompanied by an *evolution* of heat. The fact that this heat of transformation is positive, proves that *if* there exists a transition point it is to be looked for in the direction of higher temperatures [1]). The facts described in § 14, prove that such a transition point does not exist and consequently sodium is monotropic.

18. Finally it may be pointed out that HAGEN [2]), who determined the coefficient of dilation of sodium (between 0° C. and its melting point) by dilatometric measurements, was not able to observe these phenomena as the quantity of metal used by him (40 grams) has been too small.

The value of this physical constant determined by this author is consequently *fortuitous* and must be redetermined with the pure α- and β-modifications.

We express our best thanks to Dr. H. R. KRUYT to whom we are indebted for many valuable remarks.

Utrecht, April 1915. VAN 'T HOFF-Laboratory.

Chemistry. — "*Action of methylethylketone on* 2. 3. 4. 6. *tetranitrophenylmethylnitramine*". By Prof. P. VAN ROMBURGH.

(Communicated in the meeting of April 23, 1915).

As stated by me previously [3]), this nitramine reacts readily with alcohols and amines. Water also acts on it with formation of nitrous acid and of 2. 4. 6. trinitromethylnitraminophenol. Whereas at the ordinary temperature this action proceeds very slowly it takes place fairly rapidly at boiling temperature.

In order to get to know more accurately the progressive change of the reaction some previous investigations were made a few years ago by me conjointly with Dr. SINNIGE, which gave the result

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[1]) BAKHUIS ROOZEBOOM, Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre. 1, 178; Braunschweig 1901.

[2]) Wied. Ann. 19, 436 (1883).

[3]) Rec. 8, 275 (1889).

that the nitramine, when dissolved in acetone, reacts very rapidly with water even at the ordinary temperature, so that the preparation of the phenol in this manner is a very simple one.

Now it did not seem devoid of importance to know something more as to the rôle played here by the acetone and, therefore, I have studied this reaction more closely. It appeared, however, that great difficulties are experienced in the separation and identification of the products generated in addition to hydrocyanic acid, which forms abundantly, so that I thought it desirable to try whether satisfactory results can be obtained more readily by using another ketone, which then perhaps may serve to also elucidate the reaction with acetone.

It now appeared that methylethylketone lends itself very well for that purpose.

If, at the ordinary temperature, we dissolve the nitramine in so much moist ketone that a concentrated solution is obtained, we notice that the original pale yellow colour of the solution rapidly begins to darken and soon after, a yellow product crystallizes, which proved to be the 2. 4. 6. trinitromethylnitroaminophenol. In my experiments I generally used 11 grams of nitramine, which I dissolved in 16 c.c. of ketone to which 0.8 c.c. of water was added. At first, I took more nitramine (33 grams = $^1/_{10}$ gram mol.) but then towards the end of the operations explosions frequently took place.

If we decant the ketone solution from the crystals and subject the same to a distillation (in the water-bath) an intensively yellow coloured liquid with a peculiar odour passes over. It contains hydrogen cyanide which was identified by the Prussian blue test. The yellow colour, also the odour pointed to the presence of diacetyl.

If to the liquid we add a solution of silver nitrate to precipitate the hydrogen cyanide and subsequently to the filtrate an *excess* of ammonia a white voluminous precipitate is obtained which according to Fittig, Daimler, and Keller[1]) is characteristic of diacetyl. The detection of the diacetyl by means of hydroxylamine presented, owing to the excess of methylethylketone, a little difficulty.

Still, by using a liberal quantity of hydroxylamine I succeeded in obtaining crystals of dimethyglyoxime, which gave with a nickel salt and ammonia the characteristic red nickel compound.

In order to detect any volatile products eventually formed, the flask which had been heated in the waterbath at 100° was evacuated and placed in an oilbath heated at 120°. A substance began to

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[1]) Ann. **249**, 205 (1888).

distill which deposited in a crystalline form in the exit tube, when the flask exploded with a loud report.

In subsequent experiments the heating was therefore solely conducted in vacuo at 100° in a waterbath and in this way I also succeeded in obtaining small quantities of crystals, which after being pressed between paper melted at 76° and gave no depression of the melting point with *α-iso*-nitrosomethylethylketone. In addition there distilled a little of a liquid acid, which, after neutralisation with sodium carbonate solution gave with silver nitrate a white precipitate, which on heating with water turned black.

If the nitramine is heated with moist methylethylketone a rather violent action sets in, but otherwise the reaction proceeds as described above. If we take ketone that has been dried over calcium chloride we also get a yellow, diacetyl containing distillate.

If, however, we take nitramine that has been standing for some days in a desiccator over sulphuric acid and ketone that has been dried with phosphoric anhydride, no reaction takes place at the ordinary temperature even after two days. On heating in the waterbath the ketone passes over entirely colourless. If the distillation is interrupted, the nitramine in the flask crystallizes unchanged. On long continued heating in the waterbath the distillate first shows traces of hydrogen cyanide and gradually also a faint yellow coloration, which need cause no surprise because, on heating at 100°, the nitramine itself yields traces of nitrous vapours. So much, however, is pretty certain that in the experiment with moist ketone the formation of the reaction products found will have to be attributed largely to the action on the ketone of the nitrous acid generated by the water, when the strongly acid phenol will also have exerted its influence.

The fact that the reaction takes place so rapidly in the ketone solution even at the ordinary temperature may be caused by the great concentration, but there also exists the possibility that the presence of the acetone accelerat s the reaction. Experiments to make sure about this and also to study the influence of the water on the nitramine in other indifferent solvents are in progress. In water-saturated ether a conversion of nitramine into phenol also takes place fairly rapidly.

Utrecht, Org. Chem. Lab. University.

Physics. — *"The magnetic rotation of the polarisation plane in titanium tetrachloride."* I. By Prof. L. H. Siertsema. (Communicated by Prof. H. A. Lorentz).

(Communicated in the meeting of March 27, 1915).

Among the substances of which the magnetic rotation of the plane of polarisation has been observed, titanium tetrachloride occupies a particular place, first of all because it is the only diamagnetic substance known that presents negative magnetic rotation, and then because it is unique in being a liquid, for which the negative magnetic rotation can be observed without the interfering influence of a solvent, and which is free from absorption bands almost over the entire visible spectrum. Only in the extreme violet, according to my observation at $\lambda = 0.420\,\mu$, an absorption limit is found.

The diamagnetic character has been ascertained by Verdet [1]) and by H. Becquerel [2]); observations on magnetic rotation have been made by Verdet [3]), who only shows that the rotation is negative, and about of the same amount as the positive rotation of water, and by H. Becquerel [4]), who determines the magnetic rotation for six Fraunhofer lines. It appears from these measurements that the rotations are in inverse ratio to the fourth power of the wavelength, hence they follow an entirely different law from that found for the positive rotation.

An attempt to ascertain whether the later dispersion formulae derived from the theory of electrons can be applied to this substance made me realize the desirability of extending the material of observation by the carrying out of new measurements.

The measurements have been carried out by a penumbra method and spectral analysis.

The liquid was in a glass tube of a length of 265 mm. and a diameter of 25 mm., closed by plane-parallel glass plates 1 mm. thick. This tube was placed in a coil of wire 182 mm. long, so that the closing plates were a few centimetres outside the coil.

It appeared from a measurement with an empty test tube that the magnetic rotation in the glass plates was imperceptible. The coil contained 3186 windings; between the windings and the coil

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[1]) E. Verdet, Ann. de Ch. et de Ph. (3) 52 p. 156 (1858).

[2]) H. Becquerel, Ann. de Ch. et de Ph. (5) 12 p. 63 (1877).

[3]) E. Verdet, loc.cit.

[4]) H. Becquerel, Ann. de Ch. et de Ph. (5) 12 p. 35 (1877); C.R. 85 p. 1229 (1877).

there was a waterjacket, through which a stream of water could be led. The projecting ends of the test tube are enclosed in cotton wool to ensure a uniform temperature. The strength of current amounted to about 2 ampères, and was read down to 0,002 ampère on a carefully gauged ampère metre. Of the optical arrangement we should mention the source of light (quartz amalgam lamp of HERAEUS, or arclamp), from which the beam of light passed through a penumbra prism according to JELLET, with a penumbra angle of 2°, a collimator, the slit of which was immediately behind the penumbra nicol, the test tube, a nicol with 12 × 13 mm. aperture as analyzer, the rotation of which could be read in minutes on a graduated circle, and the prism with eye-piece of a HILGER spectroscope with constant deviation.

The line of demarcation of the penumbra nicol is placed horizontally, so that when the arclamp is used we observe a spectrum in the eye-glass consisting of two parts lying above each other and divided by a sharp line. Through rotation of the prism different parts of the spectrum can successively be brought in the middle of the field of vision. If the current in the coil is closed, a black band is observed in both parts of the spectrum. These two bands, however, are slightly displaced with respect to each other. Halfway between them a place can always be indicated where the intensity of the light is the same in the two parts. At this place the adjustment was brought about by means of rotation of the analyzer causing a displacement of both bands. For this purpose the eye-piece was provided with a wide ocular slit. After reversal of the current this adjustment was repeated; the angle over which the analyzer has been turned, is double the angle over which the plane of polarisation in the titanium chloride has been turned. In observations with the quartz amalgam-lamp the collimator slit was taken pretty wide, which caused a great many slit images to be seen in the reading glass, each divided into two parts by a horizontal line. Just as above the adjustment can then be made at equal luminous intensity of the two parts.

From readings of thermometers in the supply and the leading off of the water in the jacket the temperature of the test tube can be derived.

The first series of measurements have been carried out with the quartz amalgam lamp. The slit images used for this are those corresponding to the lines:

Hg 5780, the two mercury lines lying close together. The images of the two lines overlap for the greater part; the readings are reckoned to correspond to the mean of the two wavelengths.

Hg 5461, the most intense mercury line.

Cd 5086, intense cadmium line.

ZnCd 4805, a blue zinc and a cadmium line, almost coinciding.

Zn 4722, blue zinc line.

Hg 4358, ,, mercury line.

For every slit image there have been made four readings, two for every direction of current, the strength of the current having been read every time. Then the angle between the two positions of the analyzers has been derived from the means of the corresponding readings, and the angle of rotation for 1 ampère found through division by the sum of the two strengths of current that differ but little.

The results of some six series of observations are recorded in the subjoined table.

λ in μ	Magnetic rotation in minutes, for 1 amp.							$-\rho$ min./gauss.cm.
	1	2	3	4	5	6	Mean	
0.5780	59.8	60.1	60.1	60.2	60.0	60.0	60.0	0.01618
0.5461	74.9	75.2	75.3	74.9	75.1	75.0	75.1	0.02023
0.5086	101.6	101.0	100.1	100.4	98.9	100.2	100.4	0.02705
0.4805	128.1	128.4	129.4	129.3	129.2	127.8	128.7	0.03468
0.4722	140.5	139.6	140.1	141.9	138.8	141.1	140.3	0.03782
0.4358	208.7	209.6	208.8	209.5	209.2	208.3	209.0	0.05633

Then observations have been made with arc light for a number of different wavelengths. The wavelength was found by illuminating the collimator slit by means of a mirror with a quartz amalgam lamp, and adjustment to the slit images lying nearest to the place in the spectrum where observations were to be made. From this the wavelength at the place of observation was derived by means of a dispersion curve of the prism. These adjustments always took place immediately before or after those of the position of the analyzer.

To be able to calculate the rotation constant ρ per gauss cm., the test tube is then filled with distilled water, and the magnetic rotation is measured for two different wavelengths. By the aid of the constant of rotation for water and the magnetic rotation dispersion as they were before determined by the author[1]) these measurements gave two values for the reduction factor, which agreed down to 0.1 %. Besides, some measurements with carbon disulphide have been made, which sufficiently harmonized with those of water. Carbon disulphide is less satisfactory for a measurement of the magnetic field than water. The angles of rotation are then, indeed, larger, but the greater temperature coefficient renders a greater accuracy in the temperature determinations necessary, in consequence of which an accurate result is after all more difficult to reach.

Further a number of measurements have been made with the titanium chloride at different temperatures by cooling the water at its entrance into the jacket by means of ice, or by raising the temperature. The temperature coefficient of the constant of rotation appeared, however, to be so small, that it could not be determined with certainty from the observations. The thought of applying a temperature correction has, therefore, been abandoned. In the measurements with the quartz amalgam lamp the temperature was on an average 17.9°, in those with the arclamp 13.4°.

The results of the measurements with the quartz lamp are recorded in the last column of the above table; those with the arc lamp referring to observations on six different days, follow below.

The more recent theories of the magneto-optical phenomena which are founded on the theory of electrons, show that there is a connection between the magnetic rotation of the plane of polarisation and the ZEEMAN effect, which the lines of the substance's free vibrations present. By starting from simplifying suppositions, and assuming one free period, the magnetic rotation as far as the sign and the order of magnitude is concerned, can in many cases be explained by the assumption of a magnetic resolution of spectrum lines as it is given by the elementary theory[2]). For a more complete explanation it is, however, necessary to take more free vibrations into consideration.

It has appeared from investigations by DRUDE and others that the ordinary dispersion of transparent substances can generally be represented by an expression with a small number of free vibrations, among which ultrared ones, corresponding to vibrations of positively charged particles, and one or more ultraviolet free vibrations of negative particles. The ultraviolet frequencies cause the greater part of the dispersion.

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[1]) Versl. Kon. Ak. van Wet. 1896/97 p. 131. Comm. Leiden Suppl. 1. p. 76 Arch. Néerl. (2) 2 p. 366 (1899); (2) 6 p. 825 (1901).

[2]) These Proc, Vol. 5, p. 413, Comm. Leiden Nº. 82.

For a satisfactory explanation of the magnetic rotation the same frequencies will have to be taken into consideration; it should only be borne in mind that there is no occasion to assume magnetic resolution for the ultrared frequencies ascribed to positively charged particles, so that these need not occur in the expressions for the magnetic rotation.

	$-\rho$ min./gauss, cm.
0.4723	0.03689
0.5601	0.01830
0.5245	0.02349
0.5097	0.02643
0.4840	0.03325
0.4623	0.04054
0.4436	0.04927
0.4355	0.05439
0.4495	0.04686
0.4694	0.03778
0.4688	0.03843
0.4889	0.03170
0.6452	0.01083
0.5956	0.01471

For most substances the magnetic rotation is positive. Theory teaches that it can be caused by the magnetic resolution of an ultraviolet spectral line of a sign as determined by the elementary theory of the Zeeman-effect. To explain negative rotation a magnetic resolution of an ultraviolet line of the abnormal sign must be assumed. Such a resolution need not necessarily be accompanied with a positive charge, of the vibrating particles. Voigt 1) demonstrates that in consequence of couplings between vibrating electrons complicated reso-

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1) W. Voigt. Ann. d. Phys. 45 p. 457. 1914.

lution figures, and also resolutions of the abnormal sign, can appear, and that negative rotation might arise in consequence.

The thought suggests itself to try whether the observed rotation constants can be explained in this way. For this purpose it is necessary to represent these constants by a formula as required by theory, with one or more ultraviolet frequencies. It will have to appear at the same time that the index of refraction can be represented by a formula of the form required by theory, with the same frequencies, besides ultrared ones.

It will be communicated in a following paper what a treatment of the results of our observations in this sense will have yielded.

Chemistry. — *"On Tension Lines of the System Phosphorus."* IV.

By Prof. A. Smits and S. C. Bokhorst. (Communicated by Prof. J. D. van der Waals.)

(Communicated in the meeting of April 23, 1915.)

1. *New determinations of the vapour pressure of liquid white phosphorus.*

In the first communication under this title [1] among others the vapour pressure line of the liquid white phosphorus was discussed. This line, which had been determined by us according to the statical and dynamical method up to 336°, had such a course, that it could not be considered as the metastable prolongation of the vapour pressure line of the liquid violet phosphorus.

Now it appeared that this result was to be ascribed to this that the vapour pressure above 325° increased with the temperature to an abnormal degree.

This circumstance added to the fact that the temperature was always increased as quickly as possible in the vapour tension determination to prevent all the white phosphorus from being converted before the determination could be made, led us to suppose that the results might be faulty at these high temperatures in consequence of spontaneous heating of the mass brought about by the conversion:

$$\text{white } P \rightarrow \text{violet } P + a \text{ Cal.}$$

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[1] These Proc. Vol. XVI, p. 1174.

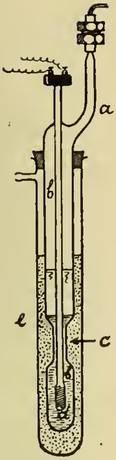

Fig. 1.

As this conversion is accompanied by a pretty great generation of heat (4.4 Cal. at the ordinary temp.), and the velocity of this reaction is already pretty great above 325°, it would be possible that the temperature of the phosphorus had been higher than that of the surrounding bath, whereas it had been assumed that inside and outside the apparatus there always prevailed the same temperature.

To avoid this possible error, not the temperature of the bath, but that of the phosphorus had to be measured.

For this purpose with application of the dynamic method according to SMITH[1]) the tube of the thermo-element was fused into the vapour pressure apparatus, so that always the temperature of the phosphorus was determined.

Afterwards when it had appeared that through the contact with stearine the boiling point of the phosphorus was absolutely not influenced, the apparatus was used represented in fig. 1. Into the inner tube *a* which has a constriction at *c* a resistance thermometer has been fused, which reaches to the lowest widening. This inner tube is filled up to above the constriction with pure white phosphorus, which is then shut off by a layer of stearine. All this takes place in vacuum. In the outer jacket *e* also stearine is brought, which is heated under different pressures. Just as for the other apparatus also now the temperature is determined at which the phosphorus under a definite pressure begins to boil. This method has this advantage that without any difficulty the experiment can be made with larger quantities, and the temperature can be indicated very quickly and very accurately.

By these two improved methods the following results were now found:

Temp.	Pressure in atm.
331.8°	2.47
332.9°	2.61
342.0	2.95
355.7	3.88

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[1]) Americ. Chem. Soc. **32**, 897 (1910).

2. *The vapour pressure formula for the liquid phosphorus.*

When we supplement our former measurements up to 300° by the above mentioned results, we get what follows:

P in atm.	t	$T \ln p$	P in atm.	t	$T \ln p$
0.04	169.0	—1423	0.69	261.4	— 198
0.07	181.3	—1208	0.74	265.5	— 162
0.09	185.5	—1104	1.00	280.5	— 0
0.18	206.9	— 823	1.38	298.6	+ 185
0.20	210.0	— 777	2.47	331.8	+ 547
0.32	229.8	— 573	2.61	332.9	+ 582
0.42	237.9	— 443	2.95	342.0	+ 665
0.54	252.0	— 323	3.88	355.7	+ 852

That the last four points fit in very well with the others, follows clearly from the following graphical representation (Fig. 2), in

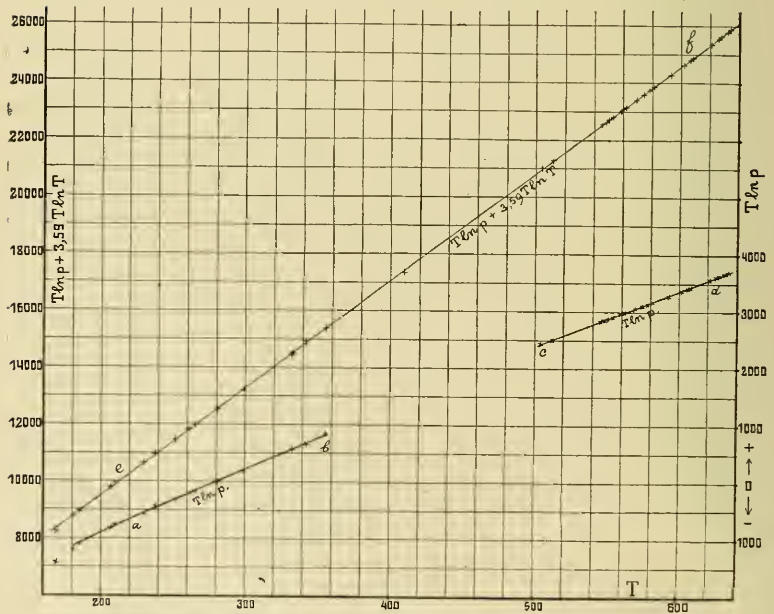

Fig. 2.

which the quantity $T\,ln\,p$ is plotted as function of T (the line ab). We see from this that the different points yield an almost straight line, whose shape is exceedingly little concave with respect to the temperature axis. This had accordingly proved that the preceding determinations had been vitiated by the spontaneous heating of the white phosphorus in conversion.

If in the same diagram we now give $T\,ln\,p$ as function of T also for the liquid violet phosphorus, we get the already discussed straight line cd.

The consideration of these two lines ab and cd brings us at once to the conviction that they belong together, i.e. that they are two parts of one and the same curve, the intermediate part of which cannot be realized here.

It follows then from this that the second part cd cannot be perfectly straight in reality, no more than the first part ab, and that there must be a rational formula to be found, which represents both portions with sufficient accuracy.

To find this formula the following course is taken.

The line ab which represents $T\,ln\,p$ as function of T for the liquid white phosphorus, is only very slightly curved. If we now assume for a moment that this line is straight, then as was already shown before, the constant C can be found by the aid of two points, on the application of the relations:

$$T_1\,lnp_1 = -\frac{Q}{R} + CT_1 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and

$$T_2\,lnp_2 = -\frac{Q}{R} + CT_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

If this value of C is substituted in one of the above equations, then follows from this the value for Q, which indicates the molecular heat of evaporation.

If this is done, we find $Q = 12.17$ kg. cal., 9.96 kg. cal. being found for the mol. heat of evaporation of the liquid violet phosphorus. The latter result was obtained in the same way as here the Q for the liquid white phosphorus was calculated viz. on the assumption that Q is no temperature function.

Now this is, evidently, indeed not the case, for $T\,ln\,p$ plotted as function of T is no perfectly straight line.

We can now accept by approximation that 12.17 kg. cal. is the mean value of the heat of evaporation of the liquid white phosphorus in the temperature interval from 160° to 360°, and that this heat of evaporation will therefore about agree with the mean temperature of 260°. Thus we can also consider the value of 9.96 kg. cal. as the mean heat of evaporation of the liquid violet phosphorus over the temperature range from 512° to 630 , so that this heat of evaporation will about hold for the mean temperature of 571°. Thus we arrive at the result that the heat of evaporation from 260° to 571° decreases by 2210 gr. cal., so that we have at a rough approximation

$$\frac{dQ}{dT} = -7{,}106 \quad \ldots\ldots\ldots \quad (4)$$

If we now start from the equation:

$$\frac{dlnp}{dT} = \frac{Q}{RT^2} \quad \ldots\ldots\ldots \quad (5)$$

and write:

$$Q_T = Q_o + aT \quad \ldots\ldots\ldots \quad (6)$$

we find by integration:

$$lnp = -\frac{Q_o}{RT} + \frac{a}{R} ln\, T + C \quad \ldots\ldots \quad (7)$$

and as according to (6)

$$\frac{d\,Q_T}{d\,T} = a$$

we can substitute the value given by (4) for a. Then equation (7) becomes

$$lnp = -\frac{Q_o}{RT} - 3.59\, ln\, T + C \;^{1)} \quad \ldots\ldots \quad (8)$$

To see whether this formula satisfied, the following graphical method was applied: Let us write equation (8) as follows:

$$Tlnp + 3.59\, Tln\, T = -\frac{Q_o}{R} + C\,T \quad \ldots\ldots \quad (9)$$

we see at once that when this relation satisfies, ($Tln\, p + 3{,}59\ Tln\ T$) plotted as function of T, will have to yield a straight line.

As appears from fig. 2, the thus obtained points lie really on a straight line *ef*, so that it has thus been proved that the relation (6) represents the change of the heat of evaporation with the temperature with sufficient accuracy.

In case of an exceptionally rapid heating, when the result was of course less accurate, a pressure of 7,36 atm. was observed at 409°,3, from which the value 1362 follows for $Tlnp$. In comparison with the

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1) We may just state here that instead of 3.59 we might as well have taken 3 or 4, for the course by which we have come to this value, is a rough approximation.

line discussed just now this value is slightly too low; this proves that the vapour was no longer perfectly saturate with respect to the white liquid phosphorus, which we think by no means astonishing.

By means of the linear relation (9) the constant C may now again be easily found in the following way from the value which the first member possesses at two different temperatures.

$$T_1 \, lnp_1 + 3.59 \, T_1 \, ln \, T_1 = -\frac{Q_0}{R} + C \, T_1 \quad . \quad . \quad . \quad . \quad (10)$$

$$T_2 \, lnp_2 + 3.59 \, T_2 \, ln \, T_2 = -\frac{Q_0}{R} + C \, T_2 . \quad . \quad . \quad . \quad (11)$$

from which follows that:

$$C = \frac{(T_2 lnp_1 + 3.59 T_2 lnT_2) - (T_1 lnp_2 + 3.59 T_1 lnT_1)}{T_2 - T_1} = tg\alpha . \quad . \quad (12)$$

In this way we find **C = 37.62**.

If we substitute this value in (9), we get:

$$T \, ln \, p + 3.59 \, T \, ln \, T = -\frac{Q_0}{R} + 37.62 \, T . \quad . \quad . \quad . \quad (13)$$

3. *Calculation of Q_0 and of the vapour tension.*

By means of this relation we can now calculate the value of $\frac{Q_0}{R}$ from the different observations.

The result of this calculation is recorded in the following table. (see p. 112).

In the fifth column the found values for $\frac{Q_0}{R}$ are given, which give as mean the value 8257, from which follows that $Q_0 = 16{,}35$ kgs. cal.

The sixth column gives the discrepancies which the different results present from the mean, and it appears from this that they are comparatively small, and now exhibit the positive sign, now the negative sign.

If this value for $\frac{Q_0}{R}$ is substituted in equation (13), we get:

$$T lnp + 3.59 \, T ln \, T = 37.62 \, T - 8257 \quad . \quad . \quad . \quad . \quad (14)$$

by the aid of which we can now calculate the pressures for the different observation temperatures.

We find the result of this calculation in column 7.

These calculated pressures harmonize on the whole as well with the observed ones, as can be desired under the given circumstances. This is shown most convincingly by the last column, which gives the difference between the calculated and the observed pressure. It is evident that this difference should not be considered in itself, but

p in atm.	t	$T \ln p$	$T \ln p + 3.59\, T \ln T$	$\frac{Q_0}{R}$	$\Delta \frac{Q_0}{R}$	Calc. p in atm.	Δp
0.04	169.0	— 1423	8242	8386	+ 129	0.05	+ 0.01
0.07	181.3	— 1208	8771	8320	+ 63	0.08	+ 0.01
0.09	185.5	— 1104	8982	8267	+ 10	0.09	0.00
0.18	206.9	— 823	9814	8240	— 17	0.17	— 0.01
0.20	210.0	— 777	9939	8232	— 25	0.19	— 0.01
0.32	229.8	— 573	10655	8261	+ 4	0.32	0.00
0.42	237.9	— 443	10995	8225	— 32	0.40	— 0.02
0.54	252.0	— 323	11482	8268	+ 11	0.55	+ 0.01
0.69	261.4	— 198	11852	8252	— 5	0.68	— 0.01
0.74	265.5	— 162	11995	8263	+ 6	0.75	+ 0.01
1	280.5	0	12554	8269	+ 12	1.02	+ 0.02
1.38	298.6	+ 185	13212	8288	+ 31	1.46	+ 0.08
2.47	331.8	547	14453	8300	+ 43	2.65	+ 0.18
2.61	332.9	582	14518	8276	+ 19	2.70	+ 0.09
2.95	342.0	665	14943	8294	+ 37	3.13	+ 0.18
3.88	355.7	852	15395	8257	0	3.88	0.00
....	....	......	......	....	.....	....	......
(7.36	409.3	1362	17346	8322	+ 65	8.10)	
....	....	......	......	....	.....	....	......
23.2	504	2443	21007	8224	— 33	22.2	— 1.0
24.3	512	2504	21288	8244	— 13	23.9	— 0.4
31.9	545.5	2834	22543	8247	— 10	31.6	— 0.3
32.4	548	2855	22633	8253	— 4	32.2	— 0.2
33.0	550	2878	22712	8249	— 8	32.7	— 0.3
33.6	553	2903	22820	8254	— 3	33.5	— 0.1
34.5	555.5	2934	22920	8248	— 9	34.2	— 0.3
35.4	559	2967	23050	8250	— 7	35.1	— 0.3
35.5	560	2973	23083	8254	— 3	35.4	— 0.1
35.9	562	2990	23156	8257	0	35.9	0.0
37.6	569	3054	23414	8268	+ 5	37.8	+ 0.2
38.8	574	3099	23598	8266	+ 9	39.2	+ 0.4
40.3	578	3146	23756	8259	+ 2	40.4	+ 0.1
41.1	581	3173	23867	8261	+ 4	41.3	+ 0.2
44.2	593	3281	24309	8270	+ 13	44.9	+ 0.7
47.0	602	3369	24648	8270	+ 13	47.7	+ 0.7
48.6	606.5	3416	24821	8266	+ 9	49.1	+ 0.5
49.0	608	3429	24876	8268	+ 11	49.6	+ 0.6
53.9	621	3564	25374	8258	+ 1	53.9	0.0
55.6	625.5	3610	25546	8256	— 1	55.5	— 0.1
56.5	627.5	3633	25625	8252	— 5	56.2	— 0.3
57.7	632	3670	25788	8258	+ 1	57.8	+ 0.1
58.6	634	3692	25866	8256	— 1	58.5	— 0.1

in connection with the absolute value found in the first or in the sixth column.

Besides the vapour pressure line of violet phosphorus, also that for liquid phosphorus is indicated in fig. 4, from which it is seen how the observed vapour pressures lie on the line drawn according to formula (14).

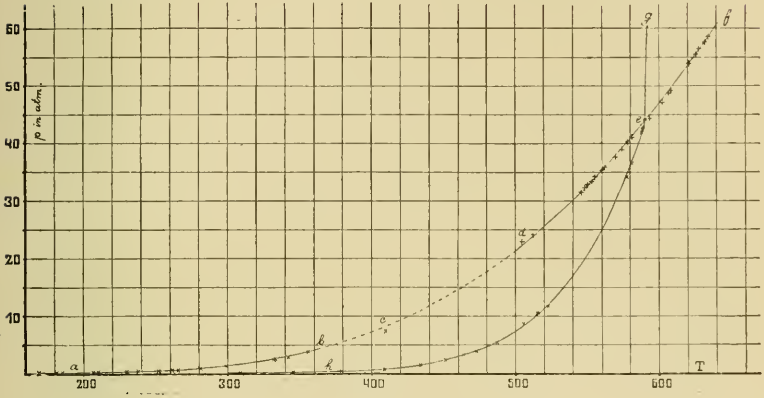

Fig. 3.

4. *Conclusions.*

The result of this investigation is so important for this reason that it was not known before whether there was any connection between the liquid white, and the liquid violet phosphorus. Bakhuis Roozeboom [1]) pointed out the possibility that the liquid white phosphorus had to be looked upon as supercooled liquid violet phosphorus, but he also expressed the opinion that it might also be that the phosphorus entirely agreed with the cyanogen, and that the vapour pressure line of the liquid white phosphorus terminated below the melting-point of the violet form in a critical point.

Up to a short time ago we thought for three reasons that this latter supposition of Bakhuis Roozeboom's would be the correct one. First of all the shape of the vapour pressure line of the liquid white phosphorus found some time ago pointed to the fact that this line could not be the prolongation of that of the liquid violet one. In the second place it could be calculated from the determinations of Aston and Ramsay [2]) of the surface tension that the liquid white phosphorus must reach its critical point at ± 422°. And in the third

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[1]) Lehrbuch Heterog. Gleichgewichte **171** and **176**.

[2]) Journ Chem Soc. **65**, 173 (1894).

place the peculiar way in which, as **Stock** and **Gomolka** [1]) were the first to find, red phosphorus can suddenly deposit from supercooled molten violet phosphorus and its vapour, seemed to point to a critical phenomenon.

In virtue of these three circumstances which seem to be in agreement with each other, we concluded phosphorus and cyanogen to be systems of the same type, and devised a diagram for the pseudo system of phosphorus, which was in close connection of that of cyanogen.

Now for the first time the question raised by **Bakhuis Roozeboom**, has been answered, and it has now appeared that the three above mentioned circumstances misled us at first. Phosphorus does not belong to the same type as cyanogen and the liquid white phosphorus must be really taken as supercooled liquid violet phosphorus.

The first determinations of the vapour tension were faulty at the highest temperature. **Aston** and **Ramsay**'s determinations of the surface tension of liquid white phosphorus (which were only two, indeed) appear not to justify a calculation of the critical temperature, and the just mentioned phenomenon, which was observed by **Stock** and **Gomolka**, must be ascribed to this that the number of nuclei possesses a strongly pronounced maximum at a definite degree of supercooling, so that a spontaneous crystallisation, which proceeds with very great velocity, suddenly occurs there.

We see with great satisfaction that the system phosphorus can be represented in a simpler way than we thought at first in consequence of the non-existence of the supposed complication.

The P,T-projection of the system phosphorus for so far as it is known now, is schematically represented in the subjoined fig. 6.

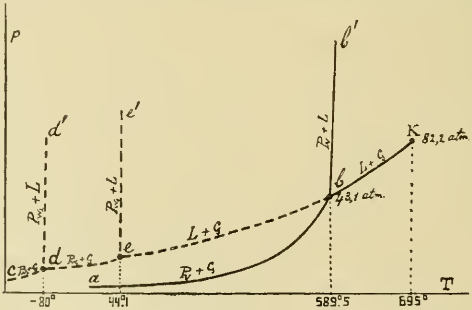

Fig. 4.

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[1]) Ber. 42, 4510 (1909).

With regard to the *TX*-fig. we must point out, that as was already remarked by us before [1]), the pseudo-system of the phosphorus is most probably ternary, and that the third kind of molecules which has been left unconsidered up to now, plays probably a principal part in the change of the point of solidification of the white phosphorus. To simplify the representation we can disregard this third kind of molecules and take the pseudo system as binary, at least when our point of consideration is the connection between the white and the violet phosphorus.

Now the difference in properties between the white and the violet phosphorus, just as the difference in volatility and melting point suggest with great probability that we have to do here with a system of molecule-kinds, which differ in *size*. Hence we have probably to do here with the case of *association*, and the violet

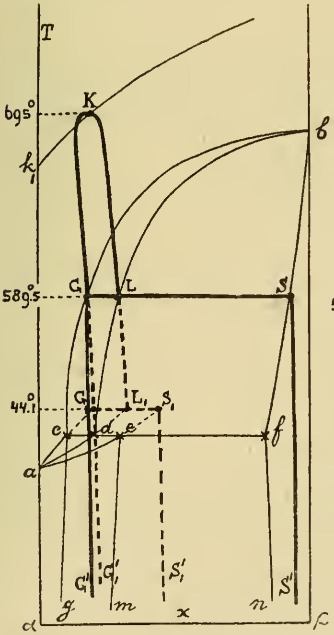

Fig. 5.

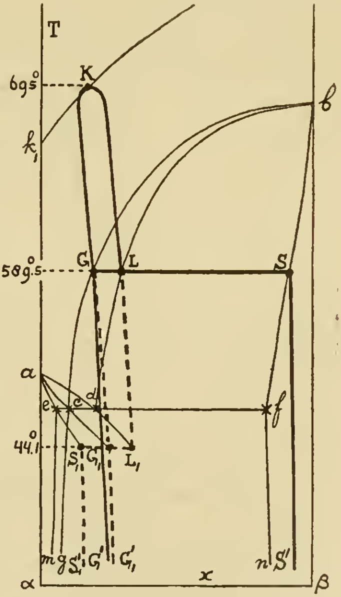

Fig. 6.

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[1]) Z. f. phys. Chem. 88, 621 (1914).

phosphorus will differ from the white chiefly in this that it contains a much larger proportion of associated molecules.

In this case the pseudo system, as was already explained several times, will possess no eutectic point, and then this pseudo system with the unary system lying in it, can be given schematically by fig. 5. If the pseudo-component β was isomer of α, also a figure like fig. 6 would be possible.

Note. When according to form. 14 we calculate the pressure corresponding with the temperature of 695°, which is the critical temperature of the liquid phosphorus according to W. A. Wahl's measurements, we find **82.2** atm. This is therefore the critical pressure, for which we found 83.56 in our preceding communication by means of the assumed linear relation.

When we calculate the b-value from the critical pressure **82,2** atm. and the absolute critical temperature of $696° + 273° =$ **968°**, and from this the size of the phosphorus molecule, we find **4.33**; we found **4.26** before, which makes no difference of any importance.

According to the formula:

$$f = 0{,}4343 \left(\frac{T_1 \, ln\, p_1 - T_2 \, ln\, p_2}{T_1 - T_2} - ln\, p_k \right)^{1)}$$

the following values are found for the value of f at different temperatures:

from 200° to 300° $f = 3{,}11$
„ 300° „ 400° $f = 2{,}84$
„ 400° „ 500° $f = 2{,}60$
„ 500° „ 600° $f = 2{,}40$

Amsterdam, April 19, 1915. *Anorg. Chemic. Laboratory of the University.*

Chemistry. — *"In-, mono- and divariant equilibria"* I. By Prof. F. A. H. Schreinemakers.

1. *Introduction.*

When $n + 2$ phases occur in an equilibrium, which is composed of n substances, then it is invariant; the composition of the phases, the pressure and the temperature are perfectly defined then. In a P,T-diagram this equilibrium is represented by a point; we shall call this pressure and this temperature P_0 and T_0.

As this equilibrium is completely determined in every respect neither the composition of the phases, nor the pressure or the temperature can change on addition or withdrawal of heat or on

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1) In the preceding communication the term lnp_k had been erroneously omitted.

a change of volume. Then, however, a reaction occurs, at which the quantities of some phases increase, those of other phases decrease, and only after disappearance of one of the phases, pressure, temperature and composition of the phases can change.

May the composition of a phase F_1 be given by the quantities

$(x_1)_1\ (x_2)_1\ (x_3)_1 \ldots (x_{n-1})_1$ and 1 or $1 - (x_1)_1 - (x_2)_1 \ldots (x_{n-1})_1$

that of a phase F_2 by:

$(x_1)_2\ (x_2)_2\ (x_3)_2 \ldots (x_{n-1})_2$ and 1 or $1 - (x_1)_2 - (x_2)_2 \ldots (x_{n-1})_2$

of the n components. We express in the same way the compositions of the phases $F_3, F_4, \ldots F_{n+2}$. Let occur between these $n+2$ phases the reaction:

$$y_1F_1 + y_2F_2 + y_3F_3 + \ldots + y_{n+2}F_{n+2} = 0 \quad . \quad . \quad . \quad (1)$$

y_1F_1 means y_1 quantities of the phase F_1, each of which has the composition given above; y_2F_2 etc. have the same meaning. It is evident that these reaction-coefficients $y_1 \ldots y_{n+2}$ cannot have all the same sign. In order to know reaction (1) it is not necessary to know the $n+2$ reactioncoefficients $y_1 \ldots y_{n+2}$ themselves, the reaction is viz. determined by their $n+1$ relations.

From the condition, that at the reaction the total quantity of each of the n components rests unchanged, the n relations follow:

$$\left.\begin{array}{l}
y_1 + y_2 + y_3 + \ldots + y_{n+2} = 0 \\
y_1\,(x_1)_1 + y_2\,(x_1)_2 + y_3\,(x_1)_3 + \ldots + y_{n+2}\,(x_1)_{n+2} = 0 \\
y_1\,(x_2)_1 + y_2\,(x_2)_2 + y_3\,(x_2)_3 + \ldots + y_{n+2}\,(x_2)_{n+2} = 0 \\
\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
y_1\,(x_{n-1})_1 + y_2\,(x_{n-1})_2 + y_3\,(x_{n-1})_3 \ldots + y_{n+2}\,(x_{n-1})_{n+2} = 0
\end{array}\right\} \quad . \quad . \quad (2)$$

As we have only n conditions for the determination of the $n+1$ ratios, (2) and therefore also (1) may be satisfied in infinitely many ways, or in other words: the reaction between the $n+2$ phases of an invariant equilibrium can take place in infinitely many ways.

Now we put the condition that the totalvolume remains the same at the reaction; the reaction is then: "isovolumetrical". When we represent the volumina of the above-mentioned quantities of the phases F_1, F_2 etc. by v_1, v_2 etc. then it follows:

$$y_1v_1 + y_2v_2 + y_3v_3 + \ldots + y_{n+2}v_{n+2} = 0 \quad . \quad . \quad . \quad . \quad (3)$$

Now we have $n+1$ equations [viz. the n equations (2) and equation (3)]; the $n+1$ ratios of the reaction-coefficients are consequently determined and therefore also the proceeding of the reaction (1). Consequently we find that an isovolumetrical reaction between the $n+2$ phases of an invariant equilibrium is completely determined.

We might just as well have posed instead of (3) the condition that the reaction takes place without addition or withdrawal of heat. As the entropy remains the same then, we call such a reaction an "isentropical reaction". When we represent the entropies by η_1, η_2 etc., then the condition is:

$$y_1\eta_1 + y_2\eta_2 + y_3\eta_3 + \cdots + y_{n+2}\eta_{n+2} = 0 \quad . \quad . \quad . \quad (4)$$

Then we have again $n + 1$ equations, so that also an isentropical reaction between the $n + 2$ phases of an invariant equilibrium is completely defined.

It is evident that the coefficients y_1, y_2 etc. in the isovolumetrical reaction (1) are others than in the isentropical reaction (1). Further it is also evident that, dependent on the direction of the reaction, we must add or withdraw heat with an isovolumetrical reaction and that we must change the volume with an isentropical reaction.

Now we imagine at T_0 and under P_0 that the $n + 2$ phases $F_1 \ldots F_{n+2}$ are together; we let the isovolumetrical or isentropical reaction take place and we let this proceed until one of the phases disappears. Then an equilibrium of n components in $n + 1$ phases arises, which is consequently monovariant. In this way $n + 2$ monovariant equilibria may occur. As in each of these equilibria one of the phases of the invariant point fails, we represent, for the sake of abbreviation, a monovariant equilibrium by putting between parentheses the missing phase. Consequently we shall represent the equilibrium $F_2 + F_3 + \ldots F_{n+2}$ by (F_1), the equilibrium $F_1 + F_3 + F_4 + \ldots F_{n+2}$ by (F_2), etc. From the invariant equilibrium, therefore, the $n + 2$ monovariant equilibria $(F_1), (F_2), (F_3) \ldots (F_{n+2})$ may occur.

Each monovariant equilibrium exists at a whole series of temperatures and corresponding pressures; consequently it is represented in the P,T-diagram by a curve, which goes through the invariant point P_0T_0. Therefore in this point $n + 2$ curves intersect one another. Each of these curves is divided by the invariant point into two parts; the one represents stable conditions the other metastable conditions. We shall always dot the metastable part. (See e. g. the fig. 1, in which these curves are indicated in the same way as the equilibria, which they represent).

When we consider only stable conditions, we may say: $n + 2$ monovariant curves proceed from an invariant point of a system of n components.

In order to define the direction of these curves in the P,T-diagram, we may use the following thesis[1]: the systems which are formed on addition of heat at an isovolumetrical reaction exist at higher — those which are formed on withdrawal of heat exist at lower temperatures. The systems which are formed on decrease of volume at an isentropical reaction exist under higher — those which are formed on increase of volume exist under lower pressures.

Let us consider now the equilibrium $(F_1) = F_2 + F_3 + \ldots F_{n+2}$, which is represented in fig. 1 by curve (F_1) at a temperature T_a and under a pressure P_a, which are represented by the point a. On addition of heat under a constant pressure or on change of volume at a constant temperature a reaction, which is completely defined, occurs between these $n+1$ phases. Let us write this reaction:

$$y_2 F_2 + y_3 F_3 + \ldots y_{n+2} F_{n+2} = 0. \quad . \quad . \quad . \quad . \quad (5)$$

The n relations between the $n+1$ reaction-coefficients are fixed then by the n equations (2) in which, however, we must omit all terms which refer to the phase F_1, [consequently y_1, $(x_1)_1$, $(x_2)_1$ etc.].

Now we let reaction (5) occur until one of the phases of the equilibrium (F_1) disappears; then an equilibrium of n phases arises, which is consequently bivariant. In all $n+1$ bivariant equilibria can arise from the equilibrium (F_1). As in each of these equilibria two of the phases of the invariant point are wanting, we represent a bivariant equilibrium by putting between parentheses the failing phases. (F_1F_2) represents consequently the equilibrium $F_3 + F_4 + \ldots F_{n+2}$. From the equilibrium (F_1), therefore, the bivariant equilibria (F_1F_2), $(F_1F_3) \ldots (F_1F_{n+2})$ may arise in the manner, which is treated above.

In a bivariant equilibrium P and T can be considered as independent variables; each bivariant equilibrium can, therefore, be represented in the P,T-diagram by the points of the plane of this diagram, consequently by a region.

Consequently $n+1$ bivariant regions, which may arise from the equilibrium (F_1), go through each monovariant curve (F_1). Each of these regions is divided into two parts by the curve (F_1); the one part represents stable conditions, the other metastable conditions. When we limit ourselves to the stable parts of these regions, we may say: in a system of n components $n+1$ bivariant regions start from each monovariant curve.

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[1] F. A. H. Schreinemakers. Heterog. Gleichgewichte von H. W. Bakhuis Roozeboom. III': we find herein the proofs for ternary systems on p. 220—221 and 298—301. These, however, are also true for systems of n components.

The $n+1$ regions starting in fig. 1 from curve (F_1), are situated partly at the one and partly at the other side of this curve; also it is evident that the regions, which are situated on the same side of the curve, cover one another. Hence it follows immediately that several bivariant equilibria can occur under a given P and at a given T.

In order to determine on which side of the curve (F_1) the stable part e.g. $(F_1 F_2)$ of a bivariant region is situated, we let the reaction (5) take place in such a way, that the phase F_2 disappears from the equilibrium (F_1). This may always take place, when the quantity of F_2 in the equilibrium (F_1) has been taken small enough. If we let this reaction proceed under a constant pressure, we have to state whether heat must be added or supplied, when we let it take place at a constant temperature, we must determine whether the volume increases or decreases. We may then apply the following rules: at the right of the curve we find the bivariant equilibria, which arise on addition of heat; at the left of the curve those which arise on withdrawal of heat. Above the curve we find the bivariant equilibria, which arise on decrease of volume; beneath the curve those, which arise on increase of volume.

For the meaning of "at the right", "at the left", "beneath" and "above" is assumed that the P- and T-axes are situated as in fig. 1.

When we apply the considerations, mentioned above, to each of the $n+2$ curves $(F_1)\ldots(F_{n+2})$ then we obtain the division of the $\frac{1}{2}(n+2)(n+1)$ divariant regions between the different curves and around the point O.

The following is apparent from the previous considerations. When we know the compositions of the phases, which occur in an invariant point and the changes in entropy and volume which take place at the reactions, then we are able to determine in the P,T-diagram the curves starting from this point and the division of the bivariant regions.

2. *Some general properties.*

Now we will put the question whether anything may be deduced concerning the position of the curves and the regions with respect to one another, when we know the compositions of the phases only and not the changes of entropy and volume which the reactions involve.

This question is already dissolved for binary [1]) and ternary [2])

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[1]) F. A. H. SCHREINEMAKERS, Z. f. Phys. Chemie **82** 59 (1913) and F. E. C. SCHEFFER, these Communications October 1912.

[2]) F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von BAKHUIS ROOZEBOOM III' 218.

systems, the way which we have followed then [viz. with the aid of the graphical representation of the ψ- and the ζ-function] is not appropriate however to be applied to systems with more components. The following method is much simpler and leads to the result desired for any system.

We consider an invariant point with the phases $F_1, F_2, \ldots F_{n+2}$ and two of the curves starting from this point, viz. $(F_1) = F_2 + + F_3 + \ldots F_{n+2}$ and $(F_2) = F_1 + F_3 \ldots F_{n+2}$. (see fig. 1). Between the stable parts of these curves the region $(F_1 F_2) = F_3 + F_4 + \ldots F_{n+2}$ is situated. When we consider stable conditions only, this region terminates at the one side in curve (F_1), at the other side in curve (F_2). Now it is the question in which of the two angles $(F_1)\, O\, (F_2)$ the region $(F_1 F_2)$ is situated, viz. in the angle which is smaller or in the angle which is larger than 180°. The first case has been drawn in fig. 1 in the latter case the region $(F_1 F_2)$ should extend itself over the metastable parts of the curve (F_1) and (F_2). We call the angle of the region $(F_1 F_2)$ in the point o the region-angle of $(F_1 F_2)$; we can prove now: "a region-angle is always smaller than 180°."

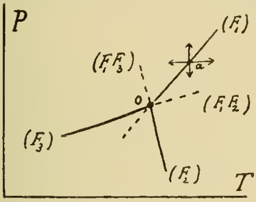

Fig. 1.

In order to prove this we imagine in fig. 1 the region $(F_1 F_2)$ in the angle $(F_1)\, o\, (F_2)$, which is larger than 180°. The stable part of this region then extends itself on both sides of the metastable part of curve (F_1) and also of (F_2). This now is in contradiction with the property that the stable part of each region, which may arise from a curve, is situated only at one side of this curve. Hence it follows, therefore, that the region-angle must be smaller than 180°.

Therefore, when we will draw in fig. 1 the region $(F_1 F_3)$, this must be situated in the angle $(F_1)\, O\, (F_3)$, which is smaller than 180°. As in fig. 1 (F_3) and (F_2) are drawn on different sides of (F_1); the regions $(F_1 F_3)$ and $(F_1 F_2)$ fall outside one another; when we had taken (F_2) and (F_3) on the same side of (F_1), the two regions should partly cover one another.

Another property is the following: every region, which extends itself over the metastable or stable part of a curve (F_p) contains the phase F_p, or in other words: each region which is intersected by the stable or the metastable part of a curve (F_p) contains the phase F_p. In an invariant point the $n+2$ phases $F_1 F_2 \ldots F_{n+2}$ occur; consequently arround this point $\frac{1}{2}(n+2)(n+1)$ bivariant regions extend themselves. In $n+1$ of these regions the phase F_1 is wanting, viz. in (F_1F_2), $(F_1F_3)\ldots(F_1F_{n+2})$; in all the other [viz. in $\frac{1}{2}n(n+1)$ regions] it is present however. The same applies to every other phase.

Now we imagine in fig 1 the curves $(F_1), (F_2)\ldots(F_{n+2})$ to be drawn. The $n+1$ regions in which the phase F_1 does not occur, all start from the stable part of the curve (F_1); none of those regions can therefore, extend itself over the stable part of curve (F_1). When, therefore a region extends itself over the stable part of the curve (F_1), then it must consequently contain the phase F_1. As every region-angle is however smaller than 180°, none of the $n+1$ regions, in which the phase F_1 does not occur, can extend itself over the metastable part of the curve (F_1); the regions, which extend themselves over this part, consequently contain all the phase F_1.

Consequently we find: each region, which extends itself over the metastable or stable part of a curve (F_p), contains the phase F_p.

We must keep in mind with this that the metastable part of a curve is always covered by one or more regions, but this is not always the case with the stable part. Further it is also apparent that the reverse of the previous thesis viz. "all regions which contain themselves the phase F_p extend themselves over the metastable or stable part of the curve (F_p)" need not be true; this is only always the case in unary systems. Later we shall still refer to these and other properties.

Now we shall deduce a thesis, which is of great importance for the determination of the position of the curves with respect to one another. For fixing the ideas we take an invariant point with the phases F_1, F_2, F_3, F_4 and F_5 and we consider the curve $(F_1) = F_2 + F_3 + F_4 + F_5$ starting from this point. Between the four phases of this equilibrium on addition or withdrawal of heat a reaction occurs, which is, as we have seen above, completely defined by the compositions of the phases. Let this reaction be for instance:

$$F_2 + F_3 \rightleftarrows F_4 + F_5 \quad \ldots\ldots\ldots \quad (6)$$

Consequently four bivariant regions start from the curve (F_1) viz. $F_2F_3F_4$, $F_2F_3F_5$, $F_2F_4F_5$ and $F_3F_4F_5$. It follows from (6) that the regions $F_2F_3F_4$ and $F_2F_3F_5$ are situated at the one side and the regions $F_2F_4F_5$ and $F_3F_4F_5$ at the other side of curve (F_1). We write this:

$$\left.\begin{array}{c|c} \multicolumn{2}{c}{F_2 + F_3 \rightleftarrows F_4 + F_5} \\ F_2F_3F_4 & F_2F_4F_5 \\ F_2F_3F_5 & F_3F_4F_5 \end{array}\right\} \quad \ldots\ldots\ldots \quad (7)$$

When we should know the changes in entropy and volume, occurring with reaction (6), then we could, as we have seen above, indicate at which side (viz. at the right, at the left, above or beneath) of curve (F_1) each of these regions is situated. As this is not the case, we only know that the regions, which are written in (7) at the right of the vertical line, are situated at the one side and those, which are written at the left of this line, are situated at the other side of (F_1). Each of the four regions is limited, besides by curve (F_1) also still by another curve, viz. the region $F_2\,F_3\,F_4$ by (F_5), $F_2F_3F_5$ by (F_4), $F_2F_4F_5$ by (F_3) and $F_3F_4F_5$ by (F_2). When we keep in mind now that every region-angle is smaller than 180°, then it is evident that the curves (F_5) and (F_4) are situated at the one side and the curves (F_3) and (F_2) at the other side of curve (F_1). We shall represent this in future in the following way:

$$F_2 + F_3 \rightleftarrows F_4 + F_5 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

$$(F_2)\,(F_3)\;\text{,}\;(F_1)\mid(F_4)\,(F_5)\,. \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

This means: when reaction 8 occurs between the phases of curve (F_1), then the curves (F_2) and (F_3) are situated at the one side and the curves (F_4) and (F_5) are situated at the other side of curve (F_1).

As the previous considerations are completely valid in general, we find the following. When we know of a system of n-components the compositions of the $n+1$ phases of a curve (F_1), then also the reaction is known between these $n+1$ phases $F_2, F_3 \ldots F_{n+2}$. With the aid of this reaction we can divide the curves $(F_2), (F_3) \ldots (F_{n+2})$ into two groups in such a way, that the one group is situated at the one side and the other group at the other side of curve (F_1).

As we may act in the same way with each of the other curves, we find:

When we know the compositions of the $n+2$ phases $F_1, F_2, \ldots F_{n+2}$, which occur in an invariant point, we can with respect to each of the curves $(F_1), (F_2) \ldots (F_{n+2})$ divide the $n+1$ remaining curves into two groups in such a way that the one group is situated at the one side and the other group is situated at the other side of the curve under consideration.

Now we shall apply the rule which is treated above, to some cases in order to deduce the position of the different curves with respect to one another. In order to simplify the discussions, we shall distinguish instead of "at the one" and "at the other side" of a curve "at the right" and "at the left". For this we imagine that we find ourselves on this curve facing the stable part and turning our back towards the stable part. Consequently in fig. 1 (F_2) is situated at the right and (F_3) at the left of (F_1); (F_3) is situated at the right and (F_1) at the left of (F_2); (F_1) is situated at the right and (F_2) at the left of (F_3).

3. *Unary systems.*

In an invariant point of a unary system three phases F_1, F_2 and F_3 occur; consequently the point is a triplepoint. Three curves (F_1), (F_2) and (F_3) start from this point, further the three regions of F_1, F_2 and F_3 occur. From our previous considerations the well-known property immediately follows: the region of F_1 covers the metastable part of curve $(F_1) = F_2 + F_3$, the region of F_2 covers the metastable part of curve $(F_2) = F_1 + F_3$ and the region of F_3 covers the metastable part of curve $(F_3) = F_1 + F_2$.

4. *Binary systems*[1].

In an invariant point of a binary system four phases occur; consequently this point is a quadruple point. When we omit, as we shall do in the following, the letter F in the notation and when we keep the index only, then we may call these phases 1, 2, 3 and 4. The four curves (1), (2), (3) and (4) are starting from this quadruple point, further we find $\frac{1}{2}(n+2)(n+1) = 6$ regions viz. 12, 13, 14, 23, 24 and 34.

We call the two components of which the system is composed, A and B; the four phases may be represented then by four points of a line AB. In fig. 2 we have assumed that each phase contains the two components; it is evident however, that F_1 can also represent the substance A and F_4 the substance B.

Now we shall deduce with the aid of the former rules the situation of the four curves with respect to one another. As F_2 is situated between F_1 and F_4 (fig. 2) we find:

$$2 \rightleftarrows 1 + 4 \quad \ldots\ldots\ldots \quad (10)$$

$$(2)\ |(3)|\ (1)\,(4) \quad \ldots\ldots\ldots \quad (11)$$

As F_3 is situated between F_2 and F_4 it follows:

$$3 \rightleftarrows 2 + 4 \quad \ldots\ldots\ldots \quad (12)$$

$$(3)\ |(1)|\ (2)\,(4) \quad \ldots\ldots\ldots \quad (13)$$

Now we draw in a P,T-diagram (fig. 2) quite arbitrarily the two curves (1) and (3); for fixing the ideas we draw (3) at the left of (1).

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[1] For another deduction see also F. A. SCHREINEMAKERS (l.c.) and F. E. C. SCHEFFER (l.c.).

We firstly determine now the position of (2). It is apparent from equation 11 that the curves (1) and (2) are situated at different sides of (3); as (1) is taken at the right of (3), (2) must, therefore, be situated at the left of (3). It is apparent from equation 13 that the curves (2) and (3) are situated at different sides of (1); as (3) has been taken at the left of (1), (2) must consequently be situated at the right of (1).

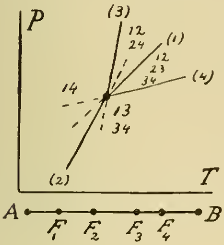

Fig. 2.

Therefore, we find: curve (2) is situated at the left of (3) and at the right of (1); it is situated, therefore, as is drawn in fig. 2 between the metastable parts of (1) and (3).

Now we determine the position of (4). It is apparent from equation 11 that (1) and (4) are situated at the same side of (3); (4) is, therefore, situated at the right of (3). It is apparent from equation (13) that (3) and (4) are situated at different sides of (1); consequently (4) is situated at the right of (1).

Consequently we find: curve (4) is situated at the right of (1) and (3); it is situated, therefore, as is also drawn in fig. 2, between the stable part of (1) and the metastable part of (3).

From fig. 2 still follow the relations:

$2 \rightleftarrows 1 + 3$ . . . . (14) $\qquad$ $3 \rightleftarrows 1 + 4$ . . . . (16)

and

$(2)\,|\,(4)\,|\,(1)\,(3)$ . . . (15) $\qquad$ $(3)\,|\,(2)\,|\,(1)\,(4)$ . . . (17)

As the position of the curves with respect to one another, is already fixed in fig. 2, we need no more the relations 14—17, they may however be useful as a confirmation. From (15) follows that (1) and (3) are situated at the one side and (2) at the other side of (4); in accordance with (17) (1) and (4) are situated at the one side and (3) at the other side of (2). We see that this is in accordance with fig. 2. Consequently we find the following rule:

when we call, going from the one component towards the other, the phases occurring in a quadruplepoint F_1, F_2, F_3 and F_4 then the order of succession of the curves, if we move in the P, T-diagram around the quadruplepoint, is 1, 3, 2, 4 or reversally.

We have assumed at the deduction above that curve (3) is situated at the left of (1); when we take (3) at the right of (1) we find the same order of succession.

Now we shall seek the position of the 6 bivariant regions. From curve $(1) = 2 + 3 + 4$ the regions 23, 24 and 34 are starting. The region 23 extends itself between the curves (1) and (4); it is indicated in fig. 2 by 23. The region 24 is situated between the curves (1) and (3); the region 34 is situated between the curves (1) and (2) and therefore, extends itself over curve (2) [fig. 2]. [We keep in mind with this that each region-angle is smaller than 180°.]

When we act in the same way with the regions which start from the curves (2), (3) and (4) we find a partition of the regions as in fig. 2.

Previously we have deduced: each region, which extends itself over the stable or metastable part of curve (F_p) contains the phase F_p. We see the confirmation of this rule in fig. 2. The metastable part of curve (1) intersects the region 14, the stable part of this curve the region 12; both the regions contain the phase 1. The metastable part of curve (2) intersects the regions 12 and 24, which contain both the phase 2; the metastable part of curve (3) intersects the regions 13 and 34 which contain both the phase 3. The metastable part of curve (4) intersects the region 14, the stable part of this curve is covered by the region 34; both the regions contain the phase 4.

The following is apparent from the preceding considerations. In all binary systems the partition and the position of the curves and the regions will respect to one another starting from a quadruplepoint, is always the same; it can be represented by fig. 2.

(*To be continued*).

Chemistry. — "*Compounds of the Arsenious Oxide.*" II. By Prof. F. A. H. SCHREINEMAKERS and Miss W. C. DE BAAT.

a. Introduction.

By RÜDORFF[1]) and others compounds are prepared of the As_2O_3 with halogenides of potassium, sodium and ammonium.

These compounds were obtained by treating solutions of arsenites (viz. solutions of As_2O_3 in a base) with the corresponding halogenides.

RÜDORFF describes the compound $As_2O_3 . NH_4Cl$, which we have found also; he also describes the compound $(As_2O_3)_2 . KCl$. which we have not found.

In order to obtain these compounds, we have, however, worked in quite another manner; for this we have brought together water,

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[1]) FR. RÜDORFF. Ber. **19** 2668 (1886), **21** 3051 (1888).

As_2O_3 and the halogenide, consequently without first dissolving As_2O_3 in a base. Therefore, we had to deal with equilibria in the ternary systems: water-As_2O_3-halogenide.

Of course we have to bear in mind in judging the results, that the possibility is never excluded that besides the compounds which have shown themselves, others might exist, that even the compounds found might be metastable.

b. The system: $H_2O — As_2O_3 — KCl$ at 30°.

In this system at 30° the two components As_2O_3 and KCl occur as solid phases and further a compound, which we shall call D. The composition of this compound is defined with the aid of the rest-method, but is not known exactly. It is sure, however, that it has not the composition: $(As_2O_3)_2\,KCl$; it is about $(As_2O_3)_6(KCl)_5$ or $(As_2O_3)_5\,(KCl)_4$; we shall refer to this further.

In fig. 1 in which the point Z indicates the component KCl the isotherm of 30° is represented schematically, this isotherm consists of three branches;

ab represents the solutions, saturated with As_2O_3
bc ,, ,, ,, ,, ,, D
cd ,, ,, ,, ,, ,, KCl.

The composition of the solution b, which is saturated with $As_2O_3 + D$, has not been defined. It is apparent from table 1 that its percentage of KCl will be between 10,37 and 11.22 $^0/_0$ and that its percentage of As_2O_3 will be somewhat higher than 2.46 $^0/_0$. Further it is apparent from table 1 that the solubility of As_2O_3 with increasing percentage of KCl of the solution increases a little, viz. from 2.26$^0/_0$ to a little over 2.46 $^0/_0$; consequently the point b is situated somewhat further from the side WZ than the point a. Further it is apparent from table 1 that the solubility of the compound D decreases at increasing percentage of KCl of the solutions, viz. of over 2.46$^0/_0$ to about 0.78$^0/_0$ (in table 1 the average of N°. 12 and 13); curve bc approaches, the side WZ in fig. 1 therefore from b. Consequently we see that the solubility of As_2O_3 increases at first a little by adding KCl, until the compound D is separated, after which the solubility decreases. [from 2.26$^0/_0$ in pure water (point a) towards 0.78 $^0/_0$ in a solution saturated with KCl (point c)].

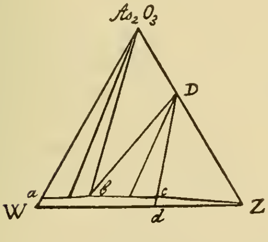

Fig. 1-

No other points besides both the terminating points *c* and *d* have been defined of curve *cd*, which represents the solutions saturated with *KCl*.

We find united in table I the results of the different analyses; all the small bottles have been shaken in a thermostat during from three to five weeks. Although the As_2O_3 and the compound *D* formed both an extremely fine powder, the eye could easily distinguish them by their different behaviour on sinking.

TABLE 1.

	Composition in percentages by weight at 30°				
	of the solution		of the rest		
N°.	% As_2O_3	% KCl	% As_2O_3	% KCl	solid phase
1	2.26	0	—	—	As_2O_3
2	2.40	6.58	84.05	1.05	»
3	2.46	10.37	82.48	2.13	»
4	2.10	11.22	36.84	17.07	D
5	1.77	13.59	18.74	15.88	»
6	1.52	15.89	37.45	20.06	»
7	1.34	17.72	32.81	20.62	»
8	1.10	20.67	19.73	21.75	»
9	0.995	22.38	23.53	22.31	»
10	0.898	22.92	11.36	23.12	»
11	0.841	25.23	26.93	24.70	»
12	0.783	26.96	12.23	28.16	D + KCl
13	0.777	27.11	(8)	(32)	D + KCl
14	0	27.2	—	—	KCl

The solubility of KCl in pure water (n°. 14 of table 1) has not been determined but has been taken from the tables of Landolt-Börnstein.

As table I shows, besides the compositions of several solutions, also the rests belonging to them, are determined; the numbers placed between parentheses in n°. 13 indicate however the composition of the complex. In order to examine if in the determinations errors might have occurred by analysis or anything else, several complexes were weighed accurately; this complex must then be situated on a straight line with the solution and the rest formed from this. This was always the case in this examination.

When in fig. 1 we draw the conjugationlines, which unite the solutions of branch *bc* with the corresponding rests, those do not go, as is drawn in fig. 1, through the same point D. When we call the percentages of As_2O_3 and water of a solution Y_l and W_l, those of the corresponding rest Y_r and W_r, and when we call Y_f the percentage of As_2O_3 of the point D (the point of intersection of the line liquid-rest with the side As_2O_3—W) then we find:

$$Y_f = Y_r + \frac{Y_r - Y_l}{W_l - W_r} \times W_r.$$

When we calculate with the aid of this formula Y_f for the determinations 4—11 of table 1, we find

76.29; 76.35; 75.52; 75.45; 75.04; 77.86; 75.65; 76.30.

As the compound $As_2O_3 . KCl$ contains 72.6 % As_2O_3 and the compound $(As_2O_3)_2\,KCl$ contains 84.1 % As_2O_3, the point D, therefore cannot represent this compound, it is more probably $(As_2O_3)_6\,(KCl)_5$. which contains 76.1% As_2O_3 or $(As_2O_3)_5\,(KCl)_4$ which contains 76.9% As_2O_3. When we take the average of the eight determinations, then we find 76.08 % As_2O_3, which is in accordance with the composition of $(As_2O_3)_6\,(KCl)_5$.

When we draw in fig. 1 the line WD, we see that this does not intersect the saturationcurve of D, but that of the As_2O_3. Consequently the compound is not soluble in water without decomposition, but is decomposed with separation of As_2O_3.

c. The system: H_2O—As_2O_3—NH_4Cl at 30°.

In this system both the components As_2O_3 and NH_4Cl and further a compound D occur at 30°. We found for the composition of this compound, which is determined with the aid of the rest-method, $As_2O_3 . NH_4Cl$

We may represent the isotherm of 30° in this system again schematically by fig. 1; the anglepoint Z represents then the NH_4Cl and the point D the compound $As_2O_3 . NH_4Cl$. Consequently the isotherm consists again of three branches, viz.:

ab, the saturationcurve of As_2O_3
bc, ,, ,, ,, $As_2O_3 . NH_4Cl = D$
cd, ,, ,, ,, NH_4Cl.

It is apparent from table 2 that the solubility of the As_2O_3 remains invariable within the errors of analysis on increasing percentage of NH_4Cl of the solutions. The solution (point *b*) which contains 7.08% NH_4Cl, contains 2.28% As_2O_3, while the aqueous saturated solution (point *a*) contains 2.26% As_2O_3. Further it appears from table 2 that the solubility of the compound decreases on increasing percentage of NH_4Cl of the solutions; in point *b* (N°. 3 in table 2) the solution contains still 2.28% As_2O_3, in the solution, saturated with $NH_4Cl + D$ (point *c*; N°. 9 in table 2) the percentage of As_2O_3 is however lowered to 0.291%. Consequently the As_2O_3 is less soluble in a solution, saturated with NH_4Cl than in a saturated solution of *KCl*.

Only the terminatingpoints *c* and *d* of curve *cd*, which represents the solutions saturated with NH_4Cl, have been determined.

In table 2 the results of the determinations are united; all the small bottles have been shaken during 3 to 5 weeks in a thermostat. Also here, although the As_2O_3 and the compound are both an extremely fine powder, the eye could easily distinguish them by their different behaviour on sinking.

TABLE 2.

Composition in percentages by weight at 30°

	of the solution		of the rest		
N°.	% As_2O_3	% NH_4Cl	% As_2O_3	% NH_4Cl	solid phase
1	2.26	0	—	—	As_2O_3
2	2.29	3.86	82.55	0.34	„
3	2.28	7.08	73.09	6.67	$As_2O_3 + As_2O_3.NH_4Cl$
4	1.31	9.08	44.59	15.90	$As_2O_3.NH_4Cl$
5	0.993	11.76	48.35	17.09	„
6	0.490	21.09	27.43	20.93	„
7	0.432	24.61	47.11	22.14	„
8	0.398	27.18	39.13	23.81	„
9	0.291	29.52	(8)	(35)	$As_2O_3.NH_4Cl + NH_4Cl$
10	0	29.3	—	—	NH_4Cl

The solubility of the NH_4Cl in pure water (N°. 10 of table 2) is not determined, but taken from the tables of LANDOLT-BÖRNSTEIN, the numbers placed between parentheses do not indicate the composition of the rest but that of the complex.

When we draw in fig. 1 the line WD, then we see that it does intersect curve ab, but not bc. The compound $As_2O_3 . NH_4Cl$ is, consequently decomposed by water with separation of As_2O_3.

d. The system H_2O—As_2O_3—$NaCl$.

In this system at 30° only the two components As_2O_3 and $NaCl$ occur as solid phases, we have not found a compound.

We may represent the isotherm schematically by fig. 2; then the anglepoint Z represents the $NaCl$. Consequently the isotherm consists of two branches, viz.:

ab the saturationcurve of As_2O_3
bc ,, ,, ,, $NaCl$.

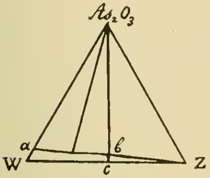

Fig. 2.

It is apparent from table 3 that the solubility of As_2O_3 decreases with increasing percentage of $NaCl$ of the solutions. The saturated aqueous solution of As_2O_3 contains viz. 2.26% As_2O_3, the solution saturated with $NaCl + As_2O_3$ contains only 1.58% As_2O_3. As a saturated solution of KCl contains 0.78% As_2O_3 and a solution saturated with NH_4Cl 0.291% As_2O_3, it is apparent that As_2O_3 is expelled least by $NaCl$ and the most by NH_4Cl from its solution.

TABLE 3.

Composition in percentages by weight at 30°

	of the solution		of the rest		
No.	% A_2O_3	% NaCl	% A_2O_3	% NaCl	solid phase
1	2.26	0	—	—	As_2O_3
2	2.18	5.93	(5)	(16)	"
3	2.04	11.49	(10)	(14)	"
4	1.88	16.86	(15)	(12)	"
5	1.71	22.06	74.12	5.90	"
6	1.58	26.17	(30)	(5)	As_2O_3+NaCl
7	0	26.5	—	—	NaCl

In table 3 the results of the determinations are united, all the small bottles have been shaken during three to five weeks in a thermostat.

The solubility of the $NaCl$ in pure water (N°. 7 of table 3) is taken from the tables of LANDOLT-BÖRNSTEIN; the numbers placed between parentheses indicate again the compositions of the complexes (consequently not of rests).

(To be continued).

(July 13, 1915).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday June 26, 1915.
Vol. XVIII.

President: Prof. H. A. Lorentz.
Secretary: Prof. P. Zeeman.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 26 Juni 1915, Dl. XXIV).

CONTENTS.

Physics. — "*The width of spectral lines.*" By Prof. H. A. LORENTZ.

(Communicated in the meeting of June 27, 1914).

§ 1. In order to account for the absorption of light we may suppose the molecules to contain electrons which are set vibrating by the incident rays and experience a resistance to their motion.

If we suppose that an electron is drawn towards its position of equilibrium by a quasi-elastic force and that the resistance is proportional to the velocity, the vibrations are determined by the equation

$$m\ddot{\mathbf{r}} = -f\mathbf{r} - g\dot{\mathbf{r}} + \mathrm{e}\mathbf{E}, \quad . \; . \; . \; . \; . \; . \; . \qquad (1)$$

where the vector $\mathbf{r}$ means the displacement from the position of equilibrium and $\mathbf{E}$ the electric force in the incident light. The mass and the charge are represented by m and e, whereas f and g are the constants for the quasi-elastic force and the resistance.

The theory takes its simplest form for a gaseous body of not too great a density; to this case I shall here confine myself. If there are several groups of electrons, those which belong to the same group being equal and equally displaced, we may write for the electric moment per unit of volume

$$\mathbf{P} = \Sigma N \mathrm{e}\mathbf{r}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (2)$$

where the sign Σ refers to the different groups and N means the number of electrons per unit of volume for each group. The dielectric displacement is given by

$$\mathbf{D} = \mathbf{E} + \mathbf{P}$$

and in addition to these formulae we have the general equations

$$rot\, \mathbf{H} = \frac{1}{c} \dot{\mathbf{D}},$$

$$rot\, \mathbf{E} = -\frac{1}{c} \dot{\mathbf{H}}.$$

($\mathbf{H}$ magnetic force, c velocity of light in the aether).

We shall, in the usual way, represent the vibrations of the system by means of complex expressions, so that, if n is the frequency, all variable quantities contain the factor

$$e^{int}.$$

Introducing

$$n_0 = \sqrt{\frac{f}{m}},$$

the frequency of the free vibrations, we find from (1) and (2)

$$\mathbf{P} = \Sigma \frac{N\mathrm{e}^2}{m(n_0^2 - n^2) + ing} \mathbf{E}.$$

A beam of light travelling in the direction of the axis of x, may be represented by expressions for $\mathbf{E}$, $\mathbf{D}$ and $\mathbf{H}$, containing the factor

$$e^{in\left(t - \frac{(\mu)x}{c}\right)},$$

where (μ) may be called the "complex index of refraction." For this quantity we find from the above equations

$$(\mu)^2 = 1 + \Sigma \frac{N\mathrm{e}^2}{m(n_0^2 - n^2) + ing} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

§ 2. If now we put

$$(\mu) = \mu - \frac{ich}{n}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

μ will be the real index of refraction and h the index of absorption. The meaning of the latter is, that the intensity of a beam of light travelling over a distance δ, is diminished in the ratio of 1 to

$$e^{-2h\delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By means of (3) μ and h may be determined for each frequency of the light.

If the values of n_0 for the different groups of electrons are sufficiently different from each other, there will be a certain number of separate maxima of absorption. In this case we may treat the phenomena belonging to each of these maxima with sufficient approximation by supposing only one group of corpuscles to be present.

Thus (3) becomes

$$(\mu)^2 = 1 + \frac{Ne^2}{m(n_0{}^2 - n^2) + ing}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

and if we put

$$\frac{Ne^2}{n_0 g} = a, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

we find the following values for the case $n = n_0$, i.e. for the maximum of absorption

$$(\mu_0)^2 = 1 - i\,a,$$
$$2\mu_0{}^2 = \sqrt{1 + a^2} + 1,$$
$$2\frac{c^2 h_0{}^2}{n_0{}^2} = \sqrt{1 + a^2} - 1.$$

The last equation shows that the smaller the coefficient of resistance g, the greater will be the value of h_0; small resistances give rise to a strong maximum of absorption. We can in this respect distinguish two extreme cases; viz. that a is much greater and that it is considerably smaller than unity. In the first case we have approximately

$$\frac{ch_0}{n_0} = \sqrt{\tfrac{1}{2}\,a}$$

and in the second case

$$\frac{ch_0}{n_0} = \tfrac{1}{2}a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

If we write λ_0 for the wave-length in the aether, corresponding to n_0, we have

$$\frac{ch_0}{n_0} = \frac{h_0 \lambda_0}{2\pi}.$$

Now, according to (5) the decrease in intensity over a wave-length's distance is given by

$$e^{-2h_0\lambda_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

and we see therefore that this decrease will be considerable if $a >> 1$ and very small if $a << 1$.

§ 3. The width of the bands of absorption may likewise be deduced from equation (6). Indeed, if n is made to differ from n_0 in one direction or the other, the term $m(n_0{}^2 - n^2)$ gains in importance in comparison with $i\,n\,g$; when it has reached a value equal to a few times ng, the index of absorption has become considerably smaller than h_0. As the ratio of $m(n_0{}^2 - n^2)$ to ng is of the same order of magnitude as that of $2mn_0(n - n_0)$ to $n_0 g$, we may say that for

$$n-n_0=\pm s\,.\,\frac{g}{2m}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where s is a moderate number, the absorption is much smaller than for $n-n_0$. Hence, the absolute value of (10) will give us some idea of half the width of the absorption band. The smaller the coefficient of resistance, the narrower the band is seen to be. A strong maximum of absorption and a small width will be found together, whereas in the case of a feeble maximum we shall find a broad band.

For values of n, differing so much from n_0 that $i\,n\,g$ may be treated as a small quantity compared with $m(n_0^2-n^2)$, we may replace (6) by

$$(\mu)^2=1+\frac{N\mathrm{e}^2}{m(n_0^2-n^2)}-\frac{i\,N\,n\,\mathrm{e}^2\,g}{m^2(n_0^2-n^2)^2}.$$

Supposing further that the real part on the right hand side is positive and much greater than the imaginary one, we find approximately

$$\mu^2=1+\frac{N\mathrm{e}^2}{m(n_0^2-n^2)},$$

$$h=\frac{N\mathrm{e}^2n^2}{2\mu c m^2(n_0^2-n^2)^2}\,g.$$

The last formula shows that the absorption at a rather large distance from the maximum increases with the coefficient of resistance, just the reverse of what we found for the maximum itself.

For values of g, so great that $a<<1$, the equations become less complicated. Indeed, for this case (6) may be written

$$(\mu)=1+\frac{1}{2}\,.\,\frac{N\mathrm{e}^2}{m(n_0^2-n^2)+i\,n\,g}$$

and this, combined with (4), leads to the values

$$\mu=1+\frac{1}{2}\,.\,\frac{N\mathrm{e}^2m(n_0^2-n^2)}{m^2(n^2-n_0^2)^2+n^2g^2},$$

$$h=\frac{1}{2c}\,.\,\frac{N\mathrm{e}^2n^2g}{m^2(n^2-n_0^2)^2+n^2g^2}.$$

This last equation shows that for $n=n_0$

$$h_0=\frac{N\mathrm{e}^2}{2\,c\,g},$$

agreeing with (8), and that at the distance from the maximum determined by (10), the index of absorption has become s^2+1 times smaller than h_0.

§ 4. The above has been known for a long time and has been repeated here as an introduction only to some further considerations. These will be limited to lines in the visible and the ultraviolet spectrum, i.e. to lines which in all probability are due to vibrations of *negative* electrons.

We shall also confine ourselves to such problems as may be treated without going deeply into the mechanism of the absorption. There are good grounds for this restriction, for it must be owned that in many cases we are very uncertain about the true nature of the phenomenon.

In the case of a vibrating electron there is always a resistance of *one* kind, viz. the force that is represented by

$$\frac{\mathsf{e}^2}{6\pi c^3}\ddot{\mathsf{v}},$$

if v is the velocity. For harmonic vibrations we may write for it

$$-\frac{\mathsf{e}^2 n^2}{6\pi c^3}\mathsf{v},$$

so that it proves to be proportional to the velocity and opposite to it. If this "radiation resistance", as it may appropriately be called, because it is intimately connected with the radiation issuing from the particle, is the only one, we must substitute in the above formulae for the coefficient g the value

$$g_1 = \frac{\mathsf{e}^2 n^2}{6\pi c^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Replacing here n by n_0 we deduce from form. (7)

$$a = \frac{6\pi N c^3}{n_0^{\ 3}} = \frac{3}{4\pi^2} N\lambda_0^{\ 3}.$$

Now $N\lambda_0^{\ 3}$, the number of vibrating electrons in a "cubic wave-length" will have in many cases a high value. Hence, on our present assumption, a would be very great and for rays of frequency n_0 the weakening would be considerable even over a distance of one wave-length only. Indeed, one finds for the exponent in (9)

$$-2h_0\lambda_0 = -\sqrt{6N\lambda_0^{\ 3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

It must be remarked here that in the case now under consideration, we cannot speak of true "absorption", i.e. of transformation of the vibrations into irregular heat motion, but only of a "scattering" of the light by the vibrating electrons, so that h may properly be called the "index of extinction".

Formula (11) leads to a very small value for the width of the dark line. Indeed, using (10) and replacing n by n_0 in (11), we easily find for the width measured by the difference of wave-length between the borders

$$\Delta\lambda = s\,\frac{g_1}{mn_0}\,\lambda_0 = s\,\frac{e^2 n_0 \lambda_0}{6\pi c^3 m},$$

or

$$\Delta\lambda = 2\pi\, sR,$$

after substitution of the well known value

$$m = \frac{e^2}{6\pi c^2 R}$$

(R radius of the electron) for the (electromagnetic) mass m.

Now we have

$$R = 1{,}25\,.\,10^{-13}\,\text{cm},$$

so that for $s = 10$

$$\Delta\lambda = 12.10^{-12}\,\text{cm} = 0{,}0012\,\text{Å U.}, \quad \ldots\ldots \quad (13)$$

This is a very small width indeed.

We shall soon see however that equations (12) and (13) apply to the ideal case only of molecules having no velocity of translation. In reality, on account of the heat motion of the molecules a "line of extinction" will be much broader than is given by (13) and less strong at the middle than we should infer from (12).

One remark more has to be made about the radiation resistance. Though the extinction to which it gives rise, quickly decreases as the frequency n deviates more and more from the frequency n_0, yet in the case of thick layers of gas it remains observable at a considerable distance from n_0. We may suppose e.g. that in the case of atmospheric air, n_0 belongs to a point in the ultraviolet. Now, if for light in the visible spectrum, we calculate the extinction corresponding to the coefficient g_1, we find exactly the well known formula of Rayleigh which agrees in a satisfactory way with observations.

§ 5. As the radiation resistance does not give rise to any true absorption, we must look for another explanation of this phenomenon. We can hardly think of a real friction or viscosity, but we may suppose that the vibrations of the electrons which are excited by the incident light cannot go on regularly for a long time, but are disturbed over and over again by collisions or impacts which convert them into irregular heat motion. It can be shown[1] that this leads to the same effect as a frictional resistance and that the

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[1] H. A. Lorentz, The absorption and emission lines of gaseous bodies, Proc. Amsterdam Acad. 8 (1905), p. 591.

formulae of §§ 1 and 2 may still be used, provided we substitute for the coefficient g the value

$$g_2 = \frac{2m}{\tau} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Here τ denotes the average time between two succeeding collisions of one and the same electron. The formula is based on the assumption that each collision wholly destroys the original vibration. If some part of it remained after an impact, we should have to take for τ a larger or smaller multiple of the time between two collisions. We may also remark that the expression (14) has a more general meaning. We may understand by τ the time during which a vibration can go on without being much disturbed or considerably damped, and use the formula, whatever be the cause of the disturbance or the damping. If there were e.g. a true frictional resistance the equation for the free vibrations would be

$$m\ddot{\mathbf{r}} = - f\mathbf{r} - g\dot{\mathbf{r}},$$

and we should have

$$\mathbf{r} = \mathbf{a}\, e^{-\frac{g}{2m}t} \cos \sqrt{\frac{f}{m} - \frac{g^2}{4m^2}}\, t.$$

The time during which the amplitude decreases in the ratio $e:1$ would therefore be

$$\tau = \frac{2m}{g},$$

which agrees with (14). Thus, the formula also applies to cases in which there is a radiation resistance only; for g we have then to substitute the value (11).

Returning to the question of impacts, we may remark that in the case of a gaseous medium, it would be natural to take for τ in (14) the mean time between two collisions of a molecule. There are, however, cases where we find in this way a value much too high for g_2.

Let us consider e.g. the propagation of yellow light ($\lambda = 6000$ Å. U.) through air of 0° and under a pressure of 76 cm, and compare the values of g_1 and g_2. In calculating this latter coefficient we shall use the values holding for nitrogen. If u denotes the mean velocity of the molecules, l the mean length of path between two collisions, we find, putting $\tau = \frac{l}{u}$, from (14) and (11)

$$\frac{g_2}{g_1} = \frac{1}{2\pi^2} \frac{u}{c} \cdot \frac{\lambda^2}{Rl}.$$

With $\lambda = 6.10^{-5}$ cm, $l = 9{,}4.10^{-6}$ cm, $u = 4{,}93.10^4$ cm/sec., and the above value of R, the ratio becomes

$$\frac{g_2}{g_1} = 172.$$

Now, we found in § 3 that, at a rather large distance from n_0, the index of absorption is proportional to g. Our calculation therefore shows that the collisions would cause an extinction 172 times stronger than that to which the radiation resistance gives rise. As the latter leads to RAYLEIGH's formula which has been confirmed by the observations, we must conclude that the effect of the collisions is much less than we supposed it to be. Thus, when light is propagated in air the electric moment which is excited in a molecule must remain nearly unchanged in direction and magnitude during an impact.

Of course, notwithstanding this, it may very well be that in the neighbourhood of n_0 and under special circumstances the collisions disturb the vibrations. Recently STARK has given good reasons for supposing that the electric field round a charged particle changes the vibrations of a neighbouring molecule in such a way that a broadening of the spectral line is brought about.

§ 6. It has often been remarked that, according to DOPPLER's principle, the molecular motion must give rise to a broadening of the spectral lines. We shall first consider this effect for the case of an emission line, on the assumption that there are no other causes for a broadening.

Let n_0, the frequency of the vibrations within the molecules, be the same for all the particles and let ξ denote the component of the velocity of a molecule along a line directed towards the observer, ξ being positive when the molecule approaches the observer, and negative in the opposite case. Then the observed frequency is given by

$$n = n_0\left(1 + \frac{\xi}{c}\right).$$

The change in frequency expressed in terms of n_0, i.e. the fraction

$$\omega = \frac{n - n_0}{n_0},$$

which also represents the ratio of the change of wave-length to λ_0, is therefore given by

$$\omega = \frac{\xi}{c} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

Let us further write N for the number of molecules per unit of volume and u^2 for the mean square of their velocity. Then we find for the number of particles for which the velocity ξ lies between ξ and $\xi + d\xi$, and the change of frequency between the corresponding values ω and $\omega + d\omega$,

$$\sqrt{\frac{3}{2\pi}}\,\frac{N}{u}\,e^{-\frac{3\xi^2}{2u^2}}\,d\xi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

or

$$\sqrt{\frac{3}{2\pi}}\,\frac{c}{u}\,Ne^{-\frac{3c^2}{2u^2}\omega^2}\,d\omega \quad . \quad . \quad . \quad . \quad . \quad . \qquad (17)$$

This last expression immediately determines the distribution of light in the emission line. The borders of the line may be taken to correspond to the values of ω for which the exponent becomes -1, i. e. to

$$\omega = \sqrt{\frac{2}{3}}\,\frac{u}{c},$$

so that the width is determined by

$$\Delta\lambda = 2\sqrt{\frac{2}{3}}\,\frac{u}{c}\,.\,\lambda_0.$$

If u is of the order of 5.10^4 cm/sec and λ_0 of the order of 6000 Å.U., this $\Delta\lambda$ will be about $^1/_{60}$ Å.U. This is a very small width; yet, it far exceeds the value which, starting from the value of g_1, we found (§ 4) for the breadth of an absorption line, and which would also belong to an emission line, if we had to reckon with the radiation resistance only. The cause of the difference is that

$$g_1 << m\,n_0\,\frac{u}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

The conclusions drawn from (17) about the width of the lines are in good agreement with the results of several physicists; they are strikingly confirmed by the experiments of Buisson and Fabry[1]) on the emission of helium, krypton, and neon in Geissler tubes. These observations show at the same time that in these rarefied gases there are no resistances whose coefficient does not fulfil the condition (18), and which, acting by themselves, would therefore give rise to a width comparable with that arising from molecular motion, or greater than it. If there had been resistances of this kind, the observed width would have been found greater than is required by Doppler's principle.

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[1]) H. Buisson et Ch. Fabry, La largeur des raies spectrales et la théorie cinétique des gaz, Journal de Physique (5) 2 (1912), p. 442.

§ 7. We shall now pass on to consider the influence of molecular motion on an absorption line. We shall suppose that there is a radiation resistance only, or at any rate that there are only resistances whose coefficients g are much smaller than $mn_0 \frac{u}{c}$ so that, acting by themselves, they would produce a much smaller width than the one we calculated in § 6. Cases of somewhat greater density are hereby excluded.

The problem is easily solved if, after having grouped the molecules according to their velocity of translation, we substitute for each group a proper value of n_0 in the expression for the electric moment and then take the sum over all the groups in the way shown in equation (3).

Let ξ be the velocity of translation of a molecule in the direction of the beam of light and let one of the groups contain particles with velocities between ξ and $\xi + d\xi$. In (3) we must then replace N by (16) or (17). Further it is clear that the particles in question will resonate with light of the frequency $n_0\left(1+\frac{\xi}{c}\right) = n_0\,(1+\omega)$ in the same way as they would with light of the frequency n_0 if they had no velocity of translation. We therefore write $n_0\,(1+\omega)$ instead of n_0. We shall also put

$$n = n_0\,(1+\mathrm{v}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

so that v determines the difference between the frequency of the incident light and n_0, and we shall confine ourselves to small values of v, as we may do in the case of narrow lines. Then, for small values of ω, the only ones for which (17) has an appreciable magnitude, we may write

$$[n_0(1+\omega)]^2 - n^2 = 2n_0^2(\omega - \mathrm{v}).$$

Moreover, since n will differ very little from n_0 we may in the term ing replace n by n_0 and consider g as a constant, though in reality this coefficient may depend on n (as g_1 does according to (11)).

Putting further

$$\frac{g}{2mn_0} = k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

we find

$$(\mu)^2 = 1 + \frac{1}{2}\sqrt{\frac{3}{2\pi}}\,\frac{Nc\,\mathrm{e}^2}{m\,u\,n_0^{\,2}} \int_{-\infty}^{+\infty} e^{-\frac{3c^2}{2u^2}\omega^2}\,\frac{d\omega}{\omega - \mathrm{v} + ik},$$

or, if we introduce

$$w = \omega - v$$

as a new variable and put

$$\sqrt{\frac{3}{2}}\cdot\frac{c}{u}=q\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$(\mu)^2 = 1 + \frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{Nce^2}{mun_0^{\,2}}\,(P-i\,Q), \quad . \quad . \quad . \quad . \quad (22)$$

where

$$P=\int_{-\infty}^{+\infty}\frac{w}{w^2+k^2}\,e^{-q^2(w+\nu)^2}\,dw\,,$$

and

$$Q=k\int_{-\infty}^{+\infty}\frac{1}{w^2+k^2}\,e^{-q^2(w+\nu)^2}\,dw.$$

We observe that these formulae determine the indices of refraction and of absorption for light whose frequency is given by (19).

§ 8. We may now avail ourselves of the circumstance that, according to (20), (21) and the inequality (18), which we suppose to hold for q,

$$kq \ll 1\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

In the first place we find by a simple transformation

$$P=\int_{0}^{\infty}\frac{w}{w^2+k^2}\left\{e^{-q^2(w+\nu)^2}-e^{-q^2(w-\nu)^2}\right\}dw\,,$$

showing that $P=0$ for $\nu=-\infty$, $\nu=0$ and $\nu=+\infty$, that the sign of P is always opposite to that of ν, and that $P(-\nu)=-P(+\nu)$. We have therefore only to consider positive values of ν. For these the absolute value of P lies beneath

$$R=\int_{0}^{\infty}\frac{1}{w}\left\{e^{-q^2(w-\nu)^2}-e^{-q^2(w+\nu)^2}\right\}dw\,,$$

or

$$R=e^{-q^2\nu^2}\int_{0}^{\infty}\frac{1}{w}\,e^{-q^2w^2}\left\{e^{2q^2\nu w}-e^{-2q^2\nu w}\right\}dw\,.$$

Developing

$$e^{2q^2\nu w}-e^{-2q^2\nu w}$$

in a series according to the ascending powers of $2q^2\nu w$ and integrating each term separately we find

$$R = 2\sqrt{\pi x}\,.\,e^{-x}\left(1 + \sum_{\varkappa=1}^{\varkappa=\infty} \frac{1}{(2\varkappa+1).\varkappa!}x^{\varkappa}\right),$$

where

$$x = q^2 v^2.$$

The expression R has a maximum for $x = 0.83$.

This greatest value is 1.92, so that in all cases

$$|P| < 1{,}92\,.$$

The integral Q can be evaluated by remarking that the fraction $\frac{1}{w^2+k^2}$ is a maximum for $w = 0$ and becomes very much smaller than this maximum when the absolute value of w exceeds a certain limit w_1, which is a moderate multiple of k. The interval $(-w_1, +w_1)$ therefore contributes by far the greater part to the value of Q. Now, in this interval, as is shown by the inequality (23), the function

$$e^{-q^2(w+\nu)^2}$$

differs very little from the value

$$e^{-q^2\nu^2},$$

corresponding to $w = 0$. We may therefore write

$$Q = k\,e^{-q^2\nu^2}\int_{-\infty}^{+\infty} \frac{dw}{w^2+k^2} = \pi\,e^{-q^2\nu^2}.$$

It is remarkable that k, and therefore the coefficient g have disappeared from the result.

We see by these considerations that P is smaller than the highest value of Q. Thus, if even for that highest value of Q the factor of i in (22) is small compared with unity, this will also be true of

$$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\,\frac{N c\,\mathrm{e}^2}{m\,u\,n_0{}^2}\,P\,;$$

we may then deduce from (22)

$$(\mu) = 1 + \frac{1}{4}\sqrt{\frac{3}{2\pi}}\,\frac{N c\,\mathrm{e}^2}{m\,u\,n_0{}^2}\,(P - i\,Q)\,.$$

Combining this with (4), we find, first the value of the real index of refraction, which we shall not now consider, and secondly that of the index of absorption h, viz. (if in (4) too we replace n by n_0)

$$h = \frac{1}{4}\sqrt{\frac{3}{2}\,\pi}\,\frac{N\mathrm{e}^2}{m\,u\,n_0}\,e^{-q^2\nu^2},$$

or

$$h = h_0\,e^{-\frac{3c^2}{2u^2}\nu^2}, \quad . \quad . \quad . \quad \quad . \quad . \quad . \quad . \quad (24)$$

if

$$h_0 = \frac{1}{4}\sqrt{\frac{3}{2}\pi}\;\frac{N\mathrm{e}^2}{m u n_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

This is the maximum value of the index of absorption which is found at the middle of the line ($\nu = 0$).

Whether the supposition that the coefficient of i in (22) is much smaller than unity be right, may be decided by calculating h_0. For it is evident that this supposition is equivalent to the inequality

$$h_0 \lambda_0 << 1\,;$$

it requires therefore that the absorption over a distance of one wave-length is small.

If this is not the case we may not use (24). However, by combining (22) and (4), we then find

$$h = \frac{h_0}{\mu}\, e^{-\frac{3c^2}{2u^2}\nu^2},$$

where μ may differ considerably from 1, and h_0 still has the value determined by (25). (This will however no longer be the index of absorption for $\nu = 0$.)

Formula (25) may be so transformed that it becomes fit for numerical calculation. If we express u in the absolute temperature T and the molecular weight M of the gas, N in T and the pressure p (in mm. of mercury), n_0 in the wave-length λ_0 (in Å.U.), substituting also the values for e and m, we find

$$h_0 = 5{,}7 . 10^4\, p\, \lambda_0 \sqrt{\frac{M}{T^3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

We shall now make some applications of these results.

§ 9. Wood's remarkable experiments[1]) on the scattering of the rays of the ultraviolet mercury line $\lambda\, 2536$ by mercury vapour have shown that even at ordinary temperatures this scattering is very considerable. The intensity of the beam decreases to half its original value over a distance of 5 mm.

The vapour pressure at this temperature is about $p = 0{,}001$ and putting $M = 200$ and $T = 290$ I find from (26) a value a little above 400 for h_0. This is much too high compared with Wood's result. It must however be borne in mind that the beam for which he measured the extinction contained a small interval of frequencies, so that we are concerned, not only with the value of h_0, but also with those of h which correspond to small positive and negative values of ν and may be considerably smaller than h_0. However,

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[1]) R. W. Wood, Selective reflexion, scattering and absorption by resonating gas-molecules, Phil. Mag. (6) **23** (1912), p. 689.

since Wood has found the scattered rays to be unpolarized, I am rather doubtful as to the propriety of applying the above theory to his experiments. For this reason, I shall no longer dwell on this question.[1] I shall only add that the value h_0 which we found, leads to a value of $h_0\lambda_0$ considerably below 1.

§ 10. The formulae (24) and (25) may also be used for calculating the total absorption, integrated over the whole width of the line, for a certain thickness of a given gas. On the other hand this absorption can be measured by a simple photometric experiment. Dr. G. J. Elias was so kind as to do this for iodine vapour.

A beam of yellow light was passed through an evacuated tube containing some small iodine crystals and heated to 89° C. The beam was obtained by isolating from the spectrum of an arc lamp a portion corresponding to the distance between the D lines. In a layer of 2 cm. the absorption amounted to 15 %.

In discussing this result, I shall remark in the first place that the distribution of light in an absorption band will depend on different circumstances, e.g. on the thickness of the gas traversed. It may be that at the middle of the line and within a certain distance from it practically all light is absorbed, the absorption diminishing gradually on both sides. However this may be, one can always define a certain width $\triangle\lambda_e$ such that the amount of light absorbed by the gas is equal to the quantity of light that is found in the incident rays within the interval $\triangle\lambda_e$. The magnitude of $\triangle\lambda_e$, which we may call the "effective" width of the line, can be immediately deduced from a photometric measurement.

The absorption spectrum of iodine vapour has a very complicated structure, containing somewhat over 100 lines between the D lines. Dr. Elias's observation shows that the effective widths of all these lines taken together amount to 15% of the distance between the D lines, i.e. to 0,9 Å.U. We shall therefore not be far from the mark if for one line we put on an average

$$\triangle\lambda_e = 0.008\ \mathring{A}.U.$$

If $I\,d\lambda$ is the intensity of the incident light within the interval $d\lambda$, we have for the absorption over the whole width of a line by a layer of thickness δ

$$I\int(1-e^{-2h\delta})\,d\lambda.$$

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[1] According to more recent measurements by A. v. Malinowsky (Resonanzstrahlung des Quecksilberdampfes, Ann. d. Physik **44** (1914), p. 935) $h_0 = 1{,}55$.

Hence

$$\int (1-e^{-2h\delta})\, d\lambda = \Delta\lambda_e,$$

by which we can calculate the maximum absorption index h_0.

For this purpose we develop $e^{-2h\delta}$ in a series and integrate between the limits $\nu = -\infty$ and $\nu = +\infty$, after having substituted for h the value (24) and replaced $d\lambda$ by $\lambda_0\, d\nu$. Putting

$$2h_0\delta = x$$

we find

$$\sum_{\varkappa=1}^{\varkappa=\infty} \frac{(-1)^{\varkappa-1}}{\varkappa!\sqrt{\varkappa}}\, x^{\varkappa} = \sqrt{\frac{3}{2\pi}} \cdot \frac{c}{u} \cdot \frac{\Delta\lambda_e}{\lambda_0}.$$

With the values $u = 1{,}88.10^4$ cm/sec and $\lambda_0 = 5893$ Å. U. the quantity on the right hand side of this equation becomes 1,50 and we find

$$x = 2h_0\delta = 4{,}1$$

approximately, showing that the absorption at the middle of the line must have been more than 98°/₀. As $\delta = 2$ cm., the index of absorption itself is found to be about

$$h_0 = 1{,}02\ {}^1/_{\mathrm{cm}}.$$

§ 11. Now this value is widely different from the one that follows from (26). At 89° C. the pressure of iodine vapour is about 24 mm. Using this value and putting $\lambda_0 = 5893$ Å.U., $T = 362$, $M = 254$, we get from (26)

$$h_0 = 1{,}9 \,.\, 10^7\ {}^1/_{\mathrm{cm}}.$$

The great difference between this number and the former one may be accounted for by supposing that a very small part (about one twenty millionth) only of the molecules are active in producing the absorption, so far as one line is concerned, a conclusion agreeing with that to which one has been led by other lines of research.

It must however be remarked that perhaps the fundamental supposition expressed in equation (1) does not correspond to reality and must be replaced by a more general one. Instead of thinking of a vibrating negative electron we may simply suppose that under the influence of the incident light an alternating electric moment $\mathbf{p}$ is induced in a particle. Equation (1) then takes the form

$$\ddot{\mathbf{p}} + \alpha\dot{\mathbf{p}} + \beta\mathbf{p} = \gamma\mathbf{E}$$

in which α, β, and γ are certain constants, the first of which determines the resistance, while β has the value n_0^2. We are again led to equation (24), but instead of (25) we get an expression which contains γ. Of this coefficient we can say nothing without making special hypotheses.

§ 12. Finally we shall shortly discuss the question whether the width of FRAUNHOFER's lines in the spectrum of the sun can teach us something about the quantity of the absorbing vapour which produces them. Let us consider an arbitrarily chosen rather fine line, the calcium line λ 5868. Its width is certainly smaller than 0,1 Å.U., by which I mean that, 0,05 Å.U. from the middle, the intensity of the light amounts to more than the part $\frac{1}{e}$ of that which is seen at a small distance from the line and which would exist in the place of the line itself if no calcium vapour were present.

If δ is the thickness of the traversed layer of calcium vapour we may write, giving to ν the value that corresponds to the above mentioned distance of 0,05 Å.U.

$$2h\delta < 1 \, ,$$

so that

$$h_0\delta < \tfrac{1}{2}\, e^{\frac{3c^2}{2u^2}\nu^2} \, .$$

We can calculate the right hand side of this inequality if we make an assumption concerning the temperature T of the absorbing layer. For $T = 6000°$ we find in this way $h_0\delta < 7{,}0$ and for $T = 3000°$ $h_0\delta < 98$.

Now, if it were allowed to use the formula (26), this upper limit for $h_0\delta$ would lead to a similar one for $p\delta$. We should have for $T = 6000°$, $p\delta < 0{,}0015$ and for $T = 3000°$, $p\delta < 0{,}0074$. As p represents the pressure expressed in mm. of mercury, whereas δ is expressed in cm., we might infer from these numbers that the quantity of calcium vapour which produces the line in question is very small. Some reserve however must be made here. It may very well be that a small part only of the calcium atoms take part in the absorption. Then the above inequalities will still hold, provided we understand by p the pressure of the "active" vapour. If we mean by p the total pressure of the calcium vapour present we should have to multiply the given numbers by 10^7, if one ten millionth part of the atoms were active (comp. § 11). For the first temperature this would give $p\delta < 15000$ and for the second $p\delta < 74000$. The last of these numbers corresponds e. g. to a thickness of 0.75 km. if the pressure is 1 mm. of mercury.

If we wish to abstain from all suppositions on the nature of the vibrating particles (comp. the end of the preceding §) we can say nothing about $p\delta$ and must confine ourselves to a conclusion concerning $h_0\delta$. However this may be, it seems rather probable that the finest lines in the spectrum of the sun are caused by relatively small quantities of the absorbing gases.

It ought also to be remarked that the problem is, strictly speaking, less simple than we have put it here. We have reasoned as if a small quantity of an absorbing vapour were present in front of a radiating body giving rise to a continuous spectrum. In this spectrum there will then be a fine absorption line. In reality, however, if there is very rare calcium vapour in a certain layer, there will be vapour of somewhat greater density at a greater depth in the sun's atmosphere. For a satisfactory theory of the phenomena it would be necessary to explain why this latter vapour does not give rise to a broader absorption line, but must rather be considered as belonging to the mass to which the continuous spectrum is due.

Chemistry. — *"Equilibria in the system Cu—S—O; the roasting reaction process with copper."* By Prof. W. Reinders and F. Goudriaan. (Communicated by Prof. Hoogewerff).

(Communicated in the meeting of May 29, 1915.)

1. In the metallurgy of copper the reactions, which may occur between the roasting products of the partly burnt copper ore, play an important role; in special conditions they can lead in a direct manner to the separation of metal. Usually it is assumed that these reactions take place according to the subjoined equations [1]:

$$Cu_2S + 2\,CuO = 4\,Cu + SO_2$$
$$Cu_2S + 2\,Cu_2O = 6\,Cu + SO_2$$
$$Cu_2S + 3\,CuO = 3\,Cu + Cu_2O + SO_2$$
$$Cu_2S + 6\,CuO = 4\,Cu_2O + SO_2$$
$$Cu_2S + CuSO_4 = 3\,Cu + 2\,SO_2$$
$$Cu_2S + 4\,CuSO_4 = 6\,CuO + 5\,SO_2\,.$$

Systematic researches as to this process, which seems very complicated owing to the large number of possible phases, are exceedingly scarce. The only observations worth mentioning are those of R. Schenck and W. Hempelmann [2]; they determined pT-lines for mixtures of $Cu_2S—Cu_2O$, $Cu_2S—CuSO_4$ and $Cu—CuSO_4$. As these observations are incomplete and their conclusions in many points unsatisfactory,

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[1] Schnabel, Handb. der Metallhüttenkunde I 176 (1901).

[2] Metall und Erz, **1**, 283 (1913). Z. f. angew. Chemie **26**, 646 (1913).

a new investigation as to the equilibria in this system appeared to us as being very desirable. The results obtained thus far, which differ in some respects from the *data* already known, will be stated here in brief.

2. The theoretical points of view which guided us here are the same as those described in the system Pb—S—O [1]).

In order to find out whether cuprous oxide forms with cuprous sulphide a stable phase-pair and also to measure the SO_2-pressures, a very intimate mixture of these substances was heated in a porcelain tube connected with an open manometer and a mercury air-pump. The heating took place in a Heraeus oven; the measuring of the temperature was carried out with a Pt-PtRh-thermocell which had been carefully set on the melting points of tin, lead, zinc, antimony and silver and which was checked a few times during the experiments.

The Cu_2O was obtained by reduction of an alkaline $CuSO_4$ solution with glucose, it was dried in a vacuum at 300°—400° and contained 88.64 °/₀ of Cu. The Cu_2S was a preparation of KAHLBAUM which, mixed with a small quantity of sulphur, was heated for some time in a current of hydrogen at 500°—600° and so got the theoretical composition.

The equilibria pressures could be attained very readily from both sides; the values obtained from SO_2-evolution and SO_2-adsorption only differed 2—3 mm. Also, after evacuation the same pressures were always again obtained; they are united in table I, where the pressure is expressed in mm. mercury at 0°.

TABLE I. $2Cu_2O + Cu_2S \rightleftarrows 6Cu + SO_2$ (fig. 3 line III).

T	*p*
586	73
607	120
636	179
650	222
669	289
691	390
710	488
730	599

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[1]) W. REINDERS, These Proc. 23, 596 (1914).

The reaction product was obtained by evacuating a few times more; it was a cindery, copper-coloured mass in which metallic particles were easily discernible; sulphate could not be detected. *$Cu_2O + Cu_2S$ thus form a stable phase-pair* and as the diagonal Cu_2O—Cu_2S cuts the diagonal Cu—$CuSO_4$ (see fig. 1), it follows *that $Cu + CuSO_4$ must be metastable in presence of each other.*

3. By now combining the other phases that are stable between ± 300° and 900° two and two with each other and heating in evacuated, sealed tubes we were able to record which of these phase-pairs can be considered as the stable ones. First of all were chosen the combinations Cu_2S —CuO and Cu_2O—$CuSO_4$.

A mixture of equal mols. of the last named substances when heated during 6—7 hours at 450°—480° remained completely unchanged, not a trace of sulphide could be detected. On the other hand, mixtures of Cu_2S and CuO appeared to undergo a very strong change at this temperature; the colour changed from black to brownish-red and on extraction with cold, recently boiled water a blue-coloured filtrate was obtained which gave a strong sulphate reaction. The sulphate soluble in water was determined quantitatively as $BaSO_4$. From 1.1182 grams of a mixture containing 2 mols. CuO on 1 mol. Cu_2S was thus obtained 0.1729 gram of $BaSO_4$ corresponding with 0.118 gram of $CuSO_4$; the mixture, after heating, therefore contained 10.6 % of $CuSO_4$. This quite agrees with the amount of $CuSO_4$ calculated on the supposition that the conversion of the mixture takes place according to the equation:

$$Cu_2S + 9\,CuO = 5Cu_2O + CuSO_4$$

namely 10.58% of $CuSO_4$.

Hence, we come to the conclusion that *$Cu_2O + CuSO_4$ forms the stable and $Cu_2S + CuO$ the metastable phase-pair.*

4. In a similar manner we investigated the combinations *CuS—Cu_2O* and *$CuSO_4$—Cu_2S*. It was *a priori* improbable that the first-named pair should be stable as according to the observations of PREUNER and BROCKMÖLLER[1]), the dissociation of CuS into Cu_2S + S becomes already measurable at 450°. In fact, it appeared that the colour of the CuS—Cu_2O mixtures had been changed from dark brown to grey after 5 hours' heating at 300°—320°; a considerable quantity of sulphate had been formed. This, after extraction with cold, recently boiled water, was determined as $BaSO_4$. From 0.8722

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[1]) Zeitschr. phys. Chem. **81**, 129, (1912).

gram of a mixture containing 9 mols CuS to 4 mols Cu_2O 0.1274 gram of $BaSO_4$ was obtained in this manner so that the mass, after heating, contains $10.0\,^0/_0$ of $CuSO_4$. If the mass had been converted entirely according to

$$9\,CuS + 4\,Cu_2O = 8\,Cu_2S + CuSO_4$$

the $CuSO_4$ content ought to be $11.15\,^0/_0$. Hence, it had been converted to a very considerable extent.

In good agreement herewith was the fact that a mixture of Cu_2S and $CuSO_4$ did not at all change at this temperature; it retained its colour and remained powdery [1]).

Hence, Cu_2S—$CuSO_4$ forms the stable, CuS—Cu_2O the metastable phase-pair.

5. On the strength of the above orientating experiments it seemed probable that we must imagine the stable equilibria in the system Cu—S—O to be as follows. Fig. 1 represents a horizontal projection on the ground plane of a figure in space which holds for a constant temperature and where the vapour pressure p is plotted on the vertical axis.

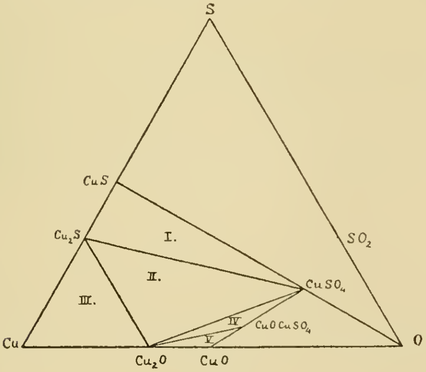

Fig. 1.

Mixtures of CuS and $CuSO_4$ will at a given temperature give the highest SO_2-pressure, namely the one related to the monovariant equilibrium:

$$3\,CuS + CuSO_4 \rightleftarrows 2Cu_2S + 2SO_2\,. \quad . \quad . \quad . \quad . \qquad (I)$$

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[1]) This is in contradiction with the observations of Schenck and Hempelmann, who record a melt between $CuSO_4$ and Cu_2S, already at 300°.

If, by removing each time the SO_2 formed, we allow this reaction to take place completely, either a mixture of CuS and Cu_2S or one of Cu_2S and $CuSO_4$ will remain.

On increasing the temperature the first will be converted completely into Cu_2S with elimination of sulphur according to $2CuS \rightleftarrows Cu_2S + S$. This reaction has been completely confirmed by the experiments of PREUNER and BROCKMÖLLER.

The mixture of Cu_2S and $CuSO_4$ will form Cu_2O with evolution of SO_2 and yield pressures appertaining to the monovariant equilibrium:

$$Cu_2S + 2\,CuSO_4 \rightleftarrows 2\,Cu_2O + 3SO_2 \quad . \quad . \quad . \quad . \quad (II)$$

Of this process the reaction product must be a mixture of Cu_2O and Cu_2S or of Cu_2O and $CuSO_4$ according to whether it contained originally an excess of Cu_2S or of $CuSO_4$.

In the first case will take place the reaction

$$2Cu_2O + Cu_2S \rightleftarrows 6Cu + SO_2 \quad . \quad . \quad . \quad . \quad . \quad (III)$$

which leads to the equilibria pressures mentioned in table I.

Mixtures of Cu_2O and $CuSO_4$ will, at a continued increase of temperature, form as a third phase either CuO, or an intermediate basic copper sulphate between CuO and $CuSO_4$. In connexion with the experiments of WÖHLER and his coadjutors[1]) it was probable that a role is played here by the basic sulphate $CuO \,.\, CuSO_4$ so that we shall obtain first of all the monovariant equilibrium:

$$4CuSO_4 + Cu_2O \rightleftarrows 3CuO\,CuSO_4 + SO_2 \quad . \quad . \quad . \quad (IV)$$

and then

$$CuOCuSO_4 + Cu_2O \rightleftarrows 4CuO + SO_2 \quad . \quad . \quad . \quad . \quad (V)$$

Finally, we will, therefore, have left a mixture of CuO and Cu_2O or of CuO and $CuO \,.\, CuSO_4$. The latter will then dissociate according to: $CuO \,.\, CuSO_4 \rightleftarrows 2CuO + SO_2$, whereas at a still higher temperature occurs the dissociation of CuO into $Cu_2O + O$[2]).

6. The above considerations have been completely confirmed by our pressure measurements.

Pressures appertaining to the monovariant equilibrium: $3CuS + CuSO_4 \rightleftarrows 2Cu_2S + 2SO_2$ were obtained by starting from an intimate mixture of CuS and $CuSO_4$.

The $CuSO_4$ was obtained by dehydrating pure crystallised $CuSO_4 \,.\, 5H_2O$ and heating at 300°—400° in order to eliminate any free sulphuric acid eventually present. CuS was prepared by precipitating a feebly acid solution of $CuSO_4$ with H_2S at the ordinary tempe-

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[1]) Ber. der deutschen chem. Gesellschaft **41**, 703 (1908).

[2]) L. WÖHLER. Zeitschr. f. Elektroch. **12**, 784 (1906).

rature and heating the precipitate so obtained, after drying at 200°—250°, in a current of H_2S. In order to remove occluded gases it was then again heated in a vacuum at 300°—350°. It contained 66.2% of Cu (theory 66.46%).

The SO_2 evolution is already perceptible at ± 150°, but the reaction velocity at this temperature is so trifling, that it is practically impossible to attain the equilibrium by heating at a constant temperature. Hence, the mass was first heated at a higher temperature (usually 220°—240°) until a considerable quantity of SO_2 had evolved and then cooled very gradually until a temperature was reached where adsorption of SO_2 occurred. Now, this temperature was kept constant for a considerable time, small quantities of SO_2 were frequently withdrawn and it was recorded whether any further absorption took place or not. In this manner it was possible to restrict the equilibrium pressure within 20—30 m.m.; closer limits could not be obtained in this very slowly progressing reaction. Table II represents the results.

TABLE II. $3CuS + CuSO_4 \rightleftarrows 2Cu_2S + 2SO_2$ (fig. 2 line I).

T	*p*
95	180
121	246
159	443
175	716

These pressures were always again attained after a few evacuations. The reaction product at the end of the measurements was still in a powdery condition, the colour had changed from black to grey. Cu_2O could not be detected. The pressures measured will, therefore, relate indeed to the above-cited monovariant equilibrium.

7. In exactly the same manner the reaction $Cu_2S + 2\,CuSO_4 \rightleftarrows 2\,Cu_2O + 3\,SO_2$ was investigated. This also proceeds very slowly at temperatures where the equilibrium pressure is less than 1 atmosphere, so that it is here also impracticable to attain the equilibrium by heating at constant temperature. Hence, it was necessary to approximate the pressure in the same manner as detailed above.

As it appeared very soon that our observations differed very much from those of SCHENCK and HEMPELMANN, we repeated the pressure measurements with mixtures of different composition. From table III wherein the results are indicated, it appears, however, that this exerts no influence on the equilibrium pressure, so that the existence of solid solutions is excluded.

TABLE III. $Cu_2S + 2CuSO_4 \rightleftarrows 2Cu_2O + 3SO_2$ (fig. 2 line II).

2 $CuSO_4$ on 1 Cu_2S.		1 $CuSO_4$ on 1 Cu_2S.	
T	*p*	*T*	*p*
300	135	327	175
310	148	351	228
350	210	375	350
360	245		
377.5	285		
390	443		
400	517		

We have not been able to confirm the phenomenon observed by the said investigators that, above 300°, the equilibrium pressure first attains a maximum value and then falls to a constant terminal value. Although we kept the mixture, after the setting in of the equilibrium, for fully 5 × 24 hours at ± 320°, no adsorption was noticed. In the case of other mixtures where the measurements were executed as rapidly as possible, we also could not notice anything of the phenomenon.

Notwithstanding the heating at 420°—425° the reaction product, after the end of the operations, was a strongly caked but *non fused* mass in which red Cu_2O particles were distinctly discernible. The above pressures therefore relate undoubtedly to the equilibrium between the solid phases Cu_2O, Cu_2S, and $CuSO_4$.

We must, therefore, utterly reject the conclusion of SCHENCK and HEMPELMANN as to the appearance of a quadruple point in this system which would be situated at 300° and ± 95 mm SO_2-pressure and where Cu_2O, CuS and $CuSO_4$ should coexist in presence of a liquid phase and a gaseous phase. Even at 430° we could *not* yet observe the appearance of a liquid phase.

8. This contradiction induced us to try and find the initial melting points of mixtures of Cu_2S and $CuSO_4$ by the thermic process. For this purpose they were heated in a glass tube placed in an electric oven whilst the heating curve could be recorded with a silver-constantane thermo-cell. The tube was furnished with an exit tube; the gas developed during the measurement was thus carried off, adsorbed in alkali and finally determined. The rise in temperature amounted to 3° per minute; the starting of the fusion was characterized by a very pronounced inflexion in the heating line. For instance, with a mixture of 25 grams of $CuSO_4$ and 25 grams of Cu_2S (about 1 mol. $CuSO_4$ to 1 mol. Cu_2S) the constancy of the temperature amounted to ± 5 minutes, after which a regular rise of 2—3° per 1′ again set in. With mixtures of different composition were obtained initial melting points which differed only 1—2°.

The mean value amounts to 484°. During the observation there was evolved, when using 25 grams of mixture, on an average 160 mg. of SO_2, from which we deduced that the mixture can have been converted at most to the extent of $2^0/_0$. The value found can, therefore, be but a very little too low.

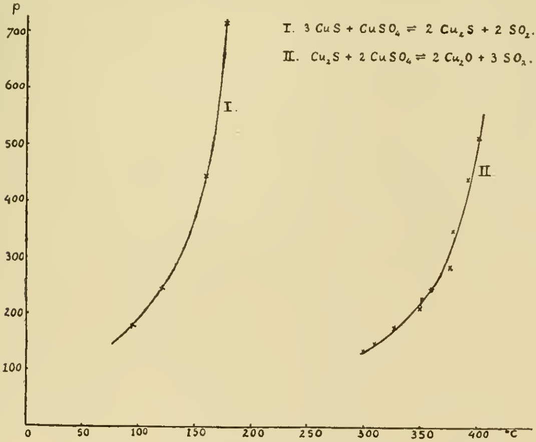

Fig. 2.

As the fused mass evolves SO_2 very powerfully, heating in a sealed apparatus was not possible.

By exactly the same method the initial melting points of ternary mixtures of $CuSO_4$, Cu_2S, and Cu_2O were recorded. Also here, the results obtained with mixtures of different composition only differed

1—2° and the thermic effect was very considerable. On an average was found: 457°. The SO_2 evolved amounted to average 40 mg. per 25 grams of mixture.

The ternary eutecticum is, therefore, situated but a little lower than the binary one of mixtures of Cu_2S and $CuSO_4$; the liquidum region in the triangle $Cu_2S—CuO—CuSO_4$ will exhibit a strongly one-sided situation towards the $Cu_2S—CuSO_4$ side. As the liquid is very viscous and the evolution of gas a violent one, we have not, up to the present, succeeded in determining the composition of the eutectica. Hence, we can only say this that they will only be permanent under a high SO_2-pressure and will, at the ordinary pressure, decompose rapidly with formation of Cu_2O. From our dissociation experiments with mixtures of $Cu_2S—CuSO_4$ we calculate for the SO_2-tension at the initial melting point ± 1.5 atmospheres. A quintuple point between the solid phases Cu_2O, CuS, $CuSO_4$, the liquid and the gaseous phase will, therefore, appear at about the above pressure.

9. Mixtures of $CuSO_4$ and Cu_2O will react with formation of the basic sulphate $CuO . CuSO_4$.

In order to study this reaction more closely, pressure measurements were executed with these mixtures also. In contrast with the former equilibria the pressure rapidly sets in; usually the equilibrium state is attained after 15—20 minutes; the adsorption also proceeds rapidly. The values attained from both sides only differed 2—3 mm.; hence, the dissociation line is sharply determinable. The SO_2-evolution became discernible at ± 480°; after evacuation the same pressures were again obtained. The results are given in table IV.

TABLE IV. $4\,CuSO_4 + Cu_2O \rightleftarrows 3\,CuO . CuSO_4 + SO_2$ (fig. 3 line IV).

t	*p*
552	48
573	71
582	87
592	114
604	168
625	317
648	502

After only a little SO_2 had been withdrawn the reaction product consisted of a powdery, but slightly caked brownish-red mass.

10. At 570°, SO_2 was now constantly being withdrawn from the mixture and each time the equilibrium pressure was measured. This remained the same until suddenly a strong depression was observed. A series of points of this newly attained equilibrium was determined; it is about equally sharply noticeable as the former. The values return, after evacuation, again very exactly. The results obtained are those of table V 1^{st} series.

In order to ascertain whether this last equilibrium really relates to the basic sulphate $CuO.CuSO_4$, and hence may be represented by:

$$CuO.CuSO_4 + Cu_2O \rightleftarrows 3\,CuO + SO_2$$

it was endeavoured to obtain this sulphate in a pure condition. WÖHLER [1]) and others recommend heating $CuSO_4$ at ± 800° in a current of SO_2; it is then, however, mixed with a small quantity of Cu_2O. We have repeated this process, but it appeared that in this manner are obtained strongly caked, red masses very rich in Cu_2O. Consequently we have abandoned this method and endeavoured to obtain the compound in a pure condition by heating $CuSO_4$ in a current of air at 720°—740°. This gave better results; the product was coloured a pure yellow and yielded on analysis 66.21 °/₀ $CuSO_4$ (theory for $CuO.CuSO_4$ 66.62 °/₀).

TABLE V. $CuO\,CuSO_4 + Cu_2O \rightleftarrows 4\,CuO + SO_2$ (fig. 3 line V).

1st series.		2nd series.	
t	p	t	p
644	39.5	655	54
666	52	679	76
684	86	699	115
703	131.5	705	133
725	215	723	205
736	292	749	386
754	419		

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[1]) L. WÖHLER, W. PLÜDDEMANN and P. WÖHLER, Ber. der deutschen chem. Ges. **41**. 710 (1908),

A mixture of equal mols. of this basic sulphate and Cu_2O yielded the pressures of table V 2nd series. As both series of observations entirely agree, we may be sure that they relate to a same monovariant equilibrium, namely between $CuO . CuSO_4$, Cu_2O, CuO and the gaseous phase. As the equilibrium pressure does not alter after withdrawal of SO_2, that is after variation in the relation of Cu_2O and CuO, the miscibility of these phases, noticed by Wöhler[1]) at *higher* temperatures, will be slight in this temperature-range, so that they will both continue to exist.

Finally, the SO_2 was withdrawn completely, so that only CuO could remain, as we had started from equimolecular quantities of basic sulphate and Cu_2O. We have been able to demonstrate that this was really the case by measuring the dissociation hereof in Cu_2O and O_2. Here we found at 944° . . . 36 m.m. and at 958° . . . 49 m.m., observations which entirely agree with those of Wöhler for pure CuO.

11. With the above mentioned equilibria in the ternary system Cu-S-O are connected the dissociation equilibria of pure $CuSO_4$ and $CuO . CuSO_4$.

These have been determined by Wöhler and his co-workers.

On a closer scrutiny of the values given by them it appeared that the p-T-lines that can be construed thereof intersect each other, which would lead to the improbable conclusion that the basic sulphate is only stable above ± 625° and must dissociate below this temperature into CuO and $CuSO_4$. Hence, we were obliged to doubt the correctness of their determinations.

As, however, the accurate knowledge of the dissociation line of the basic salt was of importance to us because — as will be seen in § 14 — the equilibrium pressure of reaction V can be calculated therefrom, we have once more determined the dissociation lines of the normal and of the basic sulphate. The results differ considerably from those of Wöhler.

Both equilibria can be attained very readily and the pressures obtained by evolution and absorption do not differ more than 2—3 m.m.; after evacuation they accurately resume the same value. By way of a check a series of observations were executed in the dissociation of the normal sulphate where platinum gauze was tied round the porcelain tube with the substance. *A priori* it was probable, however, that even without addition of this catalyst the equilibrium in the

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[1]) L. Wöhler, c.s., loc.cit.

gaseous phase would be attained because the copper compounds themselves have a catalytic action at the temperatures here employed[1]). Table VI where the 1st series has been executed without, and the 2nd with addition of platinum confirms this entirely.

12. The gas mixture was withdrawn a few times by suction until a fall took place in the equilibrium pressure; the reaction product was then analysed and gave the proportion $2CuO : SO_3 = 1 : 0.98$. This product gave afterwards the pressures of table VII, these always returned after continued evacuation, until finally the pressure fell to that of the equilibrium $4CuO \rightleftarrows 2Cu_2O + O_2$. Further basic sulphates are, therefore, not capable of existence at these temperatures.

TABLE VI. $2\,CuSO_4 \rightleftarrows CuOCuSO_4 + SO_3\,[SO_2 + {}^1/_2\,O_2]$ (fig. 3, line VI).

1st series		2nd series	
t	*p*	*t*	*p*
680	34	682	37
710	76	711	80
730	131	732	142
740	169	750	235
760	287	770	371
780	442		

TABLE VII. $CuOCuSO_4 \rightleftarrows 2\,CuO + SO_3\,[SO_2 + {}^1/_2\,O_2]$ (fig. 3, line VII).

t	*p*
740	61
760	84
780	144
800	224
810	284
820	345

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1) Bodenstein and Fink. Zeitschr. f. physik. Chem. 60, 46 (1907).
L. Wöhler, W. Plüddemann and P. Wöhler, Zeitschr. f. phys. Chem. 62, 641 (1908).

13. The bad agreement existing between the observations of Wöhler and his co-workers and our own, made us doubt for a moment whether our apparatus arrangement might be the cause of the differences. For a small quantity of SO_3 was deposited in the capillary which connected the reaction tube with the manometer. Theoretically, it is very improbable that this phenomenon can have any influence on the equilibrium pressure, for as soon as SO_3 disappears from the gas mixture which is in contact with the solid substance in the reaction tube, dissociation will again set in, until the original SO_3-pressure has again been attained. Only in those parts of the apparatus where there is no longer any contact between gas and solid substance and where moreover the temperature is low enough, in other words in the capillary, a *permanent* decrease of the SO_3-tension can take place. Here, then forms a gas mixture of SO_2 and O_2, which plays the same rôle as the interlinked air cushion in the measurements of Wöhler and co-workers. Our gas mixture, however, is not indifferent but can on cooling, be reabsorbed completely by the solid substance. It was, in fact, always observed that after heating at a higher temperature followed by cooling, the equilibrium pressure

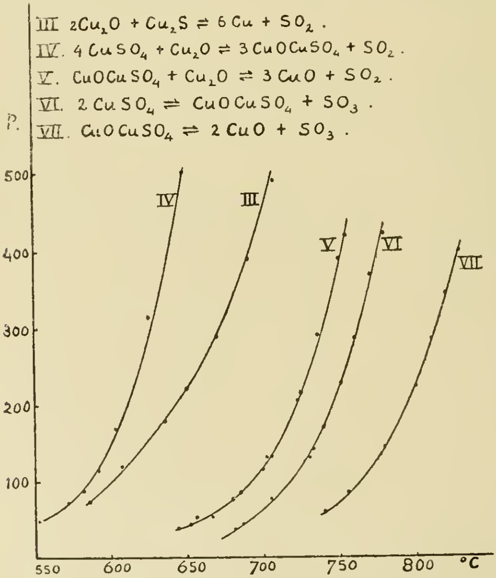

Fig. 3.

set in very exactly on the lower value appertaining to this lower temperature.

A few check experiments with ferric sulphate, executed in the same apparatus yielded equilibria pressures agreeing entirely with the values indicated by BODENSTEIN[1]).

The results are given below. The deviations answer to a difference in temperature of 1—2°.

t	$p_{\text{Bodenstein}}$	$p_{\text{R. and G.}}$
650	124	116
670	193	181
689	319	317

14. If we again consider the monovariant equilibrium,

$$CuO\,.\,CuSO_4 + Cu_2O \rightleftarrows 4\,CuO + SO_2 \;\ldots\; (V)$$

we can imagine this to have originated in the following manner:

$$CuO\,.\,CuSO_4 \rightleftarrows 2\,CuO + SO_3 \;\ldots\; (VII)$$

$$SO_3 \rightleftarrows SO_2 + \tfrac{1}{2}\,O_2 \;\ldots\; (IX)$$

$$Cu_2O + \tfrac{1}{2}\,O_2 \rightleftarrows 2\,CuO \;\ldots\; (VIII)$$

The gaseous phase consists both in reaction (V) and reaction (VII) of a mixture of SO_3, SO_2 and O_2. If we call the partial pressures of these gases at a given temperature:

for V respectively, ${}_5p_{SO_3}$, ${}_5p_{SO_2}$, ${}_5p_{O_2}$, the total pressure P_5
,, VII ,, ${}_7p_{SO_3}$, ${}_7p_{SO_2}$, ${}_7p_{O_2}$, ,, ,, ,, P_7

the homogeneous equilibrium in the gaseous phase will be as follows:

at V $K = \dfrac{{}_5p_{SO_2} \cdot {}_5p_{O_2}{}^{1/2}}{{}_5p_{SO_3}}$ and at VII $K = \dfrac{{}_7p_{SO_2} \cdot {}_7p_{O_2}{}^{1/2}}{{}_7p_{SO_3}}$.

Hence it follows that, at the same temperature

$$\frac{{}_5p_{SO_2} \cdot {}_5p_{O_2}{}^{1/2}}{{}_5p_{SO_3}} = \frac{{}_7p_{SO_2} \cdot {}_7p_{O_2}{}^{1/2}}{{}_7p_{SO_3}} \;\ldots\; (a)$$

The coexistence of the phases Cu_2O and CuO at V now demands that the partial oxygen pressure in this equilibrium is equal to a dissociation pressure of pure CuO into Cu_2O and O_2. If we call the latter P_8, then ${}_5p_{O_2}$ must be $= P_8$.

Likewise does the coexistence of the solid phases $CuO\,.\,CuSO_4$ and

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[1]) Zeitschr. f. Elektrochemie **16**, 912. (1900).

CuO at V demand that the SO_3-pressure of V is equal to that of VII so that ${}_7p_{SO_3} = {}_5p_{SO_3}$.

These relations substituted in (*a*) give:

$$ {}_7p_{SO_2} \cdot {}_7p_{O_2}{}^{1/2} = P_8{}^{1/2} \cdot {}_5p_{SO_2} \quad \ldots \ldots \quad (b)$$

In this ${}_7p_{SO_2}$ and ${}_7p_{O_2}$ may be calculated from the observations of the total pressure P_7 if the dissociation degree a of the SO_3 is known. Then we have:

$$ {}_7p_{SO_2} = \frac{2a}{2+a} P_7 \quad \text{and} \quad {}_7p_{O_2} = \frac{a}{2+a} P_7$$

and hence, substituted

$$\frac{2a}{2+a} \cdot P_7{}^{3/2} \sqrt{\frac{a}{2+a}} = P_8{}^{1/2} \cdot {}_5p_{SO_2}$$

or:

$$\left.\begin{aligned} {}_5p_{SO_2} &= \frac{P_7{}^{3/2}}{P_8{}^{1/2}} \cdot \frac{2a}{(2+a)^2} \cdot \sqrt{a(2+a)} \\ \text{and} \quad P_5 &= P_8 + {}_5p_{SO_2} + {}_7p_{SO_3} \end{aligned}\right\} \quad \ldots \ldots \quad (c)$$

In this last equation ${}_5p_{SO_2}$ will be very great in proportion to the two other terms; at the first approximation the total pressure of reaction V might be put equal to ${}_5p_{SO_2}$.

15. From the foregoing it appears that it is possible to calculate the equilibrium pressure of V if we know:

a. the dissociation pressure at the equilibrium VII;

b. the dissociation degree of the SO_3 at the pressures of VII;

c. the dissociation pressure of CuO.

The first *quantity* is known from our determinations given in table VII. The second can be calculated accurately from the careful investigations of Bodenstein and Pohl [1]). We have done this for various temperatures and pressures which are interpolated graphically from our measurements of VII (see column 5 of table VIII).

The dissociation pressure of CuO into Cu_2O and O_2 is extrapolated from the observations of Wöhler [2]) with the aid of the formula

$$\log P_8 = 13{,}077 - \frac{14000}{T},$$

which agrees excellently with his observations.

With the aid of formula (*c*) the equilibria pressures P_5 have been

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[1]) Zeitschr. f. Elektroch. **11**, 373 (1905).

[2]) Zeitschr. f. Elektroch. **12**, 704 (1906).

calculated for a series of temperatures and compared with the values found experimentally. They are collected in table VIII.

TABLE VIII.

t	T	P_7	P_8	α	P_5 (calculated)	P_5 (observed)
720°	993	33	0.0951	0.895	211	195
740	1013	55	0.1803	0.915	338	308
760	1033	90	0.3342	0.921	526	500
780	1053	144	0.6054	0.907	784	810

Considering the inaccuracy of the extrapolation of P_8 over fully 200° below the field of observation, the agreement may be called a complete one. It furnishes a proof of the correctness of our measurements as well as of those of WÖHLER in connexion with the dissociation of copper oxide.

Delft, Inorg. and phys. chem. laboratory
of the Technical University.

Physiology. — "*On measurement of sound.*" By Prof. H. ZWAARDEMAKER.

(Communicated in the meeting of April 1915.)

I have previously pointed out the benefit to be derived from Lord RAYLEIGH's arrangement, if we wish to perform a relative or even an absolute measurement of sound. Originally [1]) it was applied to the measurement of stationary sound-waves. W. KÖNIG [2]) extended its use to the theory of progressive waves in detail. It also enabled W. ZERNOV [3]) to carry out experiments on the intensity of the human voice. All earlier researchers and myself at first also, gave to the mirror, which was placed obliquely to the sound-wave, a peculiar position by attaching to it a small magnet. I now departed from this principle, at first by bifilar suspension, afterwards by simply hanging the mirror up by a long Wollaston fibre, flattened or not. [4])

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[1]) Lord RAYLEIGH. Scientific Papers. Vol II, p. 132.

[2]) W. KÖNIG. Ann. d. Physik. Bd. 42 and 43, 1891.

[3]) W. ZERNOV. Ann. d. Physik. (4). Bd 24 p. 79, 1908.

[4]) H. ZWAARDEMAKER. "On hearing-apparatus". Ned. Tijdschrift v. Geneesk. 1912, II. p. 1101. Proc. of the meeting of 27 Sept. 1913. Vol. 22. p. 273, Congress at Delft, March 1913, Multiple resonantie. Ned. Tijdschr. v. Geneesk., 1913. II. p. 640.

To my knowledge ZERNOV was the first to place the measuring mirror in a space entirely free from resonance. To increase the sensitiveness I took some years later, for application to medical problems, an afferent tube of the dimensions of the auditory canal and the auricle. This enables us to perform an accurate measurement even of whispered speechsounds. However, occasional currents of air must be arrested by putting a very small plug of cotton-wool in the artificial auditory canal. The mirror is placed at an angle of 45° close in front of the aperture of the tube, so that the sound-wave, issuing from the auditory canal is driven against it as fully as possible. The mirror is consequently tilted with maximum power to a more transversal position.

If weak sounds in the speechzone a_1 to e_3 are to be measured, it will be well to use large receiving funnels. Phonograph horns in their various shapes will be found to work very well. Small amplitudes are recorded more accurately, when the scale is placed at a great distance. Then, however, a constant position of rest is expedient, which is hardly practicable, unless the streams of air in funnel and auditory canal are removed through the insertion of an india-rubber diaphragm of the size of a phonograph membrane. Cover-glass or thin mica will do as well. Thus I was in a position to establish the ratio of the average intensities of whispered and spoken sounds. The experiment was made (together with Dr. REUTER) with 20 monosyllabic, aequisonorous and aequidistant words. The ratio appeared to be 1 : 170. (The intensity is in the ratio of 1 : 170, the distance at which sounds are heard of 1 : 13)[1]). The modifying influence of funnel and membrane may be controlled by going through the gamut first with a simple physiological conducting tube and afterwards with the same tube associated with a funnel and phonograph membrane.

In the following pages I shall briefly state the rules which have proved generally reliable in measuring sound.

§ 1. *Physiological measurement of sound.*

When the measurement of sounds with regard to their audibility is the subject under consideration, it is permissible to use an artificial auricle and an artificial auditory canal to direct the sound-wave on to the measuring mirror. Provided the resonance of the artificial conduit be equal to that of the natural canal, nothing foreign is added to the sound, for when perceived by the human ear, it is transmitted through a similar tube. The artificial canal

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[1]) Proceedings of the 14th Dutch Congress for Phys. and Med. at Delft.

used by me, has with a small plug of cotton-wool a tone of resonance equivalent to f_4, without a plug to e_4. The funnel in front of it was different in either experiment. When it was simply a flat wooden platter, a peculiar resonance was not noticeable.

The degree of sensitiveness is inversely proportional to the size of the mirror. A mirror of 2 mm. in diameter and 60 μ thickness, hung up by a Wollaston fibre of 2 μ have thus far proved to be the smallest dimensions for easy handling. In the same proportion the auditory canal should also be made narrower. Since we generally experiment on continuous waves (only e_4 yields a stationary wave), the distance at which the mirror is placed is of little consequence, provided it be axial. The sensitiveness is about inversely proportional to the distance from the aperture. It is remarkable that acoustic attraction will often concur in the case of powerful sounds. It should be precluded by all means. [1]) Electric attraction is obviated by connecting the auditory canal with the point, from which the mirror is suspended, by a small metallic chain. Should rather high tensions occur in the neigbourhood, also a conductive connection to the earth should be constituted.

In physiological experiments the walls of the space in which the mirror is suspended, are generally lined with gauze, which method was also followed by ZERNOV. To this there can be hardly any objection, when experimenting with receiving funnels, the progressive sound being in large part transmitted to the mirror along the artificial canal. What is conducted from other quarters may be disregarded altogether.

The afferent tube is fitted to a copper plate. A more accurate axial position must be effected by means of three adjusting screws at the foot of the apparatus. The distance from the mirror to the aperture of the tube is determined by a horizontal measuring microscope mounted on a heavy vertical LEITZ-stand.

§ 2. *Physical measurement.*

If instead of experimenting on the intensity of audible sounds we wish to determine the objective intensity of a pure sound-motion, auricle and auditory canal are of course disturbances. For this purpose a conduit of a more physical nature is desirable. The simplest is either a tube or a cone. A tube, if short, is liable to become a resonator with a very sharp and narrow resonance.

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[1]) Attraction seemingly acoustic, but in reality involved by eddies, will occur with any fine puncture in the canal or in the membrane.

Mr. Ws. van der Elst, assistant in our laboratory, established the resonance curves of such small resonators by shutting off one end of the tube with wax and placing a suitable mirror before the open end. In very long tubes the tone of resonance is so low, that it need not be taken into account. Earlier experiments on the propagation of sound in air showed that there is a marked decrease in the velocity of propagation, when the tubes are narrower than 4 mm. This at least is the case, when they are made of india-rubber. It must be deemed advisable, therefore, to take glass or metallic pipes of no less than ± 4 mm. in diameter. A mirror of, say 3 mm. diameter, placed just in front of a straight-cut aperture, will be found very suitable in most cases. Still, for very high tones even this pipe is too narrow, as was demonstrated by researches years ago[1]. The tones of Galton's whistle (six-legerlined octave) change, when passing through a canal of from 3—5 mm. bore, which after the foregoing need not cause surprise, the tones lying near the upper limit of musical sounds. We found it suitable to provide the afferent tubes with leaden taps[2]. The sound conducted to the measuring apparatus, may be generated at a considerable distance.

Another simple conduit is the cone. The funnel may be given an angle of 40° and a mouth of 50 cm^2. Some American hearing apparatus (operaphone) are provided with a similar funnel. Helmholtz discusses its resonance in his "Tonempfindungen". The one I used, resounds to d_2. This is easy to determine when an opening is left in the apex of 2 mm., before which the Rayleigh mirror is placed. The latter will deflect considerably, when the tone of resonance is given. With all other tones the waves will be progressive, the cone being merely an indifferent receiving funnel. Again a small plug of cotton wool had to be used to arrest disturbing streams of air.

§ 3. *Point-shaped soundsources.*

Outlets in the shape of a mere puncture are obtainable through a fine orifice, say of 1 mm. 1. in a little leaden disc that serves for a septum in a speaking tube; 2. in the covering disc of the air-chamber of a thermotelephone. In either case the mirror is placed right opposite to the fine opening, through which the sound is con-

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[1] H. T. Minkema, On the sensitiveness of the human ear to the various tones of the gamut. Dissertation Utrecht 1905.

[2] H. de Groot, Zschr. f. Sinnesphysiologie Bd. 44 S. 18 (experiments by Dr. van Mens) and these Proceedings Vol. 14 p. 758 (experiments by Dr. P. Nikiforowsky).

ducted. Either method allows of altering the sound at will, the number of sounds and intensities, transmissible through a long, wide pipe to the diaphragm, being indefinite. The tones embraced by the thermotelephone are also a great many, from the low, non-coalescent tone of an interruptor to the high hissing-sound [1]). Likewise the intensity of the thermotelephone-sound can be varied through artificial appliances within far-extended limits. Selection occurs with the latter appliance only as far as the peculiar tone of the air-chamber is concerned, but when the air-chamber is small — as is deemed advisable — it is so high, that it may be left out of calculation.

Both methods yield progressive soundwaves, whose energy is constantly procured by the generator, and emerges through the point-shaped orifice of 1 mm. If the latter is in circuit with an air-chamber, through which the sound is conveyed to the measuring mirror, the results vary roughly according to the size of the chamber. The differences are markedly perceptible with an outlet of $^1/_2$ mm. in diameter. As original sound-generator may be used a telephone, actuated by an electrically driven tuning fork or a large powerful organpipe.

§ 4. *Investigation of resonators.*

The mode of arrangement can also be easily applied to test resonators. When a puncture (2 mm.) is made in the wall of the resonator, right opposite to the mouth, the sound passing through it may readily be directed on to RAYLEIGH's mirror via a canal of the same bore [2]). It will be expedient, however, to arrest by means of a very small plug of cottonwool or a piece of lint, the streams of air escaping, like the sound, through the fine opening of the resonator. Without this precaution the mirror will never be steady, not even in a perfectly quiet environment.

The sound thus emitted through the puncture, is made up of progressive waves. By means of a long tube it can also be sent to a comparatively long distance, provided that fresh acoustic energy be constantly supplied through the orifice. The energy collected and adjusted in the resonator, emerges via the fine opening, as well as through the wide orifice. A mirror, subjected to these progressive waves, deflects, when the amplitudes are small, proportionally to the amount of acoustic energy produced. Spherical resonators yield fairly

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[1]) According to the assistant W. v. d. ELST the pitch agrees with the tone of resonance of a c_6 resonator (8000 v. d.).

[2]) H. ZWAARDEMAKER. Multiple resonantie. Ned. Tijdsch. v. Gen. 1913. II. p. 640.

symmetrical resonance curves (see l.c. p. 642); those generated by paraboloid-shaped resonators or such as are more complicated, like some hearing apparatus, are surprisingly variable [1]).

A very curious shape of resonators is offered by the familiar shells, found on the beach after stormy weather, and in which the murmuring of the rolling waves is heard. Here numerous tones coalesce into a murmur. Testing them involves peculiar difficulties for the very reason, that narrow conduits are not appropriated to the examination of high tones. Nonetheless the difficulty can be overcome by exposing the measuring mirror directly to the point-shaped outlets, afforded by the fine openings in the wall of the shell.

Chemistry. — "*The viscosity of colloidal solutions.*" By Dr. E. H. Büchner. (Communicated by Prof. A. F. Holleman.)

According to Einstein, the viscosity of a liquid, in which a great number of particles are floating, is connected with the relative total volume of the particles. If the viscosity of the pure liquid is represented by z, that of the suspension by z', and its volume by v, if further v' is the total volume of the suspended particles, then

$$\frac{z'-z}{z} = 2,5\frac{v'}{v}$$

This formula has been applied to gamboge suspensions by Bancelin, who obtained fairly satisfactory results; the factor had to be taken, however, 2,9 instead of 2,5. Admitting the formula to be correct, we may, conversely, calculate the volume of the floating particles from measurements of the viscosity. If, then, we determine the number of the particles (e. g. ultramicroscopically), the volume of one separate particle may even be deduced.

The application of this formula to colloidal solutions will greatly deepen our insight in the nature of these systems. We might feel some doubt, whether the suppositions, made by Einstein, when deducing the formula, hold good in the case of colloidal solutions, the particles of which are so much smaller. But Einstein himself has applied it to sugar solutions, and has calculated from the result, in connection with determinations of the diffusion constant, Avogadro's number. The fact, that he found in this way $6,6.10^{23}$, shows, that his assumptions are not far from being correct. For the rest, I have found, that even several observations on the viscosity of ordinary

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[1]) H. Zwaardemaker. These Proceedings, Vol. **16**, p. 496.

solutions may be represented by the same formula, as I hope to show in a more detailed paper. There is, therefore, no objection to the application of the formula to colloidal solutions, which, according to modern theory, stand between the ordinary solutions and the suspensions or emulsions, and differ from these only with regard to the size of the "dissolved" particles. For the present, it is not of much importance, that the value of the factor is not yet absolutely settled. In this communication, I only wish to show at least qualitatively, that the colloid particles are combined with a quantity of the solvent. For instance, the ultramicroscopically visible particles of a ferric hydroxide solution consist of a number of molecules ferric hydroxide and a number of molecules water; these are moving as an aggregate in the surrounding liquid. A great viscosity is to be ascribed to a great volume of the colloid particles, either they are very great themselves, or they take up much water. It must be pointed out, that, when comparing different solutions, one ought to express the concentration in volume percentage, because according to the point of view here adopted, the viscosity depends only on the volume of the dissolved particles.

The idea may also be applied to ordinary molecular solutions. The fact, that the viscosity of solutions of electrolytes is often relatively large, may be brought in connection with the property of the ions, to combine with or to envelop themselves by water, a faculty of which numerous investigators have furnished proof on the most different grounds. In accordance with this conception, the salt solutions, the ions of which show the smallest tendency to hydration, exhibit the smallest viscosity. But, for the present, I will not enter further into this question.

I have only to communicate measurements of two substances, molybdenum blue ($Mo_3\,O_8$?) and iron hydroxide. I have determined at 30° and 40° the viscosity and specific gravity of some solutions of varying concentrations. The values for the two temperatures differing only slightly, the communication of the results at 30° will be sufficient. In the subjoined table z' represents the viscosity of the solution, that of water being taken $= 1$, v' the volume of the particles, deduced from z' according to $z' - 1 = 2{,}5\,\frac{v'}{v}$; v is put equal to 1 cc. The concentration of the solutions c is expressed in g per c.c.; d' is the density thereof. As dissolved substance I regard the molybdenum blue, dried at 100°, respectively the ferric hydroxide: $Fe(OH)_3$. The concentration of the solutions of the former is known, for they are made by weighing; the content of the latter is determined iodometrically, the hydroxide having been first converted into chloride.

Molybdenum blue				Ferric hydroxide			
c	d'	z'	v'	c	d'	z'	v'
0.0199	1.014	1.042	0.017	0.014	1.011	1.034	0.014
0337	1.022	1.066	026	037	1.026	1.082	033
0511	1.034	1.091	036	074	1.051	1.192	077
0969	1.064	1.168	067				
1943	1.137	1.390	156				

From this table we deduce at once, that the volume of the dispersed particles is considerably greater than would be expected, if these particles consisted of molybdenum blue, resp. iron hydroxide only. The specific gravity of the molybdenum blue used was found to be 3,1 at 12°, that of the iron hydroxide may be put equal to about 4. The volume of .0511 g molybdenum blue in the solid state is therefore .017 c.c., and here we calculate for the dissolved particles .036 c.c., more than the double value. For the iron hydroxide the proportion is still greater, and even rises to about 4. These results show conclusively that the colloid particles condense water molecules around themselves or combine with them, and that the hydroxide takes up more water than the molybdenum blue. Although it has often been maintained that such dispersed particles would be composed of colloid and water, it has, I think, never been so clearly demonstrated by experiment.

We may also proceed in a slightly different manner, and calculate the density of the particles. Let us imagine a volume v of the liquid, in which particles having the total volume v' and the density D are floating; the total weight of the particles being consequently $v'D$. Let further d' represent the density of the solution, and vd' its weight. Now, the volume of the "free" water, that is the water, which is not combined with colloid particles, will be $v-v'$; if its density be called d, then we have

$$v'D = vd' - (v-v')\,d.$$

$$D = \frac{v}{v'}(d'-d) + d.$$

Therefore

$$D = \frac{2,5}{z'-1}(d'-d) + d.$$

As the specific gravity of the solution must be determined for the viscosity measurements, it is easy to deduce the specific gravity of the particles. We find for molybdenum blue 1,83 to 1,93; for iron hydroxide 1,66 to 1,8. In this manner too, it becomes clear, that the particles suspended in the liquid cannot consist only of dissolved substance, the density of which is 3 or 4, but must also contain water. As has already been pointed out, the qualitative value of these conclusions is not attacked, if it should appear, that instead of $2,5\frac{v'}{v}$, for instance, $3\frac{v'}{v}$ must be written. Neither would this be the case, when we introduce into EINSTEIN's formula the second power of $\frac{v'}{v}$, as is necessary for the more concentrated solutions.

I hope to discuss later from the standpoint taken in this paper, the viscosity measurements previously published by other observers. A preliminary investigation already led to remarkable results, but a great part of what is known, cannot serve my purpose; I propose to fill up this lacuna by new determinations, and to discuss then at length the many questions, which arise in this field.

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Physics. — *"Some Remarks on the Capillarity Theory of the Crystalline Form"*. By Prof. P. EHRENFEST. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 29, 1915).

§ 1. As is known, W. GIBBS[1]) and P. CURIE[2]) have set forth the following view, and given further thermodynamic grounds for it. A crystal in a solution is in thermodynamic equilibrium only when it has that shape in which its surface energy has a smaller value than for any other shape with the same content. That this equilibrium

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[1]) W. GIBBS: Thermodyn. Studiën p. 320.

[2]) P. CURIE: Bull. de la Soc. Min. de France **8** (1885) p. 145 of Oeuvres p. 153. Cf. for the relations between the theories of GIBBS and CURIE:

J. J. P. VALETON: Kristalvorm en oplosbaarheid. Proefschr. Amsterdam 1915. Ber. d. Sächs. Ges. d. Wiss. **67**, (1915).

shape is not the sphere (i.e. the form with the smallest surface) but a polyhedron, is according to GIBBS and CURIE owing to the following circumstance. The surface energy of a surface element depends in a crystalline substance on the orientation of the surface element with respect to the crystalline substance, i.e. on the indices of the surface elements, and this in different ways for different substances.

If $k_1, k_2, k_3, \ldots$ are the capillarity constants of the differently orientated bounding planes; $S_1, S_2, S_3, \ldots$ the corresponding areas of the surfaces, V the volume of the crystal, then the equilibrium form is characterised by the condition:

$$\Sigma k_h S_h = \text{min. for } V = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

G. WULFF [1]) has derived a remarkably elegant geometrical property of the equilibrium diagrams from (1), which greatly facilitates the following expositions: In a figure characterised by the minimum condition (1) there always exists a point W (we will call this WULFF's point) lying so that the distances $n_1, n_2, \ldots.$ of the different surfaces $S_1, S_2 \ldots$ from W are directly proportional to the constants $k_1, k_2, \ldots$

$$n_1 : n_2 : n_3 : \ldots = k_1 : k_2 : k_3 : \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This theorem of WULFF's immediately furnishes a construction of the equilibrium figure, if for every direction of the normal the corresponding value of k has been given. Draw from an arbitrary point W of the space in all directions lines whose lengths are proportional to the corresponding k's and apply planes normal to them through their endpoints: then there remains a space in the neighbourhood of W, where none of these planes enters — this space is the required crystalline form. It is seen here at once that surfaces with a comparatively large value of k lie so far from W, that they cannot constitute a part of the boundaries of the crystal [2]).

We derive the "law of the (small) rational indices" therefore in this theory in consequence of this that the surfaces with *small* index values in general must also possess particularly *small* capillarity constants k.

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[1]) G. WULFF: Zschr. f. Krystallogr. **34** (1901) p. 449. The proof, which WULFF had given in an imperfect form, has been improved by HILTON afterwards:

H. HILTON Centralbl. f. Miner. 1901 p. 753 = Mathem. Crystallogr. (Oxford 1903) p. 106. Cf. H. LIEBMANN. z. f. Kryst. **53** (1914) p. 171.

[2]) Let in the regular system e.g. the k's of cube planes be k_1, those of the octahedron planes k_2. It is required for the octahedron planes to occur by the side of those of the cube that:

$$\frac{1}{\sqrt{3}} < \frac{k_1}{k_2} < \sqrt{3}.$$

See: CURIE loc. cit. and WULFF loc. cit.

As is known, this theory of Gibbs and Curie's plays a very important part in the crystallographical literature. Frequent crystallographical applications have been made of it [1]; it has been now and then extended by the introduction of "side energies" and "angular point energies" by the side of "surface energies" k_1, $k_2 \ldots$, and by making the former have a share in the determination of the equilibrium figure [2]; of late years criticism has not been wanting either, which now and then even comes to a full rejection of Gibbs and Curie's view. [3]

On the other hand it seems that except Sohnke's indications [4], which concur with Bravais' views, no attempts have been made as yet to interpret the energetic theory of Gibbs and Curie in a *molecular scheme.* Such an attempt would be the more desirable as there is in this region a whole series of dark or paradoxical points to be analysed.

In view of the great difficulties which are to be overcome here, I should like to confine myself to a single of these points, and demonstrate how this can entirely be elucidated by the aid of an extreme simplified molecular scheme. It is seen the more clearly on this occasion how much there remains to be done to elucidate other points.

§ 2. *Does the capillarity constant of a crystal plane depend continuously or discontinuously on its orientation? The problem of the vicinal planes.*

The polyhedrical shape of the crystals and the law of the small rational indices easily gives rise to the supposition of a *discontinuous* dependence; accordingly it seems to have been made, at least implicitly by most crystallographers, as soon as they made use of Gibbs and Curie's theory. Explicitly it is found expressed in two often

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[1] Chiefly to be able to draw some conclusions on the structure from the crystal form see: Feodorow, Z. f. Kryst. Vol. 34—53, compare also the application to twin formations H. Hilton. The energy of twin crystals. Mineralog. Magazine **15** (1909) p. 245.

[2] Brillouin. Ann. Chim. Phys [7] 6 (1895) p. 540; Vernadsky. Bull. de la Soc. Imp. de Naturalistes de Moscou 1902 p. 495; P. Pawlow. Zschr. f. Kryst. **40** (1905) 189; **42** (1906) 120; Zschr. f. phys. Ch. 72 (1910) p. 385.

[3] A. Berthoud. Journ. de Chim. phys. **10** (1912) p. 624; G. Friedel. Journ. de chim. phys. **11** (1913) p. 478. — Cf. also J. J. P. Valeton. Thesis for the doctorate. loc. cit.

[4] F. Sohnke. Ueber Spaltungsflächen und natürliche Krystallfl. Z. f. Kryst. **13** (1888) p. 214.

cited papers by F. SOHNKE and G. WULFF[1]). Both these authors namely assume that the *capillarity constant* of a crystal plane (apart from a factor which continuously changes with the orientation) is in *inverse ratio to the net density of the plane in question*[2]).

This net density, however, is, as is known, a very discontinuous function of the orientation: thus for irrationally orientated planes, which have been rotated however little with respect to the plane (1, 1, 1), the net density would still be infinitely small in proportion to that of the plane (1, 1, 1). Here the exceptional function of the planes with the smallest indices is at once seen.

In spite of this appeal to the relation with the net density the supposition that the capillarity constant depends *discontinuously* on the orientation, will yet be thought very uncommon, if not quite paradoxical! Besides it involves a great difficulty for the frequent occurrence of the so-called "vicinal planes".[3])

For according to SOHNKE and WULFF these planes with particularly large indices (which are practically irrationally orientated) would possess extraordinarily large surface energy. Of course we are willing to admit deviations from the theoretical equilibrium figure, taking into consideration the small disturbances which are never entirely to be excluded (fluctuations of temperature, disturbances in the concentration etc.) But yet totally unexplained and even paradoxical it remains when these slight disturbances give rise exactly to those planes with extremely large surface energy, and particularly those which lie very near to the planes with particularly small surface-energy[4]).

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[1]) F. SOHNKE. Zeitschr. f. Krystallogr. **13** (1888) p. 221; G. WULFF. Zeitschr. f. Krystallogr. **4** (1901) p. 526. GIBBS and CURIE do not give any further indication on the continuous or discontinuous character of the dependence.

[2]) WULFF gives this formula and characterises the gist of SOHNKE's conception, partly in SOHNKE's own words in the following way: "Nach Sohnke muss ein Zusammenhang zwischen der Oberflächenergie einer Kristallfläche und ihrer Flächendichtigkeit bestehen. Nämlich für eine Fläche von dichtester Besetzung können die Molekularkräfte keine Arbeit mehr leisten, weil die Theilchen einander nicht weiter genähert werden können: *die potentielle Energie einer solchen Fläche muss also ein Minimum sein.* In dem Masse, als die Flächendichtigkeiten der verschiedenen Krystallflächen geringere sind, müssen die Oberflächenergieen (Capillarconstanten) grösser sein ....

[3]) By "vicinal planes" we understand planes which differ exceedingly little in situation from the planes with small indices.

[4]) H. MIERS, Rep. of the Brit. Assoc. 1894 p. 654; Z. f. Kr. **9** (1904) p. 220 has demonstrated experimentally through accurate goniometric measurements during the growth of alumn crystals, that the planes with small indices in this case (1, 1, 1), practically never occur, but nearly always vicinal planes. Cf. also C. VIOLA, Z. f. Kr. **35** p. 332.

§ 3. *Geometrical-physical interpretation of the capillary-constant for a special molecular scheme; the surface energy appears then as continuous function of the orientation, and yet produces a polyhedron as equilibrium figure. The function of the "vicinal planes".*

To throw this point into strong relief, the point which is our only purpose here, we make use of an exceedingly simplified molecular scheme:

1. a two-dimensional scheme instead of a three dimensional one;

2. we leave the thermal motion out of account and accordingly we simply seek the molecular groupings with the smallest potential energy;

3. the molecules may be squares, which tend to adjust their sides close against each other. (We might as well use circular molecules with four points of valency).

Let an enormously large number of such square molecules be given. We seek that grouping at which the maximum "saturation" of the molecules has set in. *Complete* saturation, at which all the molecule sides are occupied, is of course impossible — at least the extreme edge of the "crystal" consists of unsaturate molecule sides. Let in fig. 1 the line $ABCDE\ldots$ be a portion of the "*real*" edge, the line $ACE\ldots$ a portion of the "*apparent*" edge. Let us put:

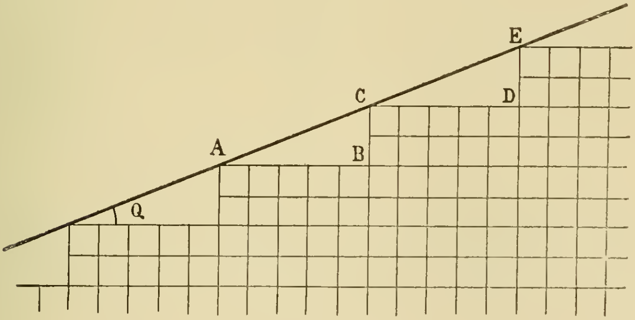

Fig. 1.

$$ABC = \Delta\sigma \quad \text{and} \quad AC = \Delta s$$

then:

$$\Delta\sigma = (\cos q + \sin q)\, \Delta s.$$

The maximum saturation has evidently been reached for that grouping of the molecules, for which the length of the real edge, i.e.:

$$\Sigma \Delta\sigma = \Sigma k \Delta s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

happens to be as small as possible. Hence the quantity:

$$k = \cos\varphi + \sin\varphi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

plays the part of the capillarity factor in our scheme.

It is seen that:

A. the capillarity factor k is here a *continuous function* of the orientation of the element of the apparent edge, which is the subject in view here. (To get a graphical representation, k should be considered as function of the direction of the normals to the edge element, and distances should be projected from a point W in all directions, which are proportional with the values of k for this direction of the normals. We obtain the curve dotted in figure (2), which is composed of 4 arcs of a circle.

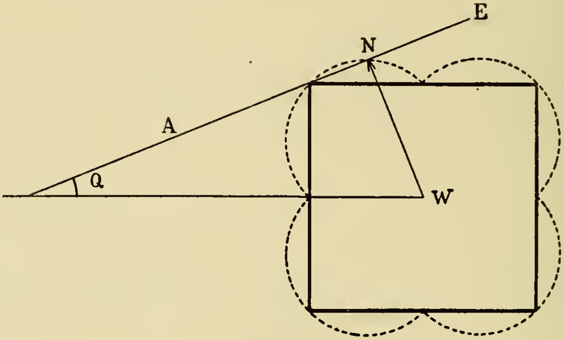

Fig. 2.

B. Yet the "equilibrium form" corresponding to it is a square. This is immediately to be seen by the aid of the construction mentioned in § 1. See fig. 2: W is **Wulff's** point: WN is proportional to k for this direction of the normal. If the straight line AE is constructed for all directions WN, they envelop conjointly the square drawn in fig. 2. 1)

C. The occurrence of "vicinal planes" involves in our scheme no deviation worth mentioning from the minimum of energy. For our k depends continuously on the orientation, and the vicinal planes are only exceedingly little rotated with respect to the planes of the form of equilibrium. Here the contrast with **Sohnke** and **Wulff's** supposition stands out very clearly.

D. Strictly speaking the form of equilibrium can do without vicinal

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1) By slight changes in the definition of the scheme another dependence of k on the orientation can be obtained, hence other equilibrium polygons.

planes only in particular cases. Indeed: if the number of molecules happens to be the square of a whole number, then the form of equilibrium is exactly a square. When however successively more molecules are added, they must adjust themselves somewhere against the square to get maximum saturation, which leads to vicinal planes. (In the formulae of § 1 this circumstance remains concealed, because there it is considered that the minimum must be determined with respect to infinitesimal changes of form. Here we realize, however, that it is a question of addition or displacement of a *whole number* of molecules).

§ 4. *Observations.* A. If a certain number of molecules is originally grouped in the form of two squares of different sizes, potential energy may be still diminished by the removal of a row of molecules from the small square, which are then laid against the large square. Decrease of energy also takes place when a rectangular grouping is changed into a square one. Until we take the temperature motion into consideration and consider the process of solution and sublimation, we can of course not ascertain whether in our molecular scheme these transitions will take place spontaneously. A somewhat trustworthy treatment of this question seems difficult to me, because for this the unevennesses of the edge are to be considered, i.e. those molecules which at a given moment are only bound singly or doubly, and not threefold.

B. It has been experimentally proved that for crystal powder e.g. of gypsum with a radius of about one micron the saturation concentration of the solution around it still appreciably depends on the radius. But for a radius of some microns this dependence already loses its significance with respect to disturbances of various nature. In virtue of this doubts will rise as to whether the changes discussed under A will appear spontaneously, and whether the actually occurring crystalline forms really agree with a minimum of surface energy ¹). Shortly ago VALETON ²) defined this view in the following way:

"For *microscopic* and *submicroscopic* crystals the surface energy has a measurable influence on the solubility. Such crystals can be in equilibrium with a solution only when their form corresponds with the minimum of surface energy. For *macroscopic* crystals this

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¹) A. BERTHOUD, Journ. de Chim. Phys. **10** (1912) p. 624. — G. FRIEDEL, Journ. de Chim. Phys. **11** (1913) p. 478.

²) l.c. p. 42. Compare there the fuller report of HULETT's experiments. Z. f. phys Chem **37** (1901) 385 with crystal powder of gypsym and barium sulphate.

influence is practically not existing. With regard to the crystalline form the equilibrium of these crystals is *indifferent*.

C. For our special model the whole still unused store of energy may be comprised in the one expression

$$\Sigma k \, \Delta s$$

with which the *surface* energy of the crystal corresponds in the three dimensional case; by the side of this there is left nothing that could answer to an energy of angular points or sides in the three-dimensional case, with which BRILLOUIN, VERNADSKY and PAWLOW[1]) work. Now however the model can be made more general by making e. g. moreover those isotropic attractive forces act between the molecules, with which LAPLACE, GAUSS, and VAN DER WAALS work with action spheres, which still contain many molecules[2]). It remains noteworthy that then actually special side and angular point energies appear, whose numerical value remains undetermined for the present[3]).

D. We have for the present not entered any further into the molecular interpretation of the cleavage directions. More recent views on this head are found in a study of P. P. EWALD[4]) on the structure of diamond. It would be interesting to ascertain whether one has also as a rule to do with vicinal planes of the ideal cleavage planes in the cleavage process. For the rest it would not be sufficient for a complete analysis of the cleavage process to ascertain what cleavage planes break a minimum of bindings; also the elastic deformation preceding the cleaving is in principle a factor to determine the orientation of the cleavage planes.

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[1]) See the citations § 1.

[2]) In this connection it may be mentioned that EINSTEIN Ann. d. Phys. **34** (1911) p. 165, comes to the conclusion from the law of EÖTVÖS that also in liquids an attraction may be assumed only between those neighbouring molecules that are in immediate contact.

[3]) In the current derivation of the fundamental equations of the capillarity the terms in question vanish, because in a certain point of the derivation the assumption is made use of that the curvature rays of the surface remain everywhere above a definite finite value. Cf. among others H. MINKOWSKI, Art. Kapillarität, Math. Encykl. V. 9, § 14, transition between equation (24) and (26). First of all this supposition does not hold for crystal sides and angles, but moreover also e.g. at the side in which three liquids are in contact with each other. BRILLOUIN, Ann Chim. et Phys. [7] 6 (1895) p. 540 has demonstrated that the structure of the groove which is formed when glass and other substances are scratched is chiefly determined by the side and angular point energy.

[4]) Ann. d. Phys. 44 (1914) p. 281.

Chemistry. — "*Action of sun-light on the cinnamic acids*". By Dr. A. W. K. de Jong.

The continued investigation has shown that the peculiar behaviour of cinnamic acid in the solid condition under the influence of sun-light must be attributed to the ease with which it passes into the metastable form. This metastable condition has been described first by O. Lehmann [1]) in 1885. Erlenmeyer Jr. has communicated a very lengthy investigation as to the existence of different forms of cinnamic acid in the Ber. D. Ch. G. and further in the Biochem. Zeitschr. He comes to the conclusion that of the normal cinnamic acid there exist four different modifications, namely α- and β-Storax cinnamic acid and α- and β-Hetero cinnamic acid. Cinnamic acid derived from plants consists of Storax cinnamic acid with but 0,5°/₀ of the Hetero-acid whilst synthetic cinnamic acid is a mixture of about equal parts of those acids. On heating their aqueous or dilute-alcoholic solutions the α-acids are converted into the β-acids. In Ber. 39 p. 1581, Ber. 42 p. 509 and Biochem. Zeitschr. 34 p. 355 some further conversions of the α- into the β-acids, and the reverse phenomenon, are communicated. The cinnamic acid used in my experiments was Storax cinnamic acid (probably derived from hydrolysed coca-acids; see previous communication) as it was deposited from alcohol in the well-formed, thick prismatic crystals of Storax cinnamic acid (in Ber. 42, p. 504 are found the photographs of the various forms). On repeatedly recrystallising from warm 95°/₀ alcohol which took place in the said experiments the α-Storax cinnamic acid is converted more or less into the β-acid. This mixture when illuminated always yielded α- and β-truxillic acid. The transformation into β-acid was much promoted, because after dissolving the cinnamic acid in alcohol the solution was made to evaporate rapidly by the shaking of the dish. For it was noticed that when an alcoholic solution of α-Storax cinnamic acid is poured on to a glass plate and the alcohol allowed to evaporate rapidly by blowing, only crystals of β-Storax cinnamic acid are formed. These crystals when illuminated gave only β-truxillic acid whereas the prismatic crystals of the α-Storax cinnamic acid gave only α-truxillic acid. The crushing of the crystals caused no change in the action of the light.

From the research is thus shown that α-Storax cinnamic acid gives α-truxillic acid when illuminated in the solid condition, whilst under the same circumstances, β-truxillic acid is formed from the β-Storax acid.

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[1]) Ber. **43**, 461 (1910); Graham Otto's Lehrbuch der Chemie Bd. I, 3e Abth., p. 57.

As to the connexion existing between α- and β-Storax cinnamic acid, nothing is as yet known with certainty.

The occurrence of differently crystallised forms of a substance may be generally attributed to polymerism, isomerism or polymorphism.

In the first case the one form is a polymeride of the other and thus possesses a double or multiple molecular weight, in the second case the molecular weight is the same but the structure of the molecule is different, whereas in the latter case where the difference exists only in the solid condition and disappears both in the liquid and the gas the arrangement of the molecules in the "Raumgitter" is accepted by some as the cause of the difference whilst others think that in this case also, a chemical difference between the solid forms is very probable [1]).

There has been no lack of efforts to determine the connexion between the different forms of the cinnamic acids.

According to ERLENMEYER Jr. [2]) there exist eight forms of cinnamic acid, namely four of the normal and four having as type *allo*cinnamic acid. The first four appertain to each other two and two and according to ERLENMEYER, these pairs should exhibit differences in the benzene nucleus.

Among the four *allo*acids we find mentioned, in addition to the three known acids, also a triclinic cinnamic acid, which he noticed a few times during his research, but of which the mode of formation is as yet quite obscure. ERLENMEYER sees in the different crystallised forms different chemical substances and endeavours to explain this case of isomerism.

I cannot find his effort, which he himself wishes to be looked upon as a *sketch*, a very happy one.

He reverts to the antiquated idea where the properties of a double bond are explained by the presence of a single bond and free affinities or as some express it, unoccupied affinity positions. Then, he assumes that on turning one of the two carbon tetrahedrons, between which the double bond exists, three different metastable forms can occur dependent on the different position of the groups on the one carbon tetrahedron in regard to that of the other one. In this manner he arrives at six different forms all capable of occurring in left- and right-handed modifications. Three thereof belong to the type of the *normal* cinnamic acid and three to that of the *allo*acid.

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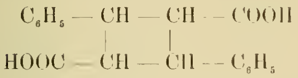
[1]) O. LEHMAN writes in "Die neue Welt der flüssigen Kristalle" 1911 p. 81: "daraus folgt aber lediglich, dass diese chemischen Methoden nicht ausreichend sind, jede Verschiedenheit der Moleküle zu entdecken und dass man polymorphe Modifikationen nicht ohne weiteres als chemisch identisch betrachten darf."

[2]) Biochem. Zeitschrift **35**, 149 (1911) and following.

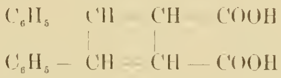
Opposed to this stands the view of Bilmann[1]) that the differences of the *allo*acids must be attributed to trimorphism whereas Riiber and Goldschmidt[2]) consider the occurrence of α- and β-Storax cinnamic acid as a typical case of dimorphism.

The changes which α- and β-Storax cinnamic acid suffer in sunlight afford us a view on the difference existing between these acids in the solid condition. The polymerisation products of these acids are, as we noticed, α- and β-truxillic acid to which are attributed the following formulae as being the most likely:

α-truxillic acid



β-truxillic acid



As to the position of the groups with regard to the plane of the 4-ring not much is known; in the case of β-truxillic acid the probability is that the COOH groups are found at the same side.

From these structural formulae it is plainly perceptible that one molecule of these truxillic acids is generated from two molecules of cinnamic acid and that the different manner in which the combination takes place gives rise to the occurrence of two truxillic acids.

Hence it must be assumed that there exists between α- and β-truxillic acid such a difference that the first, by the action of light, renders possible only a bond such as occurs in α-truxillic acid, whereas the β-Storax cinnamic acid must be such that only the binding as present in β-truxillic acid can take place exclusively.

A different placing of the groups in the molecule in regard to each other, which Erlenmeyer suggests to explain the difference between α- and β- cinnamic acid cannot avail us as even then for each formula the linking of two molecules can always take place in such a manner that both α- and β-truxillic acid can form.

If, however, we assume that the position of the molecules in the crystals is different for the two acids, a different bond due to the action of light might be coupled with this. The different behaviour of the acids might then be looked for in a different arrangement of the molecules in the "Raumgitter".

The following hypothesis may also be proposed. As is well known[3]), most probably all organic acids dissolved in hydroxyl-free solvents possess double molecules. Hence there is a great probability that in

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[1]) Ber. **42**, 184 (1909). Ber. **43**, 569 (1910).

[2]) Ber. **43**. 461 (1910).

[3]) Van 't Hoff, Vorlesungen über theoretische und physikalische Chemie, zweites Heft, pg. 52.

the solid condition at least double molecules occur The difference between α- and β-cinnamic acid might then have its origin in the manner in which the single molecules are placed in the double molecule.

The difference between these two assumptions consists in this that the first admits of a difference in the solid condition only, whereas the second renders possible a difference for the solution also.

A further investigation will have to decide which representation is in harmony with the facts. I hope to revert to this in detail, shortly.

Physics. — "*Some Remarks on the Osmotic Pressure*". By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 29, 1915).

With much interest I read Prof. EHRENFEST's paper [in the Proceedings of this Academy (April 1915)] on the kinetic interpretation of the osmotic pressure.

However, I can concur neither with the deeper ground of his interesting considerations, nor with the "Remarks" that are added to them, which in some respect may be considered as resulting from the foregoing considerations.

Prof. EHRENFEST knows that I feel a special interest in the osmotic pressure and its correct interpretation, so that he will no doubt excuse me if I once more return to it.

I will therefore briefly summarize my objections, already set forth in different papers[1]), in a number of Theses.

THESIS I. The results of a kinetic theory must necessarily be in accordance with the established results of Thermodynamics.

If the results of the kinetic theory differ from those of Thermodynamics, the kinetic theory in question is not valid.

THESIS II. Through the equating of the molecular thermodynamic potentials of the water in the solution and of the pure water outside it [there exists namely only thermodynamic equilibrium between the "*water*" on either side of the membrane, as this is supposed to be permeable only to water] the thermodynamic theory leads to[2])

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[1]) See particularly: Sechs Vorträge (1906), p. 17—36, and These Proc. of June 1906, p. 53 et seq. Also Zeitschr. f. physik. Ch. **64**, p. 629 et seq. (1908).

[2]) I gave this simple derivation already in 1894 (Zeitschr. f. physik. Ch. **15**, p, 463 et seq).

$$\mu\,(x, p) = \mu\,(0, p_0),$$

when $\mu(x, p)$ is the molecular potential of the water in the solution (in which x is the molecular concentration of the dissolved substance, p the pressure of equilibrium), and $\mu(0, p_0)$ that of the pure water (in which the concentration of the dissolved substance is 0, the pressure of equilibrium p_0).

Now:

$$\left.\begin{array}{l} \mu(x, p) = f(T) + pv_x + \alpha x^2 + RT\,log\,(1-x) \\ \mu(o, p_0) = f(T) + p_0 v_0 \end{array}\right\},$$

and hence — as in dilute solutions v_x (the molecular volume of the water in the solution) can be equated to v_0 [1]) (the molecular volume of the pure water):

$$(p-p_0)v_0 = -\,RT\,log\,(1-x) + \alpha x^2,$$

or

$$\pi = p - p_0 = \frac{RT}{v_0}\,[-\,log\,(1-x) + \alpha x^2), \quad . \quad . \quad . \quad . \quad (1)$$

when π represents the "osmotic" pressure. In this α is the so-called "influencing" coefficient in consequence of the *interaction* of the molecules of the solvent and those of the dissolved substance. It is known that α is represented by the expression [2]):

$$\alpha = \frac{a_1 b_2{}^2 + a_2 b_1{}^2 - 2a_{12} b_1 b_2}{b_1 b^2},$$

in which the numerator passes into $(b_2\sqrt{a_1} - b_1\sqrt{a_2})^2$, when $a_{12} = \sqrt{a_1 a_2}$ can be put.

Thesis III. All kinetic theories, therefore, which for *non-diluted* solutions lead to expressions which remind directly of the equation of state of gases and liquids (e.g. with $v-b$ etc., and *without logarithmic* member) must be rejected. (Therefore the theories of Wind, Stern and others).

Thesis IV. For very diluted solutions (I) passes into

$$\pi = \frac{RT}{v_0}\,x,$$

Van 't Hoff's well-known equation. Yet it is easy to see that the deviations for non-diluted solutions are much slighter than those for

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[1]) v_x and v_0 only differing in a quantity of the order x^2, the difference can always be thought included in the term αx^2.

[2]) See among others Z. f. ph. Ch. **63** (1908), p. 227—228 (Die Schmelz- und Erstarrungskurven etc.).

the corresponding non-ideal gas state. (Cf. Sechs Vorträge p. 29—30, and the cited paper in These Proc., p. 57 et seq.).

Already from this we are led to surmise that the so-called osmotic pressure has an *entirely different ground* from what the analogy of the behaviour of the dissolved substance to that of the same substance in the corresponding gas state would lead us to suspect, and that there is here no close *relation*, only *analogy*. Particularly the occurrence of the term $-\log(1-x)$ (which only passes into x at $x=0$) in the expression (1) for the osmotic pressure should have admonished to caution. This term continues to exist in the most dilute solutions.

Thesis V. If actually the osmotic pressure was caused by the pressure of the *dissolved substance* (the old theory revived!), as Ehrenfest also assumes again, the pressure of the "sugar" molecules against the semi-permeable membrane would cause the *reverse* of what is actually observed. Then there would namely no water pass from the side of the pure solvent through the membrane into the solution, and give rise to the hydrostatic counterpressure $=\pi$ in the ascension tube of the osmometer — but this water would on the contrary be checked, since the pressure in the *solution* would be greater from the outset than in the pure water!

Thesis VI. In reality the osmotic pressure is caused by the water, penetrating through the semi-permeable membrane *into* the sugar solution, which gives rise to a hydrostatic pressure, which prevents the *further intrusion* of the water. *This* excess of pressure $\pi = p - p_0$ is the so-called "osmotic pressure" of the solution.

Thesis VII. Every theory, which would try to interpret the occurrence of the osmotic pressure *kinetically*, should be based on the *diffusion* of the water molecules on both sides of the membrane. Quite generally one can assume then two solutions of different concentration x_1 and x_2 on both sides of the membrane. If one confines oneself to a solution of the concentration x and pure water, one has what follows: In the unity of time there diffuse a certain number of water molecules of the pure water towards the solution, and another number from the solution towards the water. But on account of the solution containing less water than the pure water, there will go — parallel with the prevailing diffusion pressure — more particles of the water to the solution than the reverse.

In ordinary circumstances the dissolved substance (sugar) would also diffuse, but this diffusion is now arrested by the semi-permeable membrane, so that the diffusion is only brought about by the water.

THESIS VIII. Apart from what actually takes place on or in the semi-permeable membrane — hence when simply an imaginary membrane is taken, which does allow one sort of molecules to pass through, but not the other kind — it is easy to determine the just mentioned numbers of diffusing molecules according to BOLTZMANN's method (in agreement with the kinetic interpretation of the thermodynamic potential). (See among others Sechs Vorträge p. 20—21). Then the *required logarithmic member* arises of its own accord.

THESIS IX. If there is *interaction* between the two kinds of molecules, another term αx^2 simply arises *by the side* of $-log(1-x)$. If however $\alpha = 0$, as is the case for so-called ideal solutions (this is also the "imaginary" case to which E. alludes in his Remarks) *all the above remarks continue to be valid* unimpaired — which is in contradiction with E.'s view in his Remarks. The diffusion, the *intrusion* of the water till the required excess of pressure has been reached — everything remains the same.

E.'s opinion that the rise of the water in the osmometer can only take place through the three factors named by him, of which the interaction of the two kinds of molecules is one, must therefore be rejected with the greatest decision.

To what absurdities this conception would lead appears from this that when as dissolved substance a substance is taken with a very high critical temperature, and when this substance yet forms an "ideal" solution with water, *without interaction* ($\alpha = 0$), as is the case with many organic substances (also sugar), the partial vapour pressure of that dissolved substance (e. g. sugar) is vanishingly small with respect to that of water. So there does not take place any "evaporation" at all. According to E. the vapour pressure of the sugar would become equal to the osmotic pressure — which for a normal solution amounts to no less than 24 atmospheres! In reality the partial pressure of the dissolved sugar will perhaps amount to a billionth m.m. in the imaginary case mentioned by E. (sugar is about in that case).

THESIS X. It appears in my opinion sufficiently from the above that the kinetic interpretation of the osmotic pressure — which is always reappearing again in new forms — is moving and has moved in a wrong direction, and should again be founded on the simple *diffusion phenomenon*, as was indicated by me already more than 20 years ago, and was further worked out by me ten years ago (Sechs Vorträge l. c.).

OBSERVATIONS. Though I wish a long otium cum dignitate to all incorrect kinetic theories, I would by no means be considered a personal foe to the osmotic pressure — the significance of which for the theory of the dilute solutions was set forth by van 't Hoff in the ingenious way characteristic of him.

My earlier and later opposition was only directed against two later introduced abuses (with which Prof. Ehrenfest of course entirely agrees), namely:

1. Against the extension of the idea (*thought as reality*) to *isolated homogeneous* solutions (i. e. when no semipermeable membrane is thought to exist), in which of course no real pressure of 24 atms. for every dissolved gr. mol. occurs.

2. Against the *practical application* of the idea to *non-diluted* solutions, which application I thought undesirable in view of the inaccuracies which then occur and which are not to be ascertained — which can give rise to very erroneous conclusions (and have indeed done so!). Then the general theory of the thermodynamic potential (or free energy) is the obvious and sure way.

The *existence* of the osmotic pressure has never been called in question by me. One does not give calculations and interpretations of something that does not exist! But it exists only in a solution that is *separated* by a *semi permeable membrane* from the pure solvent (or from a solution of slighter concentration) — and manifests itself then through a *diffusion pressure from* the pure solvent *towards* the solution (so just the *reverse* of what the kinetic interpreters imagine).

That the above described osmotic diffusion pressure for exceedingly diluted solutions has a value *as if* the sugar molecules in the sugar solution in the corresponding ideal gas state exert this pressure, is a mere coincidence, only owing to the term — log $(1-x)$ of the so-called Gibbs' paradox; which term, as we know, is kinetically in connection with the diffusion tendency of the components of the mixture.

Only a kinetic theory of the osmotic pressure which starts from the diffusion phenomenon, arrives at the term in question (Sechs Vorträge, S. 20—21); all other theories, which imagine the pressure *in* the sugar solution, only come to *non-logarithmical* expressions with simply x (resp. c, $^1/_v$, $^1/_{v-b}$, etc.), which owing to their derivation of course remind of the ordinary gas pressure, (law of Boyle, or for non-diluted solutions the formula of van der Waals), but which are to be called inaccurate in the most absolute sense.

Fontanivent sur Clarens, April, 1915.

Appendix during the correction.

In a correspondence on this subject with Prof. Ehrenfest (Prof. Lorentz was namely so kind as to send him my article) it has become still clearer to me to what E.'s result, which in my opinion is erroneous, is to be ascribed.

In his considerations he namely assumes (this had not appeared to me from his paper) that the molecules of the substances do not exert any action on each other, i.e. that all the forces and actions, also those in the *collisions,* are neglected. (that the attractive forces are neglected, does not affect the correctness or incorrectness of the calculations). Prof. E. expresses this by saying: The water is quite unaffected by the sugar present, and vice versa.

This is the very core of the problem. When the water is not affected by the sugar present, then $\mu(x) = \mu(0)$, and no longer $\mu(x) = \mu(0) + RT \log(1-x)$. In other words: E. works with substances for which Gibbs's paradox has disappeared, and which have therefore become entirely free from thermodynamics. Hence he could not possibly find the expression $-\log(1-x)$ corresponding to it.

Such extra-stellary, thermodynamic-free substances have of course lost all diffusion tendency — which just causes the phenomenon of the osmotic pressure. For if the water is quite unaffected by the sugar present, there exists no impetus any longer for the water to be displaced, so that the disturbed equilibrium (between concentrations x and 0, or x_1 and x_2) is reestablished.

As so many before him, Prof. E. has in my opinion allowed himself be carried away (see e.g. p. 1241 of his paper) by the striking *analogy,* which was already mentioned in Thesis IV above. That we can only speak of analogy here, is no doubt clear after all that was remarked above. The analogy pressure of E. and others acts namely precisely in the *opposite sense* from the real osmotic pressure. In the limiting case it is not x that is found instead of $-\log(1-x)$, but $-x$! This mistaken opposite pressure is of course the consequence of the perfect freedom of the sugar molecules assumed by E. and others, which molecules now begin to exert a pressure of 24 atms. per gr. mol. on the semi-permeable wall — a pressure which of course is not exerted for ordinary solutions as we know them on earth. And where E. speaks in his paper of the kinetic interpretation of *the* osmotic pressure, it seems to me that he too should work with substances as they exist on earth, and not with such where Thermodynamics is eliminated.

For through the elimination of the actions between the molecules just the "according-to-probability unordered kinetic" element (the kinetic equivalent of Thermodynamics), which is brought about by the mutual collisions has been done away with, and only the "roughly kinetic" element remains, which then, moreover, leads to to the opposite result.

In conclusion I can adduce no better evidence of the validity of my considerations than the following.

For a *gas mixture* (even if necessary of ideal gases) of e.g. O_2 in N_2 — separated from pure N_2 by a semi-permeable membrane, which does not let through O_2 — the osmotic pressure would just as for liquid mixtures, be represented by the above equation (1). Here too the *gas mixture* would rise in an ascension tube (in consequence of the diffusion tendency of the pure nitrogen) till the necessary *counter pressure* had been reached, which then prevented the further intrusion of the nitrogen. But here too "the osmotic pressure" starts from the pure nitrogen outside the mixture, and not from the O_2 *in* the mixture. That there is here no question of a separate excess of pressure of the O_2, appears from this that at the beginning of the experiment the gas pressures on the two sides of the membrane are perfectly the same, (both = 1 atm.), the sum of the partial pressures of the O_2 + that of the N_2 of course being precisely equal to the pressure of the N_2 on the other side of the membrane. The *excess of pressure* does not make its appearance until *after* the appearance of the *diffusion* — and arises, as has been said, from the *pure nitrogen*.

These observations, which in my opinion are conclusive for this problem, have already been made and elaborated in my Lehrbuch der Mathematischen Chemie (1901), p. 30—31.

4 May. 1915.

Anatomy. — *"On the metamerological signification of the cranio-vertebral interval."* By Dr. J. A. J. Barge. (Communicated by Prof. L. Bolk).

(Communicated in the meeting of May 29, 1915).

In the so exceedingly extensive literature concerning the history of the development of vertebral column and cranium two problems chiefly draw continually the attention: the so-called resegmentation of the vertebral column (Neugliederung der Wirbelsäule) and the metamery of the cranium.

Both problems have been studied circumstantially, and the bibliography of both can boast of classical essays from the best days of morphology. The more remarkable it must be called, that the two fundamental views, that served as a guide to the numerous investigators in this department, and, which, at present at least, in principle, are pretty well generally admitted, have constantly been studied separately, and never yet in their mutual relation.

It is especially to this fact that I wish to fix the attention in this communication, in order to show in this way at the same time, how for this reason the signification of important carefully stated facts has remained unobserved.

Since Goethe and Oken expressed in the "Vertebral theory of the cranium" for the first time the idea, that the bones of the cranium, at least those of mammals, could be grouped into a number of segments, which show some similarity with vertebrae, the doctrine concerning the metamery of the cranium has passed through a long period of development. It is superfluous to describe here this historical development already for this reason that most of the manuals give a summary of this idea more detailed than seems desirable in the short compass of this communication.

It may suffice to point out, that the question that was put when this problem was investigated, has constantly varied, and that the phases of development of this idea can probably be best characterized by the following formulations of the problem.

1. Are there evidences that prove, that the cranium has been constructed of a number of segments corresponding to vertebrae?

2. Is the cranium, or at least part of it, formed in its embryonal development in a similar way and of equivalent material as the vertebral column?

3. Are there indications, that make it probable, that at least part

of the cranium was segmented in a previous period of the phylogenetical development?

In this last form the problem is at the present moment still being discussed, though the arguments that are now brought forward to enable us to come to an affirmative answer of this question, are of a character quite different from those which GEGENBAUR, who was the first to formulate it in this way, developed for it. At present the state of the problem is indeed so, that a positive answer of the question is no longer contested by any of the investigators, and they only do not agree in stating how great the part of the cranium is, over which the mentioned segmentation extends.

In connection with the much earlier ontogenetical investigations of RATHKE, GEGENBAUR distinguished in the cranium 2 parts, a frontal not segmented part and a posterior segmented part. The two parts are designated as the vertebral part and the praevertebral one.

According to GEGENBAUR, who formed his theory from the phenomena of the Selachier-cranium, the vertebral part would form by far the greater part of the cranium; only the region in which the N. opticus and the N. olfactorius pierce through the skull, would belong to the praevertebral region. The vertebral part constructed by fusion of about 9 cranial vertebrae would be primary, and it is only after concrescence of these elements, that the praevertebral part would have been developed by excrescence in a frontal direction of the cartilageous part formed in the above mentioned manner, under adaptation to the olfactory groove and the optical organ.

We do not find with GEGENBAUR a primitive part of the cranium, — principally to be distinguished from the other segmented part of the cranium —, which ought to be maintained as real primordial cranium contrary to the vertebral column. The body of vertebrates consisted of a number of equivalent segments. The frontal part of these has fused for the formation of the cranium, the posterior part forms the vertebral column. Secondarily, by excrescence, an unsegmented part has still been added to the segmented part of the cranium.

STÖHR added to this the opinion that the number of segments used for the construction of the cranium is not constant, and continually increases in the series of vertebrates. The craniovertebral interval shifts consequently more and more in a caudal direction. Other investigators could confirm the correctness of this view. SAGEMEHL succeeded in showing, that the cranium of higher developed pisces and of amniotes has increased in a caudal direction with 3 vertebrae. This cranium would consequently be the Selachiercranium augmented with 3 vertebrae. With regard to the formation of the Selachiercranium Sagemehl is of the same opinion as Gegenbauer. It would namely have taken existence from metameres. It is however of great importance to remark here, that, according to Sagemehl, these metameres had not yet the character of vertebrae, and that consequently the fusion-progress of these metameres in order to form the Selachier-cranium is not equivalent to the addition of the 3 vertebrae to the Selachier-cranium, which we observe with higher pisces and amniotes.

Sagemehl calls the Selachier cranium protometamere, the cranium enlarged by the addition of 3 vertebrae auximetamere.

Van Wijhe showed that with Selachiers 9 segments (primordial vertebrae, somites) can be distinguished at the dorsal head mesoderm, which correspond entirely with and are equivalent to those of the trunkregion. Gegenbauer's view, that the head would be nothing else but a transformed part of the trunk, was certainly supported by this discovery. Van Wijhe's discoveries were however not of such great signification for the skeleton, as he could show, it is true, that sclerotomes originated from the primordial vertebrae, but it appeared likewise from his investigations, that this segmentation of the primitive formation of the skeleton was immediately again suppressed.

The investigations of Froriep are of great importance for the problem of the cranium metamery.

Froriep likewise distinguishes 2 parts of the cranium, one formerly segmented part and one unsegmented part. In this respect he consequently agrees with Gegenbaur. Not so however with regard to the place of the boundary-line between the two regions. According to Gegenbaur this boundary-line would be situated far frontally, and the unsegmented part would be restricted to the part of the cranium, formed secondarily in the neighbourhood of the olfactory groove and the optical organ. Froriep however admits as boundary-line between the two regions the spot, where the N. Vagus pierces through the base of the skull. The earlier segmented part is thus, according to Froriep, but very small and confines itself only to the occipital region. Froriep showed now that with cow and hen this occipital part behaves ontogenetically as the frontal part of the vertebral column, and consequently shows likewise the design of primordial vertrebrae, vertebral arches and nerves, whilst in the region lying before the vagus nothing is perceptible that could be compared to the segmentation in the spinal trunk-region. In accordance herewith Froriep distinguishes in the cranium a spinal and a praespinal part.

What Froriep could show with regard to the N. hypoglossus is likewise of importance. He found namely in the course of this cerebral nerve, always conceived as purely motorical, spinalganglions, and so it was obvious that this nerve would be nothing else than the complex of the nerves belonging to the spinal cranium-region.

This view of Froriep's concerning the spinal character of the occipital region of the cranium finds in reality no longer contradiction. From all sides confirmations of his discoveries have come also with other species of animals. Everywhere it has been possible to indicate that embryonally the occipital part of the cranium shows great similarity with the vertebral column. The part of the problem regarding the metamery of the cranium has ceased to be a problem. At best there is only question of the number of metameres, that can be distinguished in the spinal part. The question after the origin and the eventual segmentation of the part in front of the N. vagus still remains. On this point the views are still divided. For us it has for this moment no interest.

What is interesting for us, is the fact, that the most caudal part of the cranium, i. e. the occipital part, shows distinct proofs of a previous segmentation which corresponds entirely with that of the region of the vertebral column. It is of importance to emphasize here already that the above mentioned segmentation is a segmentation of metameres or primordial vertebrae with myotome and sclerotome, not a segmentation in vertebrae.

The second problem mentioned in the beginning is the so-called re-segmentation of the vertebral column (Neugliederung der Wirbelsäule). The quintessence of this problem is the question, whether the intervertebral joints with a full-grown individual are the same as the intervals found embryonally between the primordial vertebrae. In other terms, whether the intersegmental and the intervertebral intervals are the same, and the cartilageous and the osseous vertebrate originate from the sclerotome of one primordial vertebra (metamere.)

Remak already answered this in the negative. Van Baer admitted still that the embryonal primordial vertebrae correspond with the permanent later vertebrae. Remak showed that in the primordial vertebrae the intervertebral musculature originated, and at the same time the blastema, from which the permanent vertebrae take their origin. According to him the permanent vertebra is formed in this way: The primitive vertebral bodies (sclerotomes they are called at present) originating in the primordial vertebrae (metameres) fuse together, and, at the same time, new intervals come into existence for the secondary (permanent) vertebrae in the middle between the original intervals. A secondary (permanent) vertebra consists consequently of the caudal and cranial halves of two adjoining primitive vertebrae fused together. According to REMAK there was in the development of the vertebral column one moment, in which the blastema, from which the vertebrae will originate, is entirely unsegmented. For a considerable time REMAK's theory about the "re-segmentation of the vertebral column" has not been recognised by many anatomists. Recent investigations however have done justice to him. Especially the investigations of v. EBNER have turned the scale here, and in the first place the discovery of the so-called intervertebral-fissure.

On the frontal section through an embryo (cf. fig. 1) one sees on either side of the chorda the bodies of the primordial vertebrae.

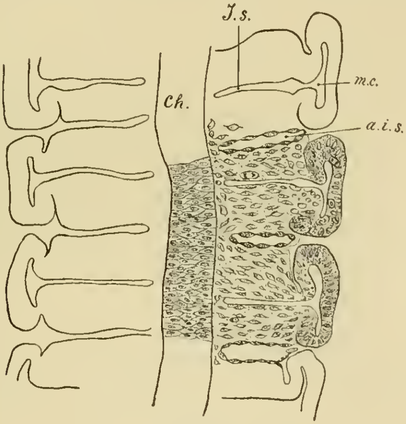

Fig. 1.
Frontal section through an embryo of Tropidonotus natrix (after v. EBNER).
ch = chorda dorsalis; *I.s.* = intervertebral fissure;
a.i.s. = arteria interprotovertebralis; *m.c.* = myocoel.

At a certain stage of the development one sees occur in it the differentiation that causes the formation of the products that are derived from it.

The primordial vertebra, in which the primordial vertebralcavity is situated, shows a medial and a lateral lamella. The lateral lamella is the cutislamella, from which the derm with adnexa takes its origin; the medial one is the muscle-lamella from which the musculature develops itself. Moreover originates from this medial lamella of the primordial segment the blastema (mesenchym) from which the skeleton will form itself, and with Amniotes a rather considerable part of it is used. This mesenchym accumulates between the chorda and the medial lamella of the primordial vertebra, so that the primordial vertebrae are pushed in a lateral direction from the chorda. The intervals between the different primordial segments are distinctly indicated by the transversal course of the intersegmental- or interprotovertebral vessels.

What is now v. Ebner's discovery?

This that from the lumen of the primordial vertebra a narrow fissure runs in a medial direction to quite near the chorda. This fissure, called by v. Ebner intervertebral-fissure divides each segment into a clearly defined anterior and a posterior (cranial and caudal) half. With Tropidonotus natrix (upon which v. Ebner made his first investigations) this fissure is most distinct in the neighbourhood of the spinalganglions. More dorsally it disappears; ventrally it can easily be followed as far as the region of the chorda. As was said this fissure was first observed by v. Ebner in Tropidonotus natrix and afterwards it was shown by the same investigator in hens, mice and bats. This discovery was soon confirmed by other investigators with other animals and also with man. The existence of the fissure is no longer contested. Van Ebner could also already show that the intervertebral fissures agreed completely with the joints of the later permanent vertebrae. According to him they disappear in the end in the dense mass of tissue, in which afterwards the articular cavities between the vertebrae occur.

The permanent vertebrae come now into existence each in the region that is limited between 2 intervertebral-fissures. Consequently each vertebra belongs to two segments and is constructed of the caudal half of a discretional segment and the cranial half of the next following one. This agrees consequently entirely with Remak's assertion cited above, with this difference however, that the intervertebral-fissures that indicate the intervals between the permanent vertebrae, can already be observed when the intervals between the segments have not yet disappeared, so that the unsegmented blastema, which, according to Remak, should exist for some time, does in reality not occur.

After this explanation it is obvious what must be understood by re-segmentation of the vertebral column. The segmentation that is expressed by the permanent vertebrae, is different from that which is given by the primordial vertebrae; a new and another segmentation has taken place.

How do now the fused caudal and cranial segments behave in the forming of the vertebra? This depends upon the species of animal in question. With some animals we see that the originally caudal half and the originally cranial half have an equal part in the forming of the vertebra. With most higher Amniotes and likewise with man we see however that, at least as regards the vertebral arch, the caudal segmenthalf becomes predominant, whilst the cranial one, partly because the spinal-nerve and the spinalganglion belonging to it always lie in it, gets more into the background. It is not my intention to enter into further particulars about the share that the two segmenthalves have in the forming of the vertebra. The statements of the divers investigators diverge, which must be partly attributed to the certainly very great difficulties of the investigation, partly to the fact mentioned already above, that the relations with the different species of animals are not the same in this respect. I will only emphatically point out, that in what way the segmenthalves may behave in definite cases in the forming of the vertebra, they naturally possess a complete potency, in such a measure that from each of the two halves under special circumstances a complete vertebra can be formed. A proof of this are the so called embolomere or rhachitome vertebrae, which occur frequently with Anamnia, but are likewise found with Amniotes, which was first shown by Goethe with Lacerta viridis, afterwards by Männer with Angius and by Schauinsland with Sphenodon, Castor fiber and Cetaceae.

After this very short explanation of what is essential in the metamery of the cranium and the re-segmentation of the vertebral column we shall examine, to what consequence these two dogmas lead in the ontogeny of the cranio-vertebral region.

If the doctrine of the metamery of the cranium according to Froriep and the later investigators is correct, and for the present there is no reason to doubt of it, then we must represent to ourselves the region of the spinal part of the cranium (the praespinal part can, as falling beyond the cranio-vertebral region, remain out of consideration) and of the vertebral column in a very young stage of embryonal development, as an uninterrupted row of anatomically (not morphologically) equivalent scleromeres, as is represented schematically in Fig. 2.

Axially the chorda(*ch.*) extends through these scleromeres, the cranial and caudal boundaries of which are indicated by the arteriae intersegmentales (*a.i.s.* interprotovertebrales). Laterally from the scleromeres one sees the myotome belonging to the connected segment

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with in it the myocoel (*m.c.*) which is continued in a medial direction in the intervertebral fissure (*f.i.v.*) of VON EBNER to quite near the chorda. The scleromere is divided, as was described above, by this intervertebral fissure into two halves, a cranial half and a caudal half. In the cranial half we see the N. spinalis (*n.s.*), the caudal half is represented striped in conformity with the fact that it is as a rule considerably stronger tinged. Somewhere in this row of scleromeres, which encloses consequently the spinal part of the skull and the immediately adjoining part of the vertebral column at some period or other of the development the cranio-vertebral interval will manifest itself.

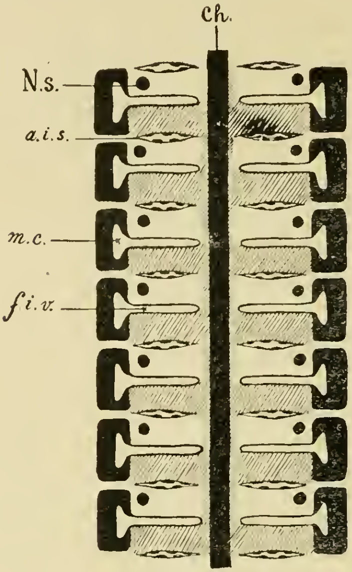

Fig. 2.

ch. = chorda dorsalis; *n.s.* = nervus spinalis; *a.i.s.* = arteria interprotovertebralis; *m.c.* = myocoel; *f.i.v.* = intervertebral fissure.

What is interesting for us at the occurrence of this interval is not the question, where it will present itself, in this sense, as if it were of importance for us, how many scleromeres will join the cranium. This problem remains here entirely out of consideration. What we want to know of the interval is, whether it coincides with the interval between the scleromeres or with the intervertebral fissure of VON EBNER. Though, as far as I know, the question as such has never been put, it can however be answered with certainty from the literature. It has indeed always been found [1]) (c.f. the well known investigations of FRORIEP, WEISS, GAUPP, BARDEEN and others) and my own investigations on sheep-embryones confirm this in every respect, that the craniovertebral interval coincides with a segment or scleromere interval, and that the most caudal part of the cranium is always formed by a caudal segment-half. This can be most easily ascertained by paying attention to the nerves. The nerve running in the cranial half of the scleromere, the caudal half of which forms the most caudal part of the cranium, forms with the two nerves of the two scleromeres lying in a cranial direction from it, the roots of the N. hypoglossus; the nerve in the cranial half of the next following segment in caudal direction, is the free 1st cervical-nerve running outside the cranium (*c.f.* Fig. 3). The caudal half of the last segment belonging to the cranium is always strongly developed and by its intensive colour distinctly to be distinguished from the weakly tinged cranial half of the in caudal direction next following segment belonging to the region of the vertebral column, in which cranial half always the first cervical-nerve is found.

If now we pay careful attention to the fact ascertained by observation, that the cranio-vertebral interval is an intersegmental one, it appears immediately that necessarily, in consequence of the process of the resegmentation of the vertebral column, one segment-half remains between the first cervical vertebra and the occipital bone. An illustration of this offers fig. 3.

We see in it as in Fig. 2 a representation of a row of segments, in which axially the chorda extends itself, and which in a lateral direction are limited by the myotomes somewhat further differentiated in comparison with Fig. 2, from which the myocoel has disappeared. Here the caudal half is likewise striped; in the cranial segment-half the spinal-nerve (*n.s.*) is indicated whilst the intersegmental vessels (*a.i.s.*) limit the segments. The line *A.B.* represents the craniovertebral interval situated intersegmentally.

In the process of the resegmentation described above, the vertebrae are formed from the segments in such a way that the caudal half of each segment fuses with the cranial half of the next following segment in a caudal direction. So e.g. the caudal half of the fourth segment (*S. IV*) will fuse with the cranial half of the fifth segment

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[1]) These statements only regard Amniotes.

(*S. V*), the caudal half of *S. III* with the cranial half of *S. IV*, the caudal half of *S. II* with the cranial half of *S. III*, and the caudal half of *S. I* with the cranial half of *S. II*, and in this way

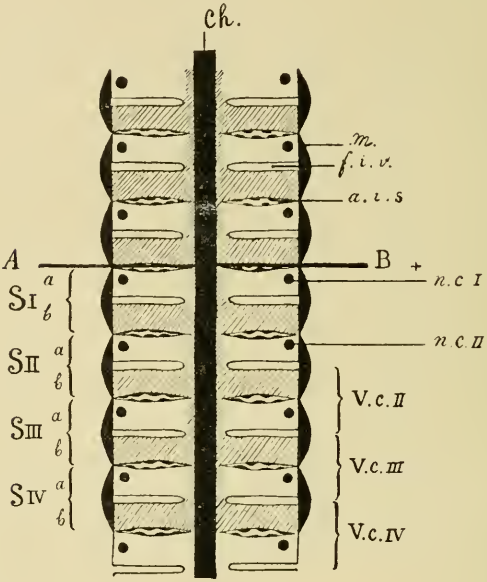

Fig 3.

ch. = chorda dorsalis; *m.* = myotome; *f.i.v* = intervertebral fissure; *a.i.s.* = arteria interprotovertebralis; *A.B.* = cranio-vertebral interval; *n.c. I* = 1st cervical nerve; *n.c. II* = 2nd cervical nerve.

resp. the 4th, 3rd, 2nd and 1st cervical vertebrae will be formed.

If we call the cranial half *a*, the caudal one *b*, we can say in general that the n^{th} vertebra is formed by the fusion of $Sn.b$ with $S(n+1)\,a$; the n^{th} vertebra has consequently for metamere formula $Sn\,b + S(n+1)\,a$. From the first segment remains now the cranial half $S.Ia$, for it remains separated from the caudal half of the segment lying cranially from it by the cranio-vertebral interval.

The conclusion from this demonstration that has issued from no other premises than from the law of the resegmentation of the vertebral column and from the fact, that the cranio-vertebral interval is an intersegmental one, must consequently be, that between the cranium and the vertebral column a free segmenthalf is found, that has certainly an osteogenetical, perhaps even a hemispondylogenetical potency.

It is now the question whether this potency is activated, and if so, what phenomena are the results of this activication. Though it is not the intention of this communication to give a categorical answer to the question submitted here, I will however indicate already the direction in which, according to my opinion, the answer must be looked for, and fix the attention to the fact that in the cranio-vertebral region a great many phenomena present themselves, the morphological signification of which has as yet not by far been defined in the same way by all investigators. I have here especially an eye to the variations of the atlas in the region of the sulcus arteriae vertebralis, to the different phenomena on which in fact the Pro-atlashypothesis of ALBRECHT is founded, to the concrescentia atlanto-occipitalis and the manifestation of the occipital vertebra.

I think, that all these phenomena can be brought under one point of view, namely the existence of the above mentioned segmenthalf *Ia*.

A further investigation into this question will form the subject of a following communication.

Anatomy. — "*The genetical signification of some atlas-variations*". By Dr. J. A. J. BARGE. (Communicated by Prof. L. BOLK).

In the previous communication, "On the metamerological signification of the cranio-vertebral interval" I have fixed the attention to the fact, verified also by investigation, that between the atlas and the caudal boundary of the cranium, in consequence of the intersegmental position of the craniovertebral interval and of the process of the re-segmentation of the vertebral column, necessarily a free half-segment must exist, indicated for the sake of brevity as the semi-segment I*a*.

At the end of this communication the question was raised, to what phenomena the activation of the osteogenetic potency, doubtlessly existing in this semi-segment, would give rise, and the provisional answer to this question was, that, in my opinion, it would probably be possible to trace a relation between the established existence of the semi-segment and a series of phenomena in the cranio-vertebral region, namely the atlas-variations, the Pro-atlas of **Albrecht**, the concrescentia atlanto-occipitalis and the manifestation of the occipital vertebra.

In this second communication I intend to trace the signification of the existence of the semi-segment for the morphological explanation of the atlas-variations.

The fact that I wish to discuss in the first place these atlas-variations finds its foundation among others in the circumstance that it is just the study of these variations that has been the nearest inducement to state the existence of the semi-segment I*a* described in the previous communication.

In the description of the human atlas it is always indicated, that the most lateral part of the arcus posterior, namely that part that borders immediately on the massa lateralis is characterized by a notch. This notch, called sulcus arteriae vertebralis, is caused by the arteria vertebralis, which after having passed through the foramen transversarium atlantis bends behind the massae laterales and crosses the arcus posterior together with the first cervical-nerve, before it pierces the membrana atlanto-occipitalis. The degree of development of this notch shows a great deal of variability. Now it is flat and shallow, now one sees that it has been transformed into a channel shut off from all sides, because an osseous bridge extends itself from the posterior rim of the massae laterale to the upper-rim of the arcus posterior, so that one must then speak of a canalis or foramen arteriae vertebralis. This latter condition occurs frequently, witness the fact, that nearly all text-books call the attention to it in their descriptions of the atlas.

The nomenclature, however, of this variation, both of the osseous bridge, mentioned above, and of the channel or foramen the cranial border of which is formed by the bridge, varies so very much, that it is almost as arbitrary to find out oneself a name for it, as to make a choice from the numerous existing names. In my opinion foramen atlantoideum posterius (**Bolk**) and foramen arcuale (**Gaupp**) are the simplest among the denominations of the above-mentioned foramen. I shall call the osseous bridge over this foramen ponticulus posterior.

Beside this variation of the human atlas a second is known, which occurs less frequently. It consists herein, that from the lateral side of the upper-rim of the massa lateralis an osseous bridge extends to the most lateral part of the upper-rim of the processus transversus atlantis. Here is consequently the arteria vertebralis [illegible] a bone, now together with the ramus anterior of the first cervical nerve, and in this way a short channel or ring-shaped opening is formed. To indicate this opening **Bolk** uses the name of foramen atlantoideum laterale, whilst **Gaupp** proposes to borrow the denomination that the veterinary surgeons (**Ellenberger** and **Baum**) give to its homologon, constantly occurring with many animals, the foramen alare. The osseous bridge that shuts off this foramen at the top I call ponticulus lateralis.

As I remarked already previously both variations are known in literature. **Le Double** [1]) indicates the frequency of the foramen atlant. posterior and the ponticulus lateralis as 11.7°/$_0$ that of the foramen atlantoideum and the ponticulus lateralis as 1.8°/$_0$.

In the collection of atlases of the Anatomical Laboratory in Amsterdam, I found among 3360 atlases 77 or 2.3°/$_0$ with foramen atlantoideum laterale and 355 or 10.6°/$_0$ with foramen atlantoideum posterius. The numbers resulting from the examination of this material, which is at least twice as large as the complete collective tables from which **Le Double** calculated his percentage do consequently not considerably deviate from the latter.

The simultaneous occurrence of these two variations at the same atlas has a.o. been described by **Bolk** [2]), who found a combination of a foramen atlantoideum laterale and a bilateral foramen atlantoideum posterius on the right side.

Le Double (l.c.s.) mentions likewise a case in which on the right side the two foramina with the ponticuli belonging to them were simultaneously present.

From the material that was at my disposal, I could select a series, in which all imaginable coincidences occur, as appears from the following summary:

1.	For. atl. lat.	bilateral	For. atl. post.	bilateral	with	2	specimens
2.	,, ,, ,,	,,	,, ,, ,,	to the left	,,	2	,,
3.	,, ,, ,,	,,	,, ,, ,,	,, ,, right	,,	1	,,
4.	,, ,, ,,	to the left	,, ,, ,,	bilateral	,,	3	,,
5.	,, ,, ,,	,, ,, ,,	,, ,, ,,	to the left	,,	4	,,
6.	,, ,, ,,	,, ,, ,,	,, ,, ,,	,, ,, right	,,	3	,,
7.	,, ,, ,,	,, ,, right	,, ,, ,,	bilateral	,,	6	,,
8.	,, ,, ,,	,, ,, ,,	,, ,, ,,	to the left	,,	3	,,
9.	,, ,, ,,	,, ,, ,,	,, ,, ,,	,, ,, right	,,	5	,,
10.	,, ,, ,,	missing	,, ,, ,,	lateral	,,	124	,,
11.	,, ,, ,,	,,	,, ,, ,,	to the left	,,	124	,,
12.	,, ,, ,,	,,	,, ,, ,,	,, ,, ,,	,,	107	,,

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[1]) **Le Double.** Les variations de la colonne vertébrale.

[2]) L. **Bolk.** De variaties in het grensgebied tusschen hoofd en halswervel-

The two most remarkable cases of this series are doubtless the two specimina mentioned first, as to my knowledge they have not yet been described. One of them is represented in Fig. 1.

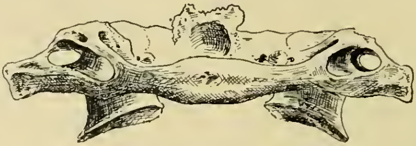

Fig. 1.
Atlas with bilateral ponticulus lateralis and bilateral ponticulus posterior.

Rises the question about the morphological signification of these variations.

Among the investigators that have tried to give an answer to this question, there are especially three, who claim the attention here, viz. Le Double, Bolk and de Burlet.

Le Double explains the occurrence of the above-described ponticuli posteriores simply mechanically and regards it as ossification of a ligament, which in most cases is found between the upper-posterior-rim of the massae laterales and the upper-rim of the most lateral part of the arcus posterior atlantis. This ossification would take place under the influence of the pulsations of the arteria vertebralis.

In consequence of the curving of this artery at this place the convexity of which is directed backwards, every pulse-gulf would push the above-described ligament backward; thereby a traction would be occasioned on the periost of the atlas on the spot where the ligament is fastened and under the influence of the stimulus the osteogenetic potency of the periost would be increased. Le Double cites, as an explanation of the occurrence of the ponticuli laterales, an ossification of a ligament occasioned by the same causes.

It seems to me very improbable that the cause of the formation of the mentioned variations is to be found in the pulsations of the A. vertebralis. In the first place it is very improbable that a so typical variation should exclusively be dependent upon outward circumstances, the more so, as these circumstances are pretty well constantly existing, and the frequency of the variation, though not unimportant, is after all not so great as might be expected in

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kolom bij den mensch en hunne beteekenis. Nederl. Tijdschr. v. Geneesk. 1899 Dl. I, II, 1900. Dl. I.

L. Bolk. Zur Frage der Assimilation des Atlas am Schädel beim Menschen. Anat. Anzeiger Bd. XXVIII.

accordance with the pretty well constant occurrence of the abovementioned ligaments and the not less constant pulsation of the A vertebralis. There are however still other considerations that, in our opinion, make Le Double's explanation appear less acceptable. Suppose even that the stimulus of the periost caused by the pulsation of the A. vertebralis should in reality be the cause of the occurrence of the ponticuli posteriores and laterales, then it would at all events be at least astonishing that the results of this process, naturally somewhat slow, could already be observed at a youthful age, and yet this is the case, as I have been able to ascertain with several atlases of the collection I have examined. The extraordinarily powerful way, in which in many cases both the ponticuli posteriores and the ponticuli laterales can be developed make us likewise doubt the correctness of Le Double's explanation of the discussed variations, the more so, as it is generally known, that osseous tissue reacts on the pulsations of the vesselwall rather with atrophy than with hypertrophy.

This doubt becomes still greater if we also consider the results of comparative anatomical investigation which were also known to Le Double. For then it appears that with many groups of mammals, and among these also primates, the ponticuli and foramini, occurring with man only as variations, are constant and normal parts of the atlas.

Bolk has laid, as far as it regards Primates, a stress upon this fact, which was already known to Merkel. He demonstrates that namely the normal human atlas has been developed by reduction from the more complete form, as it is met with among Primates a.o. with Cynocephalides. This reduction regards in the first place the topmost limitation of the canalis arteriae vertebralis, with Cynocephalides still completely extant, of which first the most lateral part (the ponticulus lateralis) afterwards also the medial part (the ponticulus posterior) disappears, by which process the channel is changed into a notch.

The repeated occurrence of these ponticuli must consequently most probably be regarded as a common atavism; ponticulus posterior and ponticulus lateralis are with the human atlas regressive variations. According to this notion the signification of this variation is in comparison with Le Double's view a quite different one. The principal cause of its occurrence is now not to be found in outward circumstances, however favourable their influence may for the rest be upon the process, but in a generally occurring inclination of reproducing phylogenetically older forms.

If we desist from trying to give an answer to the question after the influences that have brought about the reduction of the human atlas in the above-mentioned parts, the interpretation of the reoccurrence of the ponticuli laterales and posteriores as regressive variation gives certainly a satisfactory explanation of this phenomenon, as entering upon further details of the problem would immediately lead us to the department of general biology and specially to that of the phenomena of heredity.

The way in which DE BURLET[1]), the third of the above-mentioned investigators, has treated the problem differs principally from that of the former. In the views hitherto reproduced there was only an attempt to answer the question after the signification and the origin of the ponticuli posteriores and laterales with the human atlas.

DE BURLET puts the question in a different way by taking likewise into account with this question the homologa of these elements, as they constantly occur — as has already been mentioned — with many mammals. By doing so the problem assumes a more general nature, and may be formulated as follows:

"What is the signification of the foramen arcuale and alare of the mammal atlas and of the parts lying cranially from it?"

When answering this question DE BURLET points out the possibility that the arcus posterior atlantis should not be equivalent to the arcus posterior of the other vertebrae, in this sense namely, that foreign elements lying originally cranially from it should have assimilated with the arcus posterior atlantis, and as original source of these elements he indicates the so-called proatlas.

I cannot treat DE BURLET's view completely within the compass of this communication. The notion proatlas has in the course of time gradually been modified and is even now by no means accurately defined, so that an effectual discussion of DE BURLET's view that the ponticulus posterior and lateral might be homologised with the proatlas requires necessarily an accurate definition of the proatlas. I hope to do so in a subsequent communication, which will be entirely devoted to the Proatlas-problem; now I can, whilst explaining my own view, only enter upon DE BURLET's opinion in so far as he admits the possibility that elements having originally extended cranially from the arcus posterior atlantis should have assimilated with it, and the posterior arch of the atlas should consequently not be homologous with the posterior arch of the other vertebrae.

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[1]) DE BURLET. H. M. — Ueber einen rudimentären Wirbelkörper an der Spitze des Dens Epistrophei bei einem Embryo von Bradypus cuculli. Morphol. Jahrb. Bd. XLV. H 3.

In order to examine in how far the possibility expressed here is likewise a reality, we ought in the first place to remember what has been said in the previous communication on the metamerological signification of the cranio-vertebral interval about the metamere relation of the vertebrae.

From the generally admitted and in fact ascertained law of the re-segmentation of the vertebral column we have then deduced that in general the n^{th} vertebra has been constructed from the caudal half of the n^{th} scleromere and the cranial half of the $(n+1)^{\text{th}}$ scleromere, so that the metamere formula of the vertebrae is $V_{(ertebra)}\, n = Snb + S(n+1)\, a$.

If now we admit that the atlas, with regard to its metamere relations, is entirely equivalent to the other vertebrae and that consequently the above-mentioned formula likewise holds good for the atlas, then follows from it necessarily (supposing $n = 1$), that the atlas would be constructed from the caudal half of the first segment and the cranial half of the second one.

Let us now regard in this connection the position of the ponticuli posteriores and laterales.

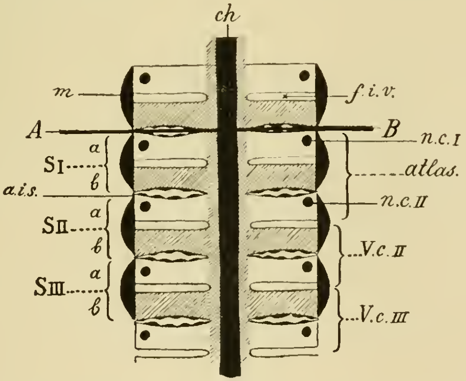

Fig. 2.

Ch = chorda m = myotome; AB = cranio-vertebral interval; S I = 1st Segment; S II = 2d Segment, etc. a = cranial semi-segment; b = caudal semi-segment; n. c. I = 1e cervicalnerve; v. c. II = axis.

To the nature of the ponticuli belongs that they form the cranial extremity resp. of the foramen arcuale and of the foramen alare, through which foramina the first cervical nerve passes. Both the ponticuli are consequently always situated cranially from this first cervical-nerve. Fig. 2 however teaches us, according to the law, that the spinal-nerve is always situated in the cranial half of the sclerotome to which it belongs, that the first cervical-nerve does not belong to the semi-segments from which the atlas is constructed, at least not, if we maintain that the atlas is equivalent to the other vertebrae and that its formula is $SIb + SIIa$. If now the 1st spinal-nerve is situated in the cranial semi-segment Ia, as is in every respect confirmed by investigation, then a fortiori the ponticulus lying cranially from this nerve must be reckoned to the same semi-segment, at all events most certainly not to the caudal semi-segment Ib. If consequently a ponticulus is present, then it follows necessarily from the fact, that the ponticulus has been formed in the cranial semi-sclerotome Ia (it remains separated from the caudal half of the last sclerotome of the cranium by the cranio-vertebral interval situated intersegmentally) that indeed the atlas is no longer equivalent to the other vertebrae, but is constructed instead of 3 semi-sclerotomes and not of 2 and consequently the formula must run: $SIa + SIb + SIIa$.

Hereby an answer is given both to the question put by DE BURLET after the signification and the origin of the ponticuli posteriores and laterales, occurring with man as a variation and with many mammals constantly, and in the first instance to the question formulated in the beginning of this communication, if activation can occur of the osteogenetic potency of the "free" semi-segment Ia, and if so, to what phenomena this activation will give rise.

The answer to the first question must be that, on account of the existence of the Ponticuli posteriores and laterales, the atlas may most decidedly not be called equivalent to the other vertebrae, but that, in comparison with the other vertebrae, it has enlarged itself, as was likewise supposed by DE BURLET by assimilation of a cranially lying element originating in the semi-segment Ia.

The answer to the second question must be, that activation of the osteogenetic potency of the semi-segment Ia is doubtlessly possible, and that one of the phenomena, by which this activation is characterized, consists in the occurrence of the ponticuli posteriores and laterales, which limit cranially the foramina arcualia and alaria. We can imagine this process thus, that in that region of the semi-segment Ia, that corresponds with the arcus posterior vertebrae (the region of the body of the vertebra remains for the present out of discussion) on account of the influence of the ossificating potency existing in it, an osseous arch is formed, be it usually only weak, which assimilates with the arcus posterior atlantis and leaves, when doing so, a necessary opening for the passage of the n. cervicalis I and the a. vertebralis, the foramen arcuale. The same holds for the region of the processus transversus. There is likewise formed in the semi-segment I*a* an osseous piece connected with the osseous arch in the region of the arcus posterior, which, whilst leaving the required room for the passage of a. vertebralis and ramus anterior n. cervicalis, (foramen alare) assimilates with the processus transversus.

If this representation is correct, it is self-evident to admit, that besides the above-mentioned ponticuli other elements can be indicated in the dorsal region of the atlas, which must be reduced to the semi-sclerotome I*a*. Hereby I have especially in view the cranial half of the massae laterales and the central part of the arcus posterior, situated between the place of insertion of the ponticuli posteriores into the posterior arch. With regard to the massae laterales we need only pay attention to the fact, that both the ponticuli originate at its upper-resp. posterior and lateral rim, and that this place of origin resp. the part of the massa lateralis projecting most posteriously and laterally is likewise always situated cranially from the 1st spinal-nerve; for on this spot we see, with somewhat strong development, the two ponticuli assimilate into each other. Consequently we are compelled to admit that here also is a part lying in the most cranial region of the massae laterales, which just like both the ponticuli has originated from the semi-segment I*a*. A difficulty however presents itself here for fixing the boundary-line between the regions of the semi-segments I*a* and I*b*. There was no difficulty in this respect for the ponticuli, as all that lies cranially from the first spinal-nerve i.e. over the foramen arcuale or alare does certainly not belong to I*b*. and there is not a single inducement to admit that anything of the region lying caudally with regard to that nerve, should belong to the semi-segment I*a*. Here however it is different, the massae laterales show neither with the full-grown atlas nor with the young one a relief of any morphological signification, as the for. arcuale or the for. alare doubtlessly is, and that would allow to indicate the boundary-line between the semi-segment I*a* and I*b*. We can consequently say indeed, that in all probability part of the massae laterales still belongs to the semi-segment I*a*, for the present it is however impossible to say which part belongs to it.

For the above-mentioned central part of the arcus posterior it is easier. Also in this region it is, as we saw, a priori probable, that the activation of the osteogenetic potency of the semi-segment I*a* does not remain restricted to the ponticuli posteriores and laterales, but extends itself between the points of insertion of the ponticuli into the arcus posterior, and consequently forms an in the median line uninterrupted osseous arch. As a rule the boundary-line between the regions belonging to SI*a* and SI*b* cannot be observed here, no more as with the massae laterales, for the simple reason that no passage required for nerve or bloodvessel keeps the regions separated.

It seems to me to be here the place to fix the attention to peculiarities occurring rather frequently at the ossification of the posterior arch of the atlas. In some cases namely one sees either in the median line, or immediately on either side of it, openings in the arcus posterior. The occurrence of these foramina is not entirely unknown. Le Double mentions them in his repeatedly cited work, when he says on p. 88 that sometimes the tuberculum posterior atlantis is replaced "par une dépression plus ou moins profonde, dans laquelle on trouve par exception un foramen minuscule, qui est l'origine d'une canalicule, qui s'ouvre en avant dans la cavité rachidienne". The author does however not attach any signification to it, nor does he try to give an explanation of it.

The mentioned opening, which might be distinguished as foramen arcuale medianum or mediale, occurs rather frequently in those atlases, where the process of ossification is not yet completed, but it is not entirely wanting in the normal, well developed atlas, as I could ascertain in the material examined by me. Usually, as likewise Le Double indicates, the variation remains restricted to a depression lying in the region of the tuberculum posterius, now of a fantastical shape, now, and this rather frequently, in the form of a rather deep notch running transversally, the two extremities of which are still a little deeper. In fig. 3, 4, and 5 I have represented some forms of this variation, as I found them in full-grown atlases

Fig. 3.
Atlas with foramen arcuale medianum.

among the material examined by me, Fig. 3 represents an atlas, in which the for the rest strongly developed arcus posterior shows in the median-line a round opening (foramen arcuale medianum) lying in a little cavity. In fig. 4 we find the representation of an atlas, the posterior part of which is characterized by a transversal notch extending over a rather large distance. In the bottom of this notch we find on either side of the median-line an opening (foramen arcuale) which is considerably larger on the left side than on the

Fig. 4.
Atlas with foramina arcualia medialia.

right one, and at last Fig. 5 gives us the representation of an atlas, which is already remarkable on account of the existence of a strongly developed bi-lateral ponticulus posterior, but which shows moreover an extraordinary deep depression (impressio mediana arcus posterioris) lying in the centre of the arcus posterior, a piercing of the posterior arch as in the specimens represented in fig. 3 and 4 is however not found here.

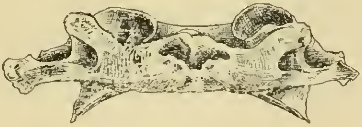

Fig. 5.
Atlas with impressio mediana arcus posterioris.

In the occurrence of these variations, to which till now but little attention has been paid, I suppose, I may see a proof for the view described above and a priori probable, that also the central part of the arcus posterior atlantis contains elements that must be reduced to the above-mentioned semi-segment I*a*. In that case the notch running transversally, and the foramina arcualia medialia or mediana, eventually occurring in it, would indicate the boundary-line between semi-segment I*a* and semi-segment I*b*.

If this supposition agrees with the actual fact, it follows from what has been said, that also in case the ponticuli posteriores and laterales have not developed, as is most frequently the case with man, the atlas cannot be called equivalent to the other vertebrae, but that also in normal circumstances it has been built of elements belonging to 3 semi-segments.

I have projected Fig. 6 (p. 212) in order to give a concise survey of the manner in which I conceive the part that the semi-segment I*a* has in the construction of the atlas with the variations described above, in proportion to the degree of the activation of the osteogenetic potency contained in it.

The figure represents 4 human atlasforms *A*, *B*, *C*, and *D*. The parts that have originated with certainty from the semi-sclerotome I*a* are represented black; those of which this is very probable and for which in many cases the region of extension can be limited are hatched.

A gives the scheme of the normal atlas without any variation. We find in it, as belonging with great probability to the semi-segment I*a*, the most cranial part of the central part of the posterior arch.

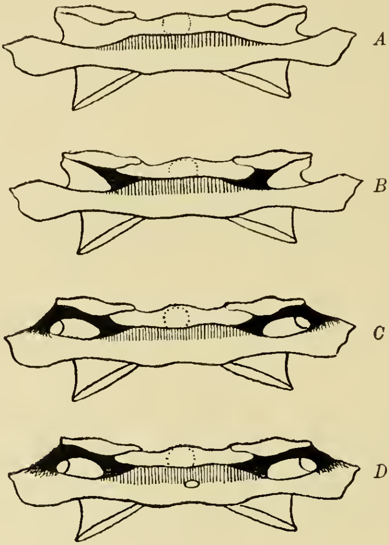

Fig. 6.

In *B* we find the ponticuli posteriores occurring bi-laterally represented black; the part of the arcus posterior lying between the two places of insertion of the ponticuli into the posterior arch is hatched as in *A*. The part of the atlas belonging to semi-segment I*a* represents now an arch lying between the posterior rim of the massae laterales and assimilated with it and with the central part of the arcus posterior.

C differs from the preceding form only by the occurrence of the ponticuli laterales, likewise represented black, by which the osseous arch originating from semi-segment I*a* has been enlarged in a lateral direction; whilst in *D* the foramen arcuale medianum is indicated as the very probable natural limitation of semi-segment I*a* opposite to semi-segment I*b*.

A indicates consequently the minimal degree, *D* the maximal degree of activation of the osteogenetic potency in the semi-segment I*a*.

On purpose I have not represented in these schemes the share that semi-segment I*a* would have in the structure of the massae laterales. As long as this part of the atlas does not show a relief, by which we could indicate the boundary-line between the semi-segments I*a* and I*b*, I do not think myself justified to insert it in a scheme, however probable the view may be theoretically.

Briefly expressed the following has been demonstrated in this communication:

1st. As was ascertained by Bolk, we have to see in the occurrence of ponticuli posteriores and laterales in the human atlas nothing else than an atavistic variation, as the form of the atlas occurring normally with man has originated by reduction from the mammal-atlas, in which the mentioned ponticuli usually occur constantly.

2. The ponticuli posteriores and laterales, whether they occur as a variation, as with man, or are constant, as with most of the mammals, belong to the semi-segment I*a*

In all cases in which the mentioned ponticuli are extant, the atlas is certainly not equivalent to the other vertebrae, as the formula for the atlas must then be $SIa + SIb + SIIa$. Consequently de Burlet's supposition that elements that originally were situated cranially, have assimilated with the atlas, is correct.

3. The variations of the atlas designated as foramina arcualia medialia or mediana are most likely the proof, that also the part of the arcus posterior, in so far as it is situated cranially from the mentioned foramina, extending between the two places of insertion of the ponticuli posteriores must be reduced to the semi-segment I*a*.

4. The fact that the two mentioned ponticuli belong to the semi-segment I*a* is the proof, that activation of the osteogenetic potency existing in this semi-segment is possible.

Mineralogy. — "*On phosphorite of the isle of Ajawi*". By Prof. A. Wichmann.

(Communicated in the meeting of May 29, 1915).

The isle of Ajawi or Mios Kairú, situated at $0^\circ 16^1/_2{}'$ S. Lat. and 135°5′ E. Long. northwest of the Schouten Islands was discovered on Febr. the 15th 1700 by William Dampier. When he intended to sail between this island and the neighbouring isle of Aifondi he scarcely escaped being shipwrecked. This fortunate escape induced him to call this group the Providence Islands 1). Though it was afterwards often enough seen, Ajawi was never visited by Europeans. When the New Guinea Expedition of 1903 was on their way to the Mapia Islands, they were of opinion that they should not let the opportunity pass by to take likewise a view of this isolated island.

After Aifondi was left in the morning of the 19th of July by the government steamer "Zeemeeuw", Ajawi was reached after $3^1/_2$ hours' steaming. Already from a distance it appeared that the island, covered with forests, was low, but that the eastern part was formed by rocks of a] phantastic shape. At about 2 km. distance from the south-coast the ship cast anchor in 13 fathoms, whereupon the yawl took all the participants to the south-west-corner. This part, rising hardly 3 m. above the level of the sea, consists of coral sand with blocks of coral besides boulders of a white rather gross-grained and hard but porous limestone which contains, according to L. Rutten, numerous specimens of *Rotalia*. They call the attention to the fact that the rock must be considered as subrecent 2). The ground is covered by a thin forest, consisting of specimens of *Pandanus*, about 16 m. high, in which enormous flocks of the beautiful Nicobara pigeons (*Caloenas nicobarica*) nestle 3). There were no human inhabitants and from the absence of coconut-palms the conclusion may be drawn, that permanent settlements have never existed.

In the eastern and north-eastern part of the island compact limestones occur, which however differ from the above-mentioned ones.

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1) A Voyage to New Holland, etc. in the year 1699. A Collection of Voyages 3d ed. 3. London 1729, p. 195. On the map Ajawi was indicated as Little Providence and Aifondi as Great Providence.

2) Foraminiferen-führende Gesteine von Niederländisch Neu-Guinea. Nova Guinea 6. 2. Leiden 1914, p. 30.

3) Maatschappij ter bevordering van het Natuurkundig Onderzoek der Nederlandsche Koloniën. Bulletin No. 46. 1903, p.p. 35—36. — H. A. Lorentz, Eenige maanden onder de Papoea's. Leiden 1905, p p. 201—202.

They are dense, of a whitish grey colour, and contain specimens of *Globigerina*, so that they are perhaps of equal age as similar rocks that are found likewise in islands to the North of New Guinea, and according to Rutten are not younger than old-miocene[1]).

The most important rock of the island is however formed by the above-mentioned ± 16 m. high phantastic rocks, some of which are likewise found isolated in the neighbourhood of the eastern shore. This rock, hitherto unknown in the Dutch East Indies, is a phosphorite which shows great resemblance to the phosphates of other islands of the Pacific. It is of a yellow to reddish-brown colour and sometimes of a pitchlike appearance. Angular, yellowish-white parts give to the rock a brecciated character. The specific weight amounts to 2.78 and the hardness is = 6.

In thin sections the rock has under the microscope the appearance of a light-yellowish, structureless mass, intersected with fine and irregular fissures. Some parts of the thin sections are rather opaque, but everywhere dispersed are dark dots which are apparently of an organic origin. Though amorphous the phosphorite shows a slight double-refraction, in which the interference-colours do not surpass the iron-grey of the first order. In some parts one discovers through the phosphate cavities filled up in zones that remind entirely of the formation of agates (fig. 1), a phenomenon that is quite common in phosphates from the Pacific[2]).

Fig. 1.

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[1]) l. c. p. 29—31.

[2]) Carl Elschner. Corallogene Phosphat-Inseln Austral-Oceaniens und ihre Produkte. Lübeck 1913, p. 55, pl. IIa. Such like phosphate-agates are found in the Isle of Nauru itself in rather large pieces (l. c. pl. VIIIb).

An incomplete analysis made by Dr. Max Buchner at Heidelberg gave the following result:

P^2O^5	31.53
CO^2	7.31
Fe^2O^3	2.83
CaO	37.38
MgO	2.17
H^2O to 110° C. . . .	1.48
H^2O from 110—1250° C.	3.86
insoluble residue . . .	0.19
	86.75

Qualitatively still a considerably large quantity of organic matter and moreover fluorine and traces of chlorine was shown. The composition points to the fact, that 68.90°/₀ tricalcium-phosphate ought to be present in the rock, which is less than with most of the phosphates from the Pacific, whose typical representatives contain 38 to 40°/₀ P^2O^5.

Whereas 31.53°/₀ P^2O^5 require for the formation of the calcium-triphosphate 37.37°/₀ CaO, for the likewise occurring 7.31°/₀ CO^2 however no less than 9.30°/₀ CaO is required for $CaCO^3$, there is a residue of phosphoric acid extant that can only be bound to the magnesium and the iron. Further it appeared that not the entire $CaCO^3$ is mechanically mixed with the other substances. When it was namely removed by means of acetic acid, the treatment with hydrochloric acid showed a very perceptible development of carbondioxyde, so that we have decidedly to do with a carbono-phosphate, which are likewise the minerals Dahllite, Podolite and Francolite. The Nauruite, moreover always contains fluorine, as likewise the phosphorite of Ajawi.

P. Hambruch gives as formula for this mineral

$$3\,(Ca^3P^2O^8)\,.\,CaCO^3\,.\,CaF^2,$$ [1])

C. Elschner on the contrary

$$x\,Ca^2P^2O^8 + \left\{\begin{matrix} CaO \\ Ca(OH)^2 \\ CaF^2 \end{matrix}\right\}, \text{ in which } x = 3 \text{ to } 5$$ [2])

It is however clear, that with the impurities, that are found in all phosphates from the Pacific, it is for the present decidedly impossible to find a satisfactory formula.

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[1]) l. c. p. 680.

[2]) Entstehung, Bildung und Lagerung des Phosphats auf Nauru. Zeitschr. Gesellsch. f. Erdkunde. Berlin 1912, p. 59.

With regard to the origin of the phosphorite of Ajawi there can exist no doubt, but it was formed in the same way as the other phosphates from the Pacific. From the investigations made in this respect appeared that those islands were in former times atolls or at least contained lagoons, into which the excrements of the birds producing guano were washed by the atmospheric waters. The phosphoric acid that had become free by the dissolution was the cause that the coral-limestone surrounding the lagoons was changed into phosphorite. The coral fragments that had come down to the bottom of the lagoons, the boulders of limestone etc. were likewise submitted to a similar metamorphosis, and were afterwards cemented into a compact rock ¹).

Wherever such like phosphorites of coral islands make themselves apparent, it can only be the consequence of negative level-changes. For this reason the rocks of Ajawi are to be considered as the ruins of an original atoll, which has obtained its present shape after subsequent upheaval by the waves of the sea.

Now the question still needs to be answered, in what way the absence of phosphorite in the islands of the Indian Archipelago can be explained. For Ajawi belongs already to the territory of the Pacific Ocean, and Christmas Island, 10°25′, S. Lat. 105°42′ E. Long. ²), rich in phosphorite is, it is true, situated in the Indian Ocean, but its distance from the west-point of Java amounts to 420 km., so that it does not form any longer part of the Archipelago.

As we have seen the conditions for the formation of phosphorite in the Pacific were: the existence of coral islands with lagoons and further deposits of guano. There is no doubt but there existed also during the tertiary period a great number of coral islands. Neither is it hazardous to suppose that in some of them settlements of guano-producing birds were found. Consequently it seems to me that the third condition — the existence of lagoons — was not complied with, from which would follow that no more at that time than at the present moment there were atolls in existence. At any case,

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¹) O. Stutzer. Ueber Phosphatlagerstätten. Zeitschrift für praktische Geologie **19**. Berlin 1911, pp. 81—82. — O. Stutzer. Die wichtigsten Lagerstätten der Nichterze **1**. Berlin 1911, pp. 438—440. — Paul Hambruch. Entstehung, Bildung und Lagerung des Phosphats auf Nauru. Zeitschr. Gesellsch. f. Erdkunde. Berlin 1912, p. 679. — Already as early as 1896 Ad. Carnot (Sur la mode de formation des gîtes sédimentaires de phosphate de chaux. Compt. rend. Acad. des Sc. **123**. Paris, pp. 724—729) proved, that in general phosphorite and phosphate-chalk are to be considered as shore- and lagoon-formations.

²) Charles W. Andrews. A Monograph of Christmas Island (Indian Ocean). London 1900, pp. 289—291.

they cannot have played a significant part. All this is of greater significance, if we cast a look at the condition of the few guano-deposits that are found in the Indian Archipelago.

For a long time it has been known that guano occurs in the Baars Island, or Kabia[1] the west-point of which is situated at 6°50'55" S.Lat. and 122°12'20" E.Long.[2]. In 1877 an application for preliminary exploration was made but "it was found inappropriate for being granted"[3]. Apparently that refusal was the consequence of an investigation made by J. Bensbach and G. A. L. W. Sol in the beginning of Dec. 1877 the result of which was not favourable[4]. Notwithstanding this we read in a report over 1879, that a concession was granted for the time of 10 years against payment of *f* 1 per bouw (7096$^{1}/_{2}$ m^{2}.) to J. H. de Siso and Th. C. Drysdale at Kupang[5]. According to C. C. Tromp a certain quantity of that guano had already been shipped to England, but the exploration had afterwards to be stopped on account of the depressed market[6].

When Carl Ribbe had however paid a visit to the island in 1882 he wrote, that "ein durch die tropischen Regengüsse sehr ausgelaugter und deshalb minderwertiger Guano ausgeführt wird."[7] At last Max Weber described Kabia as an upheaved coral reef, the rocks and trees of which were covered by a white bed of excrements originating from *Sula pisatrix, Sula fusca and Tachypetes ariël*[8].

The second finding-place of guano has become known by F. H. Guillemard, who found it on the cliffs of Batu Kapal situated near the north-point of the isle of Lembé (eastward of the N.E. point of the isle of Celebes, but it was taken for chalk[9]. As appeared

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[1] According to H. D. E. Engelhard the real name is Kawi Kawijang. (Het eiland Saleyer. Bijdr. tot de T. L en Vk. (4) **8.** 's Gravenhage 1884, p. 264).

[2] J. A. C. Oudemans. Verslag van de bepaling der geographische ligging van punten in Straat Makassar etc. Natuurk. Tijdschr. Ned. Indië. **31.** Batavia 1871, p. 146 (table).

[3] Jaarboek van het Mijnwezen in Ned. Indië. 1878. **2.** p. 233.

[4] J. E. Teysmann. Bekort verslag eener Botanische dienstreis naar het Gouvernement Celebes etc. Natuurk. Tijdschr. v. Ned. Ind. **30.** Batavia 1878, p. 119.

[5] Jaarboek van het Mijnwezen. Amsterdam 1879. **2**, p. 201.

[6] Tijdschr. voor Nijverheid en Landbouw Ned. Ind **25.** Batavia 1880, p. 554.

[7] Oscar Schneider. Carl Ribbe's Reisen in der Südsee. Deutsche geograph. Blätter 8. Bremen 1885 p. 374

[8] Maatschappij ter bevordering van het Natuurk. Onderzoek der Nederl. Koloniën Bulletin No. 33. 1900, p 7. — Max Weber, Introduction et description de l'expédition. Siboga Expeditie **1.** Leiden 1902, p. 94

[9] The Cruise of the *Marchesa* to Kamschatka and New Guinea. **2.** 2d ed. London 1889, p. 333.

however from the investigations of Sidney J. Hickson, the cliffs consisting of limestone were covered by a thin bed of guano, which seen from a distance looked like chalk [1]).

The third and last finding-place was traced by J. J. Pannekoek van Rheden in Pulu Batu, a little island near Pulu Seraya ketjil, westward of Flores [2]). The guano forms there only a thin bed spread over the surface of a few ares, the quantity was valued at only about one hundred cubic meters [8]).

From the description, at all events of that of the two first-mentioned places, it appears that the guano was leached, i.e. a not unimportant part of the phosphoric acic had found its way to the sea, by which the formation of phosphorite, as under equal circumstances in every monsoon-territory, was prevented.

The guano-beds in limestone-grottoes originating chiefly from bats will be preserved from such a fate. The quantity of these formations is however usually very slight, as will appear from the following summary.

In the S. and E. department of Borneo the grottoes of Mount Hapu are especially known, in these grottoes the existing guano-bed attains a thickness of at least 2 m. The quantity of guano that is found in the grottoes of Mount Lampinet was even valued at 10000 tons [3]). It is however far surpassed by that of the grottoes of Gomanton on the river Kinabatangan in British North Borneo where it is said that the thickness of the guano-beds amounts to 50 feet [4]).

The bottom of the numerous limestone-grottoes in Sarawak is likewise usually covered with a bed of bat- and bird-guano sometimes mixed with river-mud. It is however of no significance [5]).

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[1]) Omzwervingen in Noord Celebes. Tijdschr. Ned. Aard. Genootsch. (2) **4**. M. U. A. 1887, p. 135. — A Naturalist in Celebes. London 1889, p. 33.

[2]) Overzicht van de geographische en geologische gegevens verkregen bij de Mijnbouwkundig-geologische verkenning van het Eiland Flores in 1910 en 1911. Jaarboek van het Mijnwezen **40**, 1911. Batavia 1913, p. 226.

[3]) P. J. Maier, Scheikundig onderzoek van Vogelmest, afkomstig uit de grotten van den Goenoeng Hapoe in de afdeeling Riam Kanan en Kiwa (Zuid- en Ooster-afdeeling van Borneo). Natuurk. Tijdschr. Ned. Ind. **29**, Batavia 1867, p. 114—129.

[4]) Die Vogelnestgrotten von Gomanton auf Nord Borneo. Globus **46**. 1884, p. 31, according to the North Borneo Herald of 1st March 1884. — H. Pryer. An Account of a Visit to the Bird's nest Caves of British North Borneo. Proceed. Zoolog. Soc. London 1884, p. 532—538. — D. D. Daly, On the Caves containing Edible bird's nests in Britisch North Borneo. Ibid. 1888, p. 108—116.

[5]) A. Hart Everett. Report on the Exploration of the Caves of Borneo. Proc. Roy. Soc. **30**. London 1880, blz. 310—313. — Th. Posewitz. Höhlenforschungen in Borneo. Das Ausland **61**. Stuttgart-München 1880, pp. 612—613.

In Sumatra the Lyang-na-Muwap in the department of Padang Lawas, residency of Tapanuli, is especially known, the bottom of which is covered by a bed of guano of a thickness of 2 feet[1]). The grotto in the isle of Kluwang (5°8′ S. Lat., 95°17′ E. Long.), near the west-coast of Atjeh, contains likewise rather much guano[2]).

Numerous are the cavities in limestone in Java, that contain guano. Similar deposits are nowhere missing where swallows or bats are nestling. Some of them were carefully examined, but not a single one is of any significance[3]).

Nothing has ever become known of an investigation whether in any of the above-mentioned grottoes phosphatisation has taken place i. e. whether the existing guano has caused a metamorphosis of the limestone into phosphorite.

Botany. — "*On the germination of the seeds of some Javanese Loranthaceae.*" By Dr. W. and Mrs. J. DOCTERS VAN LEEUWEN-REIJNVAAN. (Communicated by Prof. F. A. F. C. WENT).

(Communicated in the meeting of April 23, 1915).

1. *Introduction.*

Only a few investigations have been published on the Javanese Loranthaceae. The last carried out by KOERNICKE[4]) appeared in the Annales du Jardin botanique de Buitenzorg some years ago. It deals chiefly with the adult life of these plants. Already long before this article appeared we had occasionally been occupied with experiments on the germination of various species of *Loranthus*. Mr. KOERNICKE wrote to us (in 1911) that he had also taken with him material

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[1]) R. C. VAN DER BOR De Lijang na Moewap en de legende daaraan verbonden. Tijdschr. voor Ind. Taal-, Land- en Volkenk. 37, Batavia 1894, p. 201.

[2]) L. H. WALLON, Klouwang et ses Grottes. Côtes ouest d'Atchin. Ann. de l'Extrême Orient 2. Paris 1879—80, p. 41. — X. BRAU DE SAINT-POL-LIAS. La Côte de Poivre. Voyage à Sumatra. Paris 1891, p. 224. — Zeemansgids voor den Oost-Indischen Archipel 1, 2e druk. 's Gravenhage 1904, p. 450.

[3]) D. W. ROST VAN TONNINGEN. Scheikundig onderzoek van eene meststof (guano) afkomstig uit de afdeeling Grissee. Natuurk. Tijdsch. Ned. Indië 9. Batavia 1855, pp. 157 168. — P. F. H. FROMBERG. Verslag over den aard en de bruikbaarheid der dierlijke meststof aanwezig in de grot Poetjakwang te Grissee. Ibid. pp. 169—190. J. C. BERNELOT MOENS. Guano van Telok Djambi, residentie Krawang. Ibid. 35. 1863, p. 327—328.

[4]) M. KOERNICKE, Biologische Studien an Loranthaceae. Ann. d. Jard. Bot. de Buitenzorg, 3e Supplément, p. 665. 1910.

from Java for the study of the germination and would shortly publish a paper on the subject. We thereupon abandoned the investigation, but having heard nothing further from KOERNICKE, we took it up again and were thus able to collect a fairly large quantity of material.

Some time ago, however, we learned that KOERNICKE had read a paper on this subject at Vienna, but we did not receive a copy of this, so that we are still in ignorance as to what was dealt with in this paper. For the present we do not intend therefore to give a complete survey of our work. Our results concerning germination form, however, a complete whole and this instalment can probably confirm or extend KOERNICKE's paper. Later we may have an opportunity of considering some points further.

A few notes on the germination of these species are given in GOEBEL's work [1]) and WIESNER [2]) also discusses certain points.

As is known, the fruits or rather pseudocarps of *Loranthus* are one-seeded. The pericarp is succulent and contains a large amount of sugar. The testa is very thin and is surrounded by a layer of mucilage varying in thickness, which is very sticky in some species, e. g. in *Loranthus pentandrus*. Within the testa lies the endosperm and in the longitudinal axis of the latter the green embryo is found consisting of a hypocotyl and two small, thin cotyledons.

We had at our disposal material from *Viscum articulatum* L. and *V. orientale* Bl., also the following species of *Loranthus* whose names were determined by the kindness of Dr. J. J. SMITH: first a species indicated as N°. 5, which is probably identical with *L. subumbellatus* Bl., further *Loranthus chrysanthus* Bl., *L. fasciculatus* Bl., *L. pentandrus* L., *L. ferrugineus* Bl., a species indicated as N°. 6 which resembles *L. Schultesii* Don. as well as *L. atropurpureus* Bl., but whose flowers are larger and leaves less hirsute, also N°. 8 which is probably identical with *L. fuscus* Bl. and finally *L. praelongus* Bl.

It is not always easy to collect a sufficient supply of ripe fruits. Various birds are very fond of them and look for them especially in the early morning. Moreover they eat the seeds before they are quite ripe. We succeeded in getting together a sufficient quantity of fruits either by enclosing the plants or by collecting the fruits of those plants which had been strongly occupied by the great red, vicious

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[1]) K. GOEBEL, Pflanzenbiologische Schilderungen. Teil I, 1889, p. 156.

[2]) J. WIESNER, Vergleich. physiol. Studien über die Keimung europäischer und tropischer Arten von Viscum und Loranthus, Sitz. Ber. d. Kais Ak. d. Wissensch. Wien, Bd. 103. Abt. I. 1894, p. 403.

tree ants, *Oecophila smaragdina* Em., which are evidently avoided by birds.

At first it appeared to us that the germination varies greatly among different species of Loranthaceae, but on closer investigation we found that a number of types of germination can be distinguished which are readily deducible from one another.

2. *Viscum articulatum* L.

So far as is known, these plants are almost exclusively found parasitic on *Loranthus pentandrus*. Cases have, however, been recorded in which this plant occurred on other hosts. We only succeeded in finding one such case. The *Viscum*-plants were growing on a young tree of a *Symplocos* species in the Tolomaja mountains in such numbers on the branches and stem and had such a peculiar habit, that we did not at first recognise them.

Sometimes it seems as if a plant of *V. articulatum* is growing on a host other than *Loranthus* but on closer examination this is found not to be the case. The leaves of the *Loranthus* are sometimes entirely eaten away by caterpillars (*Delias* species). Microscopic examination of the branch on which the *Viscum* grows alone can give certainty in this case.

At various times we sowed seeds of this species of *Viscum* on many kinds of plants, but none germinated. If the seeds are sown on *Loranthus pentandrus*, then development takes place with great certainty. We do not know the reason for this.

The fruits are almost spherical and in colour white. The seeds are juicy and flat, 3 by 2½ m.m. and about ½ m.m. thick. They easily adhere and germination takes place fairly quickly. The first day after the seeds have been set, no great change is observable. On the second day a small green point appears from the edge of the seed. This gradually develops into a thin green filament of about ½ m.m. in length. The apex of this bends towards the branch of the host in consequence of negative heliotropism, as can easily be demonstrated and as has long been known in the case of European *Viscum*. The green filament is none other than the hypocotyl of the seedling grown out. Its apex attaches itself to the bark of the host and then begins to swell up a little to a small discoid sucker.

The seed sometimes remains for several weeks in this stage of development. It swells up so as to become rounder. After about four weeks (in the rainy season somewhat earlier, in the dry somewhat later) the seed becomes loosened from the substratum, whereupon the hypocotyl extends. The seed then stands on a straight green stalk. The cotyledons now draw nourishment from the endosperm, the testa shrivels and falls off and the cotyledons bend away from each other. In the meantime the haustorium has also penetrated into the bark of the host and the plant begins its proper mode of life. In comparison with European species of *Viscum*, germination proceeds quickly and the further development in particular takes place more quickly, but in the species of *Loranthus* which we have investigated the development of the seeds proceeds even much more rapidly.

3. *Viscum orientale* Bl.

In our neighbourhood this plant is not so common as the previous species. We had therefore not much material at our disposal. The fruits and seeds closely resemble those of *Viscum articulatum*, but are somewhat smaller. Germination proceeds exactly in the same way, although somewhat more slowly. Seeds, which were set on November 26th, showed four days later commencement of growth of the hypocotyl. On December 6th the apex of the hypocotyl had become applied to the substratum. There was no trace of any thickening of the extremity. At the end of January the hypocotyl was again straightened out and only after a few weeks the cotyledons made their appearance from the seed.

4. *Species of Loranthus.*

Among the species of *Loranthus* which we investigated three types of germination can be distinguished. The simplest case is that in which germination takes place in much the same manner as in *Viscum*.

We have not been able to find from the literature at our disposal in what manner germination takes place in the European species of *Loranthus*. H. York[1]) describes the development of an American *Loranthacea*: *Phoradendron flavescens* Nutt., where germination, as we shall later show in greater detail, corresponds in many respects with that of the species of *Loranthus* which we have investigated.

5. *Loranthus subumbellatus* Bl. (?)

This species is very common, both in the plains and on the

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[1]) H. York. The anatomy and some of the biological aspects of the "American" Mistletoe. Bull. of the University of Texas. No. 20. 1909.

mountains. The plants grow on all kinds of hosts, and, in contrast with most other members of this genus, are also often found on species of *Ficus*. They are rather conspicuous by reason of their bright green foliage and the bright yellow colour of their ripe fruits. These fruits are spindle-shaped and pointed at both ends. The green seeds are also spindle shaped and are enclosed in a thick layer of juicy fruit-flesh. The layer of mucilage is not so strongly developed as in other species of *Loranthus* and is really found only at one end of the seed.

This is the part of the seed which in the fruit is turned towards the fruit-stalk. The seeds are not attached by their lateral edge, but at the extremity, and the connection with the substratum is not so firm as in other species. After a good shower of rain the seeds may be seen hanging by a thread of mucilage, loosened from the substratum. On drying they usually attach themselves again to the stem. In the course of a day the mucilage becomes, however, so hard that the seed remains fixed in its place. There appear on the side of the seed opposite the substratum five small, soft, white protuberances, which are placed in a ring round the apex. If these portions are removed, the extremity of the endosperm and the apex of the hypocotyl become visible.

The embryo consists of a well-developed hypocotyl, whose extremity is already enlarged in the seed to a discoid sucker with glutinous apex, and of two cotyledons. The latter are bright green like the rest of the embryo and about 1 m.m. long. The germination of these seeds is attached to a branch, the apex of the hypocotyl begins to emerge from between the soft bosses. After 24 hours the hypocotyl already projects one or two m.m. from the seed. The hypocotyl continues to develop until it is a green filament 5—7 m.m. in length. The apex becomes broader and broader and continually more sticky, After 36 hours a curvature of the filament becomes visible and usually the substratum is already reached after two days. The disc is then attached to the surface of the host and becomes very much broader.

After a few days the mucilage layer by means of which the seed was fastened to the substratum becomes loose and the hypocotyl now begins to straighten itself again. The seed is thus drawn away from the branch and then stands up erect on a green stalk 7—9 m.m. in length. The endosperm is now used up and the testa falls off after a few days and then the two cotyledons spread themselves out flat.

This brings germination proper to an end. In the meantime the haustorium has made itself a way into the host.

As can be seen from the above description, this species of *Loranthus* develops in much the same way as *Viscum*.

A clear figure of the germination of this *Loranthus* is given in the well-known work of GOEBEL[1]), already quoted. The name of the *Loranthus* described is however not given there.

6 and 7. *Loranthus spec.* 6 *and L. chrysanthus Bl.*

The first species of *Loranthus* is very common in several places in the neighbourhood of Semarang, especially on neglected coffee-plants of the natives. We found the second species in large numbers on the slopes of Merbabu and Telamaja at a height of 1000—2000 metres. The fruits of the two species, closely resemble each other, as do the plants themselves. Those of *L. spec.* 6 are somewhat smaller and less thickly covered with brown scales. The fruits are pear-shaped with a fairly long stalk which becomes much curved on ripening. The ripe berries are orange-brown in colour. They are greedily eaten by birds, which swallow the entire fruit. The seeds are dropped with the faeces and sometimes attach themselves in masses to the branches.

The shape of the seed differs from that of the previously described species of *Loranthus*. The latter was round in transverse section, whilst a section of the seed of *L. spec.* 6 is square. At one end it is broad and there occur in a line with the four edges four small, succulent, white protuberances. At their other end the seeds become gradually narrower and terminate in a long, thin white stalk. This stalk is the central portion of the fruit stalk. Although this white stalk easily breaks off, it is almost always seen in seeds when germinating in the open. These seeds have traversed the intestinal canal. Round the seed itself and the stalk there is a thin, but very glutinous, partly green layer of mucilage, by means of which the seeds of this species of *Loranthus* are very firmly fastened to their substratum.

The greater part of the seed consists of a white endosperm in which the small green embryo is imbedded. This embryo is composed of a short, thin cylindrical hypocotyl ending in a point, and of two very small cotyledons. They are rather difficult to distinguish, since they form a prolongation, as it were, of the cylindrical hypocotyl. The latter, whose apex, in contradistinction to that of the previous species of *Loranthus*, is not at all broadened, lies entirely within the testa. The testa is however perforated in the middle, exactly at the spot where the hypocotyl is applied to the testa. The

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[1]) R. GOEBEL loc. cit p. 156. Figure 64 A.

hole is small and quite difficult to see, but yet large enough to form an outlet for the thin hypocotyl.

Germination takes place fairly rapidly. Its commencement is difficult to distinguish through the tough green layer of mucilage. This must be removed by means of a needle, which is hardly possible until the seeds have been soaked for some time in water to soften them. A few hours after the seed has become fixed, the apex of the hypocotyl begins to emerge and the next day there can be clearly seen a fine green point protruding from the hole in the testa.

As soon as this protrudes half a millimetre out of the seed, the growing stem begins to turn towards the substratum, keeping close to the testa, so that it cannot be traced through the layer of mucilage. Later it often bends still further and grows for a short distance between the testa and the substratum. The apex of the hypocotyl is not broadened and does not apply itself with its extreme point to the substratum, but sideways. Gradually there is a broadening of that part of the hypocotyl, which lies against the branch. The hypocotyl is now as it were drawn out of the testa and the basal portions of the cotyledons also appear outside the seed. For the most part, however, the cotyledons remain hidden within the seed. The upper side of the hypocotyl and the bases of the cotyledons also soon appear outside the layer of mucilage and are very obvious by reason of their bright green colour. The seed reaches this stage after two or three days according to circumstances. Still a day later a small green point appears on the upper side of the hypocotyl, and later yet another. After a short time these are seen to be the first green leaves of the plant. At first we took this to be the development of adventitious buds, but the process is, however, much simpler. The two cotyledons separate a little at their base, so that a narrow slit is visible, from which the growing point of the embryo grows out. Generally the embryo turns itself in coming out, in such a way that the slit between the two cotyledons faces upwards. Occasionally this opening lies more to the side and then the leaves of course also appear laterally.

The two leaves grow very slowly and the hypocotyl broadens itself at the same time. After a few weeks the haustorium penetrates into the bark of the host.

8. *Loranthus fuscus Bl.* (?)

We found this species in large quantities as a parasite on plants of *Lespedeza cytisoides,* which were very common on the slopes of the Merbabu Mountain at a height of 2000—2500 Metres. With regard to its manner of growth this species of *Loranthus* resembles the two previous ones, but the leaves are not covered with scales, and the flowers and fruits are much smaller. The seeds are also quadrangular and quite of the same structure as those of *Loranthus spec.* 6. The mucilage layer was also the same, as were the first stages of germination as far as we saw them — we remained for two days on the top of Merbabu.

9. *Loranthus fasciculatus Bl.*

We found a species of *Loranthus* which was noticeable because of its small leaves and the flowers coloured dark-red at their base on a gigantic tree of *Ficus retusa* in the neighbourhood of Getasan, a village at an altitude of about 1100 Metres at the foot of Merbabu.

The fruits resemble in shape those of *L. subumbellatus*, but were somewhat smaller and of a beautiful red colour like currants. The fleshy part of the fruit was especially well developed, so that the seeds were very small, hardly 2 millimetres in length. Moreover the mucilage layer was not so strongly developed. The seeds of this species also were quadrangular, the edges more or less rounded off. We were only able to observe the germination for a few days. The first stages completely agreed with those of the three foregoing species of *Loranthus*.

10. *Loranthus pentandrus L.*

This species is, in Semarang at any rate, the commonest *Loranthus*. It is a vigorous plant which grows very quickly and of which the stems, a metre in length, for the most part hang down from the branches of the host. The fruits are fairly large, about 10 millimeters long and 4—5 mm. thick. They have the shape of a truncated cone and are orange-red in colour. Mature fruits are seldom found on the plants, because when still green and almost ripe, they are eaten by birds. The germination of these nearly ripe fruits, however, takes place just as well as that of the completely ripe ones. Naturally the latter germinate more rapidly, but germination takes place so quickly in this species, that one sees little difference.

In contradistinction to the fruits of the foregoing species of *Loranthus* which are usually swallowed entire by birds, so that the seeds arrive on the branches of the host with the ejecta, the fruits of

L. pentandrus are generally pealed by the birds one by one. Then the birds, usually species of thrushes rub off the very sticky seeds from their beaks on to the branches. It is obvious that by such a method, the chance of a seed arriving at a place suitable for its development is much greater than was the case in the previously mentioned species.

Naturally they are often found on branches of *Loranthus pentandrus* itself and young seedlings can always be found on it in great numbers. This fact was also observed by KOERNICKE [1]). But this does not imply, that we can now speak of *Loranthus* as a parasite on *Loranthus* itself. All the cases figured by KOERNICKE refer only to seedlings. We have never yet met with adult plants of *Loranthus* growing on another species of *Loranthus*. Seedlings are often also found on dead branches, which, because they are leafless, offer a favourite support to birds. But this does not permit us to say that species of *Loranthus* can be parasitic on dead wood.

In comparison with the size of the fruit the seeds are relatively small, about 4—5 mm. The testa is, as in the other species, very thin and encloses a great quantity of endosperm. At the extremity which is in the fruit turned towards the apex, there are 5 mucilaginous, filamentous protuberances, about 3 mm. long, which cover the apex of the seed and make it appear to be therefore about 7 mm. long.

Their removal from the seed is not prejudicial to germination and is indeed often brought about by the agency of birds. The green apex of the hypocotyl is then seen which hence protrudes slightly from the seed. The apex is already markedly swollen, when the fruit is still not quite ripe. In proportion to the quantity of endosperm the embryo is rather small. It consists of a short hypocotyl, which, as has already been said, is swollen at its free extremity into a knob and of a pair of very short, flat cotyledons, which reach to about the centre of the endosperm.

If the seeds are stuck on a branch, then, at least if it does not rain, a few hours afterwards the mucilaginous protuberances of the seed are seen to begin to dry up and the green knob of the hypocotyl becomes visible.

At the same time this knob swells up and grows with one lateral edge towards the branch, so that a large swelling arises at the extremity of the seed. Its lower side lies against the branch and adheres to it. This occurs in the course of one to three days. Gradually also that part of the hypocotyl which was concealed in

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[1]) M. KOERNICKE. loc. cit. p. 690.

the seed, is drawn out in consequence of the growth of its anterior part, but since this concealed portion is very short, very little of this can be seen in the beginning. The bases of the cotyledons also just become visible and the terminal bud, which is concealed between the two cotyledons grows out. First a small leaf appears, then another. But this growth is much slower than at the commencement of germination. After a few weeks they are usually one centimetre in length. It is only when the stem begins to lengthen, sometimes not until after a few months, that development proceeds again at a greater rate. Long before this the white haustorium has already penetrated into the host.

11. *Loranthus praelongus* Bl.

This is the largest species of *Loranthus* which we found in Java. It can grow on a variety of trees, but for the most part we found them on *Ficus* species, including *Ficus elastica*. Specimens with pendulous branches 4—5 meters in length, are not uncommon. The inflorescence is a thick crowded raceme. The flowers are very long and orange-yellow in colour. The fruits are sessile, as broad as those of the former species, but somewhat shorter. Moreover the seeds are somewhat more crowded. The structure is identical with that of *Loranthus pentandrus* and germination takes place in the same way.

12. *Conclusion.*

The first impression gained with regard to the germination of species of *Loranthus* is that it proceeds very differently in various species. But investigation has shown that this difference is only apparent.

The germination, as described above for species of *Viscum* and agreeing completely with that of *Viscum album*, might be considered the simplest stage. This germination-process may be compared with that of epiphyte seeds, as Goebel[1]) has already noticed. In species of *Aeschynanthus*[2]) and *Dischidia*[3]) the hypocotyl also appears first from the seed. It bends towards the bark of the host and attaches

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[1]) K. Goebel. loc. cit. p. 156.

[2]) Idem p. 155. Figure 63.

[3]) W. and J. Docters van Leeuwen—Reijnvaan. Beiträge zur Kenntnis der Lebensweise einiger Dischidia-Arten. Ann. d. Jard. bot. de Buitenzorg. XXVII. 1913. p. 68.

itself to it by means of a ring of fine hairs. Not until later do the cotyledons appear.

The germination of *Loranthus subumbellatus* (?) quite agrees with this. In this species also the cotyledons become the first leaves of the young plant. In the other species of *Loranthus* which we investigated this is no longer the case. In these the cotyledons (except their bases) remain completely concealed in the endosperm, and serve to carry the food hence to the hypocotyl and do not later function as leaves of the plant.

In *Loranthus spec. N°.* 6, *chrysanthus*, *fuscus* (?) and *fasciculatus* the hypocotyl is still placed completely within the testa. On germination it becomes visible and grows along the testa towards the bark of the host. The embryo now pushes itself so far out of the seed that the bases of the cotyledons appear and the terminal bud is able to grow out.

In *Loranthus pentandrus* and *praelongus* the apex of the hypocotyl is in the first place already outside the testa and in the second place the apex is swollen into a knob. Here there is no question of a curvature of the hypocotyl, as in all the other species. The knob grows, at the side which is turned to the host, towards the latter's bark. The hypocotyl in the seed is further so short that the bases of the cotyledons almost at once come to lie outside the seed. So far as germination is concerned this species of *Loranthus* may be considered the most specialised. The germination is here the most rapid and the seedlings are the earliest to reach their host.

The germination of an American *Loranthacea* i. e. *Phoradendron flavescens* Nutt. has been investigated by YORK[1]), who found that in this species germination takes place in the same way as in *Loranthus spec.* 6 investigated by us. But the cotyledons remain functional much longer. First the embryonic root is formed; the endosperm often remains united to the cotyledons for more than a year. Generally these shrivel up and disappear. Rarely the stem develops from the terminal bud between the cotyledons. Usually the shoots arise from adventitious buds, which develop on the terminal disc of the hypocotyl by means of which the latter is united to the host.

Semarang, Java.

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[1]) loc. cit. p. 8.

Physiology. — *"On the heart-rhythm.* 4th Communication. *Heart-alternation."* By Dr. S. de Boer. (Communicated by Prof. J. K. A. Wertheim Salomonson.)

(Communicated in the meeting of May 25, 1915).

Physiologists and clinical men have repeatedly discovered an alternating activity of the central organ of the circulation of the blood. By experiments this phenomenon was likewise brought about in different ways. So could Hoffmann (1) cause his stopping frog's heart preparations to make for some time alternatingly stronger and weaker pulsations by passing from a slow stimulation-frequency to a quicker. Rümke (2) made frog's hearts alternate by poisoning them with antiarine. Muskens (3) obtained heart-alternation by poisoning frog's hearts with digitalisdyalysate. Also by other poisons as aconitine and glyoxyle-acid an alternating activity of the heart is obtained. Gaskell (4) could make the heart-alternation in frog's hearts disappear by Vagus-stimulation, whilst Frédéricq (5) could produce heart-alternation in narcotized dogs by stimulation of the accelerantes. There exists very little certainty about the explanation of this phenomenon. Muskens, Trendelenburg (6) and Hering (7) on one side attribute the alternating weak pulsations of the heart to asystoly of part of the ventricle-musculature. Wenckebach (8) contradicts this view, he admits likewise this cause for the alternating activity of the heart, but distinguishes moreover another reason for the phenomenon. Clinical experience taught him that p. alternans, apart from its occurrence in paroxysmal tachycardies, is almost exclusively discovered, when the arterial pressure of the blood has increased (chron. nephritis) and the elasticity of the arterial wall has decreased. He considers in this respect alternation more as a pulse-phenomenon than as a heart-phenomenon. Under the influence of little irregularities the filling of the ventricle and the arterial resistance vary alternatingly, so that with constant contractility of the heart-muscle the result of the systoles varied alternatingly.

My experiments [1]) treat of extirpated frog's hearts: for the alternating activity of these this peripheric cause is consequently excluded. If a frog's heart is extirpated and suspended, sometimes alternatingly high and low curves are obtained. I give an example of this in fig. 1. (next page).

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[1]) The experiments were made on hibernated specimens of rana esculenta in the months of February and March 1915. Preliminary communication published in the Zentrallblatt für Physiologie (9).

During the large systoles I saw in this experiment the whole ventricle contract, whilst during the little systoles the point remained in rest. After this suspended heart had written for some time alternation-curves, these curves suddenly changed into curves of equal height. This transition can be seen in the figure. For a very short time these curves continued to be of equal height, to change again into alternation. The second row of curves of the figure was written down 5 minutes after the first. The transition of the alternation into the curves of equal height is brought about, because the little curves increase in height, whilst the height of the large curves gradually decreases. The height of the normal curves is in the end between that of the large ones and the little ones of the alternation. I found this confirmed in a great number of experiments. This can be beautifully seen in fig. 1. I have not observed here the transition of these normal curves into the alternation. After I had replaced the drum to begin the second row, the alternation existed already again. The distances between the initial points of the ventricle-systoles of the alternation-row are equal, but because the large systoles are wider, the ventricle-pauses are of unequal duration. The little systoles follow after a shorter pause than the large ones. And it is the preceding pause that is of consequence. The dimension of the systole is in general dependent upon the duration of the preceding pause and of the dimension of the systole that has preceded this pause. If a systole after a short pause succeeds

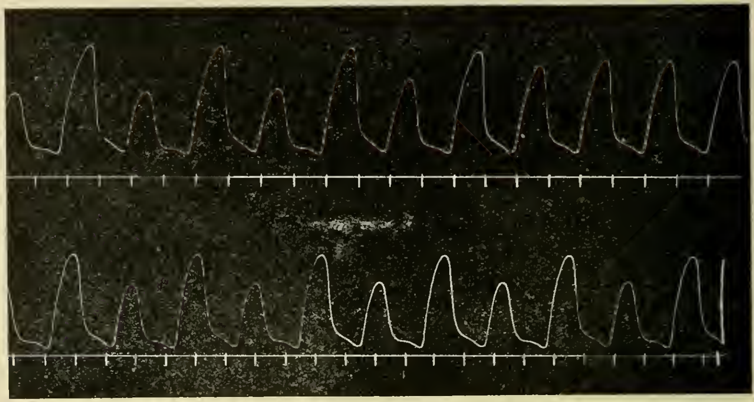

Fig. 1.

a large systole then it is little, and on the other hand a systole is large, when the preceding systole is little and the preceding pause long.

Repeatedly I saw the alternation change into halving of rhythm. Fig. 2, lower row of curves, shows an instance of it. After I had suspended this heart, the systoles were all equally high; after a short time this row of curves changed into alternation. When this

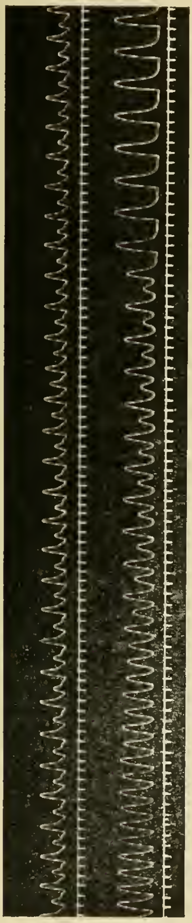

Fig. 2.

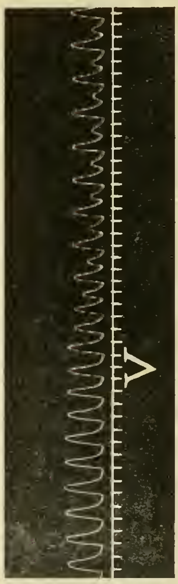

Fig. 3.

had existed for about one minute, halving of rhythm occurred. In this halved rhythm the heart continued to pulsate for more than $2^1/_2$ minutes, after which the usual rhythm returned, in the beginning with systoles of equal height. After this slow rhythm the height of the systoles gradually decreases. The preceding slow rhythm had contributed to make the first systoles higher. The first systole of Fig. 2 is the 15th after the halved stage. The systoles continue here to decrease in height. From the 6th systole in this figure the alternation is distinctly extant. We see now the little systole constantly diminish in height, till the rhythm halves again. I hope to give an explanation of this fact at the end. Conducted by this observation which I made several times myself, from which appeared, that alternation occurs as a transition from the normal rhythm into the halved one, and conducted by the well known clinical observation that p. alternation occurs especially with paroxysmal tachycardies, I have tried to produce heart-alternation in my frogs in a simple way. The result answered entirely to my expectations. I suspended in the usual way an extirpated frog's heart, and raised then the temperature of the sinus venosus by making a hot Ringersolution trickle on it.

My intention was to make the impulsions proceed from the sinus venosus to the ventricle in a quicker tempo, whilst the temperature of the ventricle remained the same. As I expected the ventricle began indeed to pulsate in alternation. Fig. 3 (at V. sinus venosus calefied). In this way I could cause nearly every extirpated frog's heart to pulsate alternatingly. Thus I suspended e.g. 28 March 10 frog's hearts and found with 9 of these alternation after calefaction of the sinus venosus, with the 10th polygeminy occurred. (Every 4 to 8 systoles 1 ventricle-systole fell out here). Refrigeration of the sinus venosus was then again sufficient to change the alternation again into the normal rhythm. (Fig. 4 at A sin. venosus refrigerated).

Alternation as transition between the normal and the halved rhythm occurred hereby likewise frequently.

So we see in Fig. 5 upper row at V, on account of calefaction of the sinus venosus, alternation appear which disappears again at A in consequence of refrigeration. In the lower row occur a few curves of another heart in the halved rhythm between the alternation-pulsations (at V the sin. venosus is here likewise calefied, at A refrigerated).

Sometimes I obtained in this experiment for a short time heart-alternation, but often also the heart continued to pulsate for a long time in alternation. It makes the impression that the average normal height of the systole lies between the two of the alternation, whilst during the alternation there exists an oscillation round this average. This is in accordance with the conception that the height of the systole is direct proportional to the duration of the preceding pauses. The duration of the pause in the normal rhythm is also the average

Fig 4.

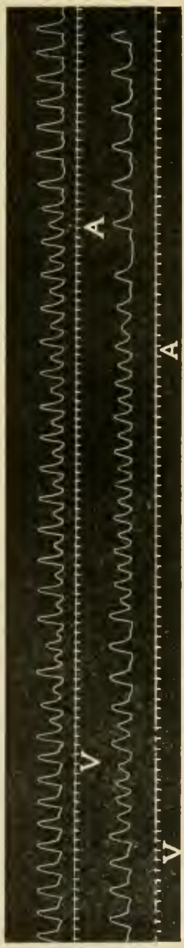

Fig. 5.

of the long and the short pauses during the alternation. When once pulsating in alternation the heart continues of itself to oscillate round this average. Every large systole is followed by a shorter pause, so that there are two reasons, why every following systole will be little, namely:

1. the short preceding pause.
2. the fact that the preceding systoles are large.

And so, conversely, every little systole will be followed by a large one. This will be so, because the preceding systole is little, and the preceding pause long. For this reason a once existing alternation easily continues.

Now I thought it desirable to study this heart-phenomenon likewise with the string-galvanometer. The communications on this subject are so contradictory that I felt the desire to study the action-currents of the simple frog's heart possessing but one ventricle during the alternation. My experiment facilitated my investigations considerably; I could now at any time by any method make hearts pulsate alternatingly; I deducted the action-currents in the usual way from the point and the basis or auricle. I represent here in Fig. 6 the suspension-curve and the electrogram of a frog's heart that by itself was pulsating alternatingly. (Fig. 6. Time in $^1/_5$ sec.) After the sixth systole I refrigerated the sinus venosus by pouring a little chloric ethyl on it.

We see in the row of curves the *R*-oscillations remain equally large. The slow *T*-oscillations are for the little systoles considerably larger than for the large ones. The consequence of this is, that the electric curves alternate over against the mechanical ones in an opposite sense.

And this can easily be explained. The negativities of the basis and of the point are transmitted from the ventricle to the measuring-apparatus. *These negativities demonstrate themselves there in opposite signs.* In so far as consequently the basis- and the point-negativities coincide, they are subtracted from each other. *In the mechanical curves however the point and the basisalterations sum up.* The greater the mechanical curve is, i.e. the more the point takes part in it, the smaller the electric curve becomes. With the low curves consequently is in the electrogram the incision from the top into the electrograms smaller than with the large curves (indicated by two arrows in Fig. 6). The depth of the incision is indicated by the measure in which the point interferes with the basis.

That indeed during the little curves the point is in rest can especially distinctly be seen, when the difference in dimension of the two systoles is strongly pronounced. The little curves of the alternation-pairs express themselves in the electrograms more as monophasic curves, whilst the large ones represent more diphasic curves. The part of the point consequently participates, also in an electric

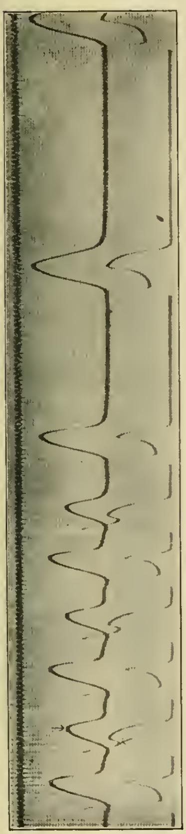

Fig. 6

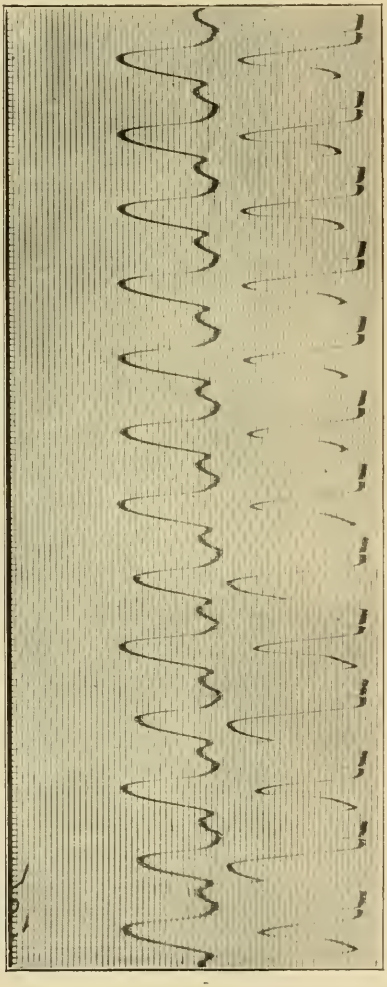

Fig. 7

sense little, for the little curves. According to this notion it is also obvious, that the R-oscillations of all curves are of equal height. The height of these oscillations is determined by the transmission

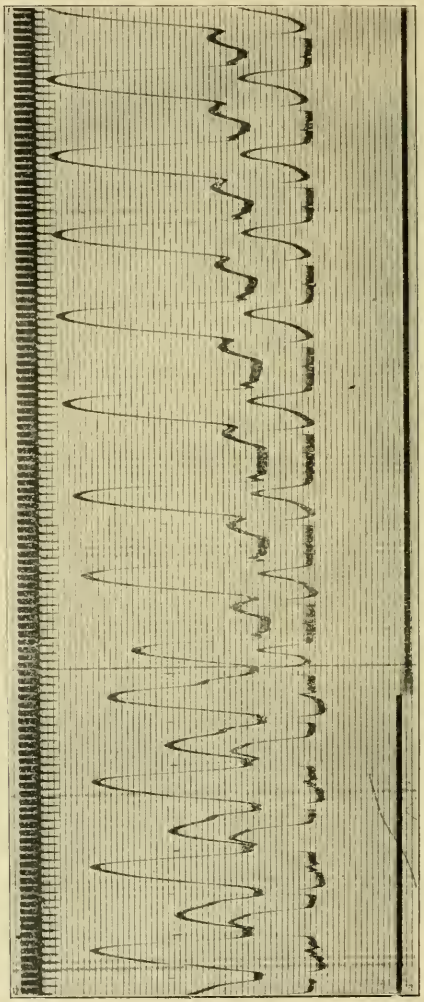

Fig. 8.

of stimula through the basis-part, till the stimulus has proceeded so far, that the negativity begins to show itself also at the point-pole. As long as the basis-region continues to pulsate in its full extent, the *R* will consequently remain equally high. (If at least the

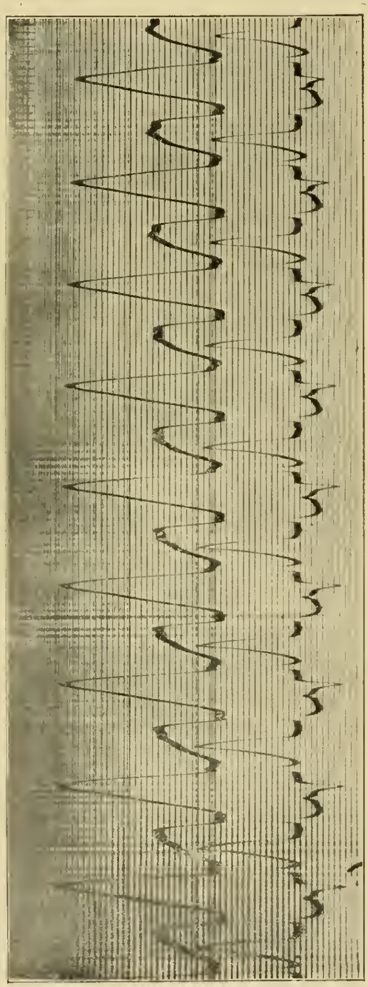

Fig. 9.

transmission-velocity of the stimulus is not considerably disturbed; for if the stimulus transmits itself slower, the point will interfere later with the basis, and thereby the height will be able to increase already). The influence of the refrigeration of the sinus venosus on the electrograms and the mechanical curves is here entirely a consequence of variation of frequency. The duration of the *R*-oscillation becomes shorter on account of the improved transmission of excitation after the longer pauses, but the duration and height of the *T*-oscillation likewise increase considerably. The mechanogram likewise increases in height and duration.

A well-defined example of transition of alternation into the normal rhythm represents Fig. 7. The height of the mechanograms of the normal rhythm stands between the heights of the alternation-systoles. In the electrograms the same proportion is found back for the heights of the *T*-oscillations, and likewise for the depths of the incisions, caused in the electrograms by the interference of the apex negativity with the negativity of the basis.

In Fig. 8 (page 238) we see an alternation that I had caused by calefaction of the sinus venosus, change again into the normal one by refrigeration of the sinus (the moment of refrigeration is indicated by the signal) Occasionally the alternation was only to be ascertained by a difference in height of the *T*-oscillations. The highest *T*'s belonged then to the lowest systoles. This can only be explained by an inferior interference of the apex-part with the basis.

Not always, however, does the point participate less during the little systoles; in some cases the electogram can only be understood, if alternatingly we admit a diminished participation of the basis, or also, if alternatingly now the basis, now the point pulsated.

So Fig. 9 (page 239) allows us to doubt, whether here the little systoles are occasioned by exclusively basis-systoles.

I have another representation in which during the little systoles for the greater part the point pulsates, and during the large systoles the basis does so. These however are exceptions. As a rule I observed that during the little systoles the point does not participate. In nearly all representations the large systole begins later after the expiration of the preceding systole than the little one. This can distinctly be observed from the electrograms. Consequently besides the systoles the pauses alternate also, whilst an alternation in the duration of the heartperiods does not occur. After it has appeared from the electrograms, that the heart-alternation of the extirpated frog's heart is caused by partial asystole of part of the ventricle-musculature (mostly of the point), Fig. 2 suddenly becomes also more intelligible.

We see here alternation gradually change into halving of the rhythm, most probably of the ventricle only. I often observed this halving of the rhythm after alternation. The alternation is here consequently a form of transition between the normal rhythm and the halved one, as I found in my frog's hearts poisoned with veratrine repeatedly bi- and trigeminus as transition between these two rhythms. The transition is here gradual; the more we approach the halved rhythm, the lower the little alternation-systole becomes. During the little systole a constantly greater part of the heartpoint remains in rest. In Fig. 10 I have indicated by lines drawn transversally over the ventricle the frontier between the part of the ventricle that pulsates during the little systole, and the part that remains in rest. The part under the line pulsates consequently during one alternationpair once, and this part becomes constantly larger, the line rises gradually. So we come to the conclusion that as soon as the alternation occurs, halving of rhythm of part of the ventricle-musculature takes place. The part of which the rhythm halves becomes constantly larger and larger, till at last the rhythm of the whole ventricle halves. The lines in the fig. indicate thus, how far the contraction continues alternatingly in the ventricle.

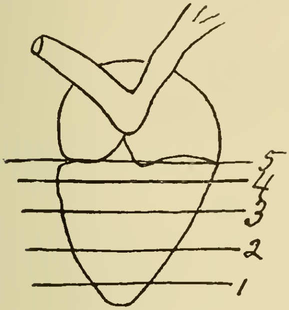

Fig. 10.

By this investigation into the potential differences which exist in the ventricle during the alternation-curves it is at the same time clearly indicated that we must conceive the ventricle-electrogram as a product of interference of the negativities at the basis and the point.

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Physiology. — "*Upon the simultaneous registration of electric phenomena by means of two or more galvanometers, and upon its application to electro-cardiography.*" By W. EINTHOVEN, F. L. BERGANSIUS, and J. BIJTEL.

(Communicated in the meeting of May 29, 1915).

For a long time the need has been felt of a simultaneous registration of electric phenomena by means of two, or three galvanometers. This is evident from the experiments made by BULL, GARTEN, HOFFMAN, LEWIS, WILLIAMS, and others.

Speaking generally, three methods may be distinguished:

A. That in which two galvanometers are placed side by side. Each of the instruments is illuminated by a separate lamp, while the rays which proceed from the projection-oculars form two fields of illumination one beside the other on the horizontal slit, behind which the photographic plate is moved in a vertical direction.

The time-registration can be obtained by a single spoke-disc, the number of spokes of which may be 10, or a multiple of ten. The disc must be placed in such a position that its centre falls in the line, which, running about parallel with the slit, connects the optical axes of the two galvanometers. This can easily be done with great accuracy, so that no greater error need occur than say 0,01 part of the distance which divides one spoke from another. Care must also be taken that by a suitable placing of the lenses the images of the spokes on the slit are sharply defined.

B. Another method consists in stretching two strings across the same magnetic field. The Cambridge Scientific Instrument Comp. provides a double string-holder on their model of galvanometer, in which two strings are held at a distance of 0.5 mm. from each other.

If a strong magnification were used with this arrangement without any further arrangements the images in the field of projection would fall so far apart that the apparatus would be useless in practice. With a magnification of 600, the images of the strings would lie 30 cm. apart. To avoid this difficulty, the rays which are directed upon the slit by the projection-ocular, are changed in direction by a pair of achromatic prisms in such a manner, that the images of the strings come to lie at a convenient distance from one another upon the slit. A rectangular screen, placed at some distance in front of the slit, divides the two fields formed by the prisms, and forms a fine line of shadow upon the sensitive plate.

C. The third method of combination of galvanometers may perhaps be called the most elegant, but it demands a very careful adjustment. The principle of this method is that the two galvanometers are placed one behind the other, with the optical axes falling in the same line.

Midway between the projection-objective of the first galvanometer and the illumination-objective of the second a combination of lenses is introduced which may be compared to a double ocular, and which the firm of CARL ZEISS have been kind enough to construct at our request. This system is placed at such a distance from the two above mentioned objectives, that the spherical and chromatic aberrations of the image are compensated as well as possible.

The string which is nearest to the lamp is first projected in the new ZEISS-system, a second time in the optical field of the second string; a third time in the projection-ocular, and finally a fourth time upon the sensitive plate.

Although great demands are made upon the optical apparatus in order to insure sharpness in this fourth image, yet the curves show that the method leads to very satisfactory results. The images are so sharp and full of contrast, that it is sometimes almost impossible to distinguish between the image of the first and that of the second string. This may be seen for instance in the curves in the thesis of Dr. BATTAERD, in which heart sounds and E.K.G. were simultaneously registered by the method in question.

In applying the method of simultaneous registration to electrocardiography special precautions must be taken. In this paper we discuss the use of three galvanometers at once.

If an E.K.G. is made with only one derivation, regulating the sensitivity of the galvanometer in the usual way, each centimetre of an ordinate of the curve represents a potential difference of 1 millivolt, and this potential difference would actually exist between the places of derivation, if these were *not* connected to the galvanometer.

If the body is connected to a second galvanometer, the deflections of the first will be diminished, and this will be increasingly the case in proportion as the second galvanometer possesses less resistance. By a third connection the results are again reduced, and the question therefore arises: How is the sensitivity of the three galvanometers to be regulated, so that they will simultaneously inscribe curves which will fulfil the conditions required: The centimetres of the ordinates must always represent the millivolts of the potential oscillations which occur between two points of derivation of a body, when the body itself is still free from all connections.

As long as only one galvanometer is connected to the body, at the sudden application of e millivolts in the circuit the image of the string must be deflected by e cms. If there are three galvanometers connected to the body at the same time, by the application of e millivolts the deflection must be more than e cms. In a particular case with the simultaneous derivations I, II, and III, we will call the deflections required E_1, E_2, and E_3. These deflections can be calculated by means of the laws of distribution of currents from the potential difference e applied each time, the resistances of the body l_1, l_2 and l_3, and the galvanometer resistances g_1, g_2, and g_3.

The result may be obtained in the simplest and at the same time most practical way, by using the method of the equilateral triangle.[1]

In this model of the human body the resistances of the body in the three derivations are equal. If l_1, l_2, and l_3 really differ from one another, they can be made equal by means of rheostats, or in the adjustments a mean resistance $l = \frac{l_1 + l_2 + l_3}{3}$ may be used. In almost all cases this last method which is simpler in practice, is amply accurate enough.

The galvanometer-resistances must be actually made equal to each other, by the addition of rheostat resistances to the two smallest ones. We then write $g_1 = g_2 = g_3 = g$.

If $\frac{l}{2g} = a$, the deflection required is for each of the three string images $E = e\,(1 + a)$ centimetres.

We may remark in passing that at the application of e millivolts

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[1] Comp. "Ueber die Richtung und die manifeste Grösse der Potentialschwankungen im menschlichen Herzen", u. s. w. Pflüger's Archiv für die ges. Physiologie. Bd. 150. p. 275, 1913.

in one of the galvanometer circuits all three of the string images show a deflection. If the sensitivity of the strings is properly regulated the string image into the circuit of which the potential difference is introduced will be deflected by E cms and each of the other string images by $E-e$ cms.

The following case may serve as an example. In the experimental subject *Hu* the resistances of the body are

$$l_1 = 1200 \text{ Ohms}$$
$$l_2 = 1000 \quad ,,$$
$$l_3 = 800 \quad ,,$$

from which it follows that the mean resistance is $l = 1000$ Ohms.

Two galvanometer resistances of 4400 and 4000 Ohms are raised by means of rheostats to 6200 Ohms and thus made equal to the third galvanometer resistance. We then get

$$g = 6200,\ a = \frac{l}{2g} = 0{,}08, \text{ and } E = e(1+a) = 1{,}08 \text{ cm.}$$

The sensitivity of each galvanometer must therefore be regulated in such a way that when in one of the circuits one millivolt is introduced, the string image that belongs to that circuit will show a deflection of 10.8 mms. The other string images will be deflected by 0.8 mms.

The curves obtained in this way show a complete agreement within the limits of observation with the formula quoted. In the measurement of a curve of complicated shape with a strongly negative peak R_{III} no deviation was found to be larger than 0.1 mm.

The simultaneous registration of the E. K. G. by three derivations has provided a new and not unwelcome proof of the accuracy with which the string galvanometer is capable of reproducing the potential oscillations of the human heart. For the direct practical proof that the formula for the three derivations is right, can only be given, when each of the three curves is accurate in itself.

It is worth mentioning, that the object can be obtained with the ordinary commercial string galvanometers. Our curves are obtained partly with the original model, partly with the double string-holder of the Cambridge model.

The method here described further opens the possibility of determining the manifest value and the direction of the potential difference in the heart itself, in an easy and certain way. If, in the measurements, one is obliged to use curves which have been registered one after the other, one often meets with difficulties. If the curves have a complicated form it is not always easy to ascertain the corresponding phases of a heart period that has been registered by derivation I, for instance, and of another period by derivation II or III.

Moreover, one heart contraction is not exactly like another. At a superficial glance the E.K.G. of the same series, appear so similar to one another, that one would take one period for the reproduction of another, but, when measured, numerous small differences appear which impede the accurate calculation of the direction and the manifest value of the potential difference. All these difficulties disappear when the E.K.G. is registered by the three derivations simultaneously.

The method is of service not only physiologically, but also clinically. For the object of practical cardiography is not to ascertain the potential difference that exists between one hand and another, or a hand and a foot, but to obtain an insight into the working of the heart itself [1]).

Physics. — "*The magnetic susceptibility and the number of magnetons of nickel in solutions of nickelsalts.*" By P. Weiss and Miss E. D. Bruins. (Communicated by Prof. H. A. Lorentz.)

§ 1. The purpose of this research was to investigate, how in connection with the magnetontheory the magnetic susceptibility of nickel in solutions of nickelsalts depends on the concentration of nickel in the solution. The research was made after Quincke's method improved by Piccard [2]).

Before and after every series of measurements water was measured of which the specific susceptibility or coefficient of magnetisation has of late years been determined with great accuracy after different methods.

For this coefficient Séve gives : $-0.725.10^{-6}$ at 22° C. [3])
Piccard : $-0.7193.10^{-6}$ „ 20° C. [2])
de Haas and Drapier : $-0.721.10^{-6}$ „ 21° C. [4])

In the following calculations has been used the value given by Piccard $\chi_{water\ 20^\circ C.} = -0.7193.10^{-6}$.

The coefficient of magnetisation χ_L of the solution is calculated with the formula:

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[1]) The complete account of the above investigation will appear elsewhere.

[2]) Die Magnetisierungskoeffizienten des Wassers und des Sauerstoffs. Promotionsarbeit von A. Piccard. Arch. de Genève 1913.

[3]) Sève. Paris 1912. Thêse. Ann. Chim. phys. (8) 27 p. 189—244. 1912.

[4]) De Haas und Drapier. Annalen der Physik. Band 42. p. 673—684. 1913.

$$\chi_L = \frac{k_1}{\gamma_1} + \frac{h_1}{h}\left(\chi_{water} - \frac{k}{\gamma}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

where: h_1 = the measured ascension of the solution.

k_1 = the susceptibility of the air which is above the meniscus of the solution. At 20° C. and a pressure of 760 m m. $k = 0.0294 \,.\, 10^{-6}$.

Therefore $k_1 = 0.0294.10^{-6} \frac{p_1}{760}\left(\frac{293}{T}\right)^2$,

where p_1 indicates the atmospheric pressure decreased with the moisture of the air.

γ_1 = the density of the solution.

h = the measured ascension of the water.

k = the susceptibility of the air which is above the meniscus of the water.

γ = the density of the water.

If the solution contains $x^0/_0$ of the nickelsalt, we have according to WIEDEMANN'S law:

$$\chi_L = \frac{(100 - x)\,\chi_{water} + x\chi_{Ni\,salt}}{100} \quad . \quad . \quad . \quad . \quad (II)$$

This $\chi_{Ni\,salt}$ multiplied by the molecular weight of the nickelsalt in question gives the molecular coefficient of magnetisation χ^m. From χ^m the coefficient of magnetisation χ^a_{Ni} of the nickelatom has been deduced by making a correction for the diamagnetism of the anion.

These were taken:

$$\chi^m_{Cl_2} = -0.40 \,.\, 10^{-6}$$
$$\chi^m_{SO_4} = -0.37 \,.\, 10^{-6}$$
$$\chi^m_{(NO_3)_2} = -0.36 \,.\, 10^{-6}$$

which values have been deduced from those given by PASCAL by making a correction for the value of χ_{water}, which PASCAL has taken $-0.75 \,.\, 10^{-6}$.

The formula $\sigma_0 = \sqrt{(\chi^a_{Ni} \,.\, 3RT)}$ gives σ_0 the magnetic moment of the nickel pro gramatom at the absolute zero of temperature.

$n = \frac{\sigma_0}{1123{,}5}$ finally gives the number of magnetons of the nickelatom.

§ 2. In the first place the aqueous solutions of $NiSO_4$, $NiCl_2$ and $Ni(NO_3)_2$ were investigated.

They have been prepared from distilled water and cobaltfree nickelsalts from KAHLBAUM.

The concentration has been determined by analyzing the most concentrated solution after the electrolytic method [1]) with a platinum net for cathode and a platinum spiral for anode. The rest of the solutions were obtained from the analyzed by dilution. In order to insure accuracy some have been analyzed. For example the results of two analyses of a solution, which ought to contain 3,641 $^0/_0$ $NiCl_2$ according to the way it was prepared, were found to be 3,643 $^0/_0$ and 3,640 $^0/_0$ $NiCl_2$.

The following table gives the results obtained; in the fifth column are mentioned the values of χ^a_{Ni} reduced to 20° C. according to Curie's law (comp. § 5).

Aqueous solutions of $NiSO_4$.

	$^0/_0$ $NiSO_4$	T	$\chi^m_{NiSO_4}\cdot 10^5$	$\chi^a_{Ni}\cdot 10^5$	$\chi^a_{Ni\,20^\circ C.}\cdot 10^5$	n
param.	24.154 [2])	$291\overset{\circ}{.}6$	443.7	447.3	445.2	16.05
param.	16.345	291.3	444.0	447.7	445.0	16.05
param.	10.341	290.4	444.7	448.4	444.4	16.05
param.	3.116	290.2	446.6	450.3	446.0	16.07
				Average:	445.1	16.06

Aqueous solutions of $NiCl_2$.

	$^0/_0$ $NiCl_2$	T	$\chi^m_{NiCl_2}\cdot 10^5$	$\chi^a_{Ni}\cdot 10^5$	$\chi^a_{Ni\,20^\circ C.}\cdot 10^5$	n
param.	22.690 [3])	$289\overset{\circ}{.}3$	446.6	450.7	445.0	16.05
param.	16.121	289.3	447.2	451.2	445.5	16.06
param.	9.516 [4])	291.2	444.8	448.8	446.1	16.07
param.	5.890	291.1	443.6	447.6	444.7	16.05
param.	3.641	290.9	443.4	447.5	444.3	16.04
param.	3.156	289.2	446.2	450.2	444.4	16.02
diam.	1.244	290.8	444.3	448.3	444.9	16.05
diam.	0.623	290.8	442.8	446.8	443.4	16.03
				Average:	444.8	16.05

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[1]) Treadwell. Quantitative Analyse.

[2]) Average of the results of two analyses: 24.154 and 24.154.

[3]) Average of the results of two analyses: 22,695 and 22,685.

[4]) Average of the results of two analyses: 9,513 and 9,519.

Aqueous solutions of $Ni(NO_3)_2$.

	$^0/_0 Ni(NO_3)_2$	T	$\chi^m_{Ni(NO_3)_2} \cdot 10^5$	$\chi^a_{Ni} \cdot 10^5$	$\chi^a_{Ni\,20^\circ C.} \cdot 10^5$	n
param.	37.164 1)	$289\overset{\circ}{.}4$	445.9	449.5	444.0	16.03
param.	26.953	289.4	447.9	451.5	445.9	16.07
param.	14.873	289.3	447.9	451.5	445.8	16.07
param.	7.098	289.3	448.0	451.7	446.0	16.07
diam.	1.016	289.2	447.8	451.4	445.5	16.06
				Average:	445.4	16.06

Before we draw conclusions from the results obtained their accuracy must be tested. The error in the value used for χ_{water} is not greater than $3^0/_{00}$ at most 2), from these, $2^0/_{00}$ are a consequence of the error in the measurement of the normal electromagnetic field. The proportion of the susceptibility of the solution to that of the water, however, is independent of the error in the field; as in this research the proportion of the susceptibility of the solution to that of the water has really been determined, it is only the inaccuracy in the determination of the ascension, which was $1^0/_{00}$ at most, which consists in that proportion obtained, while in the final results the error of χ_{water} remains as well. From the results of the analyses it is evident, that the error in the concentration always remains below $1^0/_{00}$.

Thus within the limits of experimental accuracy the value of $\chi^a_{Ni\,20^0C}$ and also the number of magnetons seems to be independent of the nature of the salt and of the concentration of the solution. This result agrees with that of CABRERA 3), who from his research about the aqueous solutions of nickelsalts also concluded the atomsusceptibility to be independent of the concentration and the nature of the salt. For the number of magnetons of the nickelatom in solutions of $NiSO_4$, $NiCl_2$, and $Ni(NO_3)_2$ he respectively gives the numbers 16,07, 16,03 and 16,02.

The number of magnetons of nickel in dissolved nickelsalts thus seems to be a whole number within the limits of experimental accuracy and as such supports the magneton theory.

§ 3. Then the ammoniacal solutions of nickelsalts were investigated.

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1) The analyses gave $37{,}164^0/_0$ and $37.131^0/_0$, the former value has been taken, because the second is less reliable.

2) A. PICCARD, ibid. p. 53.

3) CABRERA, MOLES et GUZMAN, Arch. de Genève T. XXXVII, p. 330, 1914.

If ammonia is added to an aqueous solution of a nickelsalt, we get the blue coloured solution of the complex nickel-ammonia compound. As with these solutions the strong evaporation of the ammonia makes it impossible to determine with sufficient accuracy the correction for the magnetic susceptibility of the air, these measurements were carried out under an atmosphere of hydrogen and ammonia, which was obtained by leading the hydrogen through an aqueous NH_3-solution of about the same NH_3-concentration as the solution to be investigated. The magnetic susceptibility of this atmosphere is so small, that it may be taken equal to zero, thus formula (I) becomes, as with these measurements the water measurements also were made under a hydrogenatmosphere:

$$\chi_L = \frac{h_1}{h}\,\chi_{water} \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I')$$

The calculation of $\chi_{\text{Ni salt}}$ from χ_L with the ammoniacal solutions is performed analogous to the calculation of $\chi_{\text{Ni salt}}$ from χ_L with the aqueous solutions. However not only the susceptibility of the water but also that of the ammonia must be taken into account.

The measurements of aqueous ammonia solutions gave for χ_{NH_3}:

$$\begin{array}{rl} & -\,0{,}947.10^{-6} \\ & -\,0{,}950.10^{-6} \\ & -\,0{,}942.10^{-6} \\ & -\,0{,}954.10^{-6} \\ \hline \text{Average:} & -\,0{,}948.10^{-6} \end{array}$$

while Pascal gives: $\chi_{NH_3} = -\,0{,}881.10^{-6}$.

Instead of formula (II) we get:

$$\chi_L = \frac{(100-x-y)\,\chi_{\text{water}} + y\,\chi_{NH_3} + x\,\chi_{\text{Ni salt}}}{100} \quad . \quad . \quad . \quad (II')$$

where x indicates the percentage of nickelsalt, y that of ammonia.

As from some experiments in the beginning it was evident, that with a *certain* concentration of the nickelsalt within the limits of experimental accuracy a fixed value was found for $\chi_{\text{Ni salt}}$ calculated with formula (II) for *different* NH_3-concentrations, the conclusion may be drawn that χ_{NH_3} has the same value no matter in what degree the ammonia is bound to the nickelsalt or finds itself free in the solution. The susceptibility therefore may be assumed as an additive property and the correction for the ammonia may be deduced from the whole ammonia quantity.

The following table gives the results obtained with the ammonical solutions:

Ammoniacal solutions of $NiSO_4$.1)

	$^0/_0$ $NiSO_4$	$^0/_0$ NH_3	T	$\chi^m_{NiSO_4}\cdot 10^5$	$\chi^a_{Ni}\cdot 10^5$	$\chi^a_{Ni\ 20^\circ C.}\cdot 10^5$	n
param.	4.441	8.628	290°1	419.7	423.4	419.2	15.58
param.	3.244	8.061	290.0	419.9	423.6	419.3	15.58
diam.	2.527	6.225	290.0	420.3	424.0	419.7	15.59
diam.	1.522	6.557	293.1	415.1	418.7	418.9	15.57
diam.	1.078	3.479	291.0	420.5	424.2	421.2	15.62
diam.	0.535	2.937	291.1	421.0	424.7	421.9	15.63
					Average :	420.0	15.59

Ammoniacal solutions of $NiCl_2$.2)

	$^0/_0$ $NiCl_2$	$^0/_0$ NH_3	T	$\chi^m_{NiCl_2}\cdot 10^5$	$\chi^a_{Ni}\cdot 10^5$	$\chi^a_{Ni\ 20^\circ C.}\cdot 10^5$	n
param.	4.342	6.875	290°.9	417.6	421.6	418.6	15.57
param.	3.141	7.517	291.0	417.0	421.0	418.2	15.56
diam.	2.209	6.704	289.4	418.2	422.3	417.1	15.54
diam.	1.688	4.478	290.8	417.5	421.5	418.4	15.56
diam.	1.197	3.744	289.4	420.1	424.2	419.0	15.58
diam.	0.569	1.901	289.5	421.5	425.6	420.5	15.60
					Average :	418.6	15.57

Ammoniacal solutions of $Ni(NO_3)_2$.3)

	$^0/_0$ $Ni(NO_3)_2$	$^0/_0$ NH_3	T	$\chi^m_{Ni(NO_3)_2}\cdot 10^5$	$\chi^a_{Ni}\cdot 10^5$	$\chi^a_{Ni\ 20^\circ C.}\ 10^5$.	n
param.	5.276	5.520	290°.9	417.2	420.8	417.8	15.55
param.	4.262	6.692	290.9	417.5	421.2	418.1	15.56
diam.	3.032	4.566	291.2	418.5	422.1	419.5	15.58
diam.	2.556	5.639	289.6	421.0	424.6	419.7	15.59
diam.	1.919	5.512	289.5	421.0	424.7	419.6	15.59
diam.	1.041	4.918	289.5	420.7	424.4	419.3	15.58
					Average :	419.0	15.57

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1) These solutions were prepared by dilution, and mixture of an aqueous $NiSO_4$-solution, for which two analyses gave 16,587 and 16,592 $^0/_0$ $NiSO_4$ and a solution of ammonia in water, for which two analyses gave 11,53 and 11,49 $^0/_0$ NH_3. The ammonia analyses were performed by titration with $^1/_2$ normal chloric acid.

2) These solutions were prepared by dilution and mixture of an aqueous $NiCl_2$-solution for which two analyses gave 17.216 and 17.190 $^0/_0$ $NiCl_2$ and a solution of ammona in water for which two analyses gave 11.782 and 11.783 $^0/_0$ NH_3.

3) These solutions were prepared by dilution and mixture of an aqueous solution of $Ni(NO_3)_2$, for which two analyses gave 19.539 and 19.514 $^0/_0$ $Ni(NO_3)_2$ and the same NH_3-solution in water as with the ammoniacal $NiCl_2$-solutions.

From the results obtained the conclusion may be drawn, that for the ammoniacal solutions $\chi^a_{Ni\,20^\circ C.}$ and also the numbers of magnetons are somewhat smaller than the corresponding quantities for the aqueous solutions. For the three salts investigated this difference is the same within the limits of experimental accuracy, for instance this difference is for the number of magnetons 0.47 0.48 and 0.49 respectively for the $NiSO_4$, $NiCl_2$ and $Ni(NO_3)_2$ solution.

§ 4. Addition of H_2SO_4 to a aqueous solution of $NiSO_4$ and of $(NH_4)_2SO_4$ to an ammonical solution of $NiSO_4$ evidently was without influence on the number of magnetons:

% $NiSO_4$	% H_2SO_4	n
3.619		16.01
3.241	9.493	16.02

% $NiSO_4$	% NH_3	% $(NH_4)_2SO_4$	n
3.659	8.308		15.46
3.187	7.238	12.884	15.48

§ 5. Finally it has been investigated how χ^a_{Ni} depends on the temperature, by measurements of a aqueous $NiCl_2$-solution at 6°.0, 16°.7 and 89°.7 C. and of an ammoniacal $NiCl_2$-solution at 6°.7, 18°.8, 20°.2 and 56°.2 C.

As only that part of the tube which was in the magnetic field had the temperature T, while the rest of the tube and the basin in which the end of the tube had been immersed were at the temperature t° C. of the room, a correction must be made for the inhomogeneity of the liquid in the tube and the basin; therefore formula (I′) becomes:

$$\chi_L = \frac{h_1 \dfrac{\gamma^T}{\gamma_t}}{h} \chi_{water}$$

where γ^T indicates the density of the solution at the temperature T, and γ_t the density of the solution at the temperature t.

The coefficients of dilatation necessary for the calculation of γ_T have been determined:

Coefficient of dilatation of an aqueous $NiCl_2$-solution containing 4.614 % $NiCl_2$ between 5°.0 C. and 18°.8 C.: 0.00021

between 5°.9 C. and 22°.0 C,: 0.00017

Average: 0.00019

between 18°.8 C. and 89°.5 C.: 0.00042
between 22°.0 C. and 90°.3 C : 0.00044
Average: 0.00043

Coefficient of dilatation of the solution containing 4.611 % $NiCl_2$ and 6.782 % NH_3 between 4°.8 C. and 19°.1 C.: 0.00023
between 3°.7 C. and 19°.8 C.: 0.00018
Average: 0.00020

between 19°.1 C. and 59°.0 C.: 0.00037
between 19°.8 C. and 60°.8 C.: 0.00039
Average: 0.00038

These measurements were also executed under a hydrogen atmosphere and gave the following results:

% $NiCl_2$	T	$\chi^a_{Ni} \cdot 10^5$	$\chi^a_{Ni} \cdot T$	t
4.614	279°.0	466.7	1.302	19°.1 C.
4.614	289.7	450.7	1.306	16.7
4.614	362.7	357.7	1.297	18.4
		Average:	1.302	

$\chi^a_{Ni} \cdot T$ calculated from the above average 444.8 for $\chi^a_{Ni\ 20^\circ C.}$ gives **1.303**.

% $NiCl_2$	% NH_3	T	$\chi^a_{Ni} \cdot 10^5$	$\chi^a_{Ni} \cdot T$	t
4.611	6.782	297°.7	434.9	1.216	20°.9 C.
4.611	6.782	291.8	418.9	1.222	18.8
4.605	6.800	293.2	418.2	1.226	21.2
4.605	6.800	329.2	372.3	1.226	20.6
			Average:	1.223	

$\chi_a^{Ni} \cdot T$ calculated from the above average 418.6 for $\chi^a_{Ni\ 20^\circ C.}$ gives **1.226**.

From the results obtained it is evident, that within the limits of experimental accuracy the atomsusceptibility of nickel in solutions of nickelsalts follows CURIE's law.

Zürich, July 1914. *Eidgenössisches Physikgebäude.*

Physics. — *"Magneto-chemical researches on ferrous salts in solution"*. By P. Weiss and Miss C. A. Frankamp. (Communicated by Prof. H. A. Lorentz).

The investigation included ferrous sulfate 7 aq. and the ammoniacal double-salt thereof, ferrous-ammonium sulfate 6 aq.

According to the method of Quincke, as it has been finally improved by Piccard [1]), the ascension is measured of the solution, placed between the pole-pieces of a Weiss-magnet. Standard-liquid is distilled water, which is also used in preparing the solutions.

According to the equation:

$$\chi = \frac{k_{o_1}}{\varrho_{\text{sol.}}} + \frac{h}{h'}\left(\chi' - \frac{k_{o_2}}{\varrho'}\right)$$

we are able to deduce the coefficient of magnetisation from the ascension; χ being this coefficient, χ' the one, belonging to water, k_{o_1} and k_{o_2} the susceptibilities of air at the average temperatures of the experiment, finally h and h' the ascensions of the solution and of water respectively.

The meaning of the ϱ's is evident.

By means of the theorem of Wiedemann

$$\chi = \left(1 - \frac{x}{100}\right)\chi' + \frac{x}{100}\chi_v,$$

x being the percentage in weight of the salt without aq, χ_v has been calculated, which, multiplied by the molecular weight of the salt, gives the molecular coefficient of magnetisation.

After correction as to the diamagnetism of the other elements, the atomic coefficient of magnetisation of iron χ_a is obtained, from which, by means of the well-known formulae:

$$\sigma_{m_0} = \sqrt{3RT\chi_a}$$

and

$$n = \frac{\sigma_{m_0}}{1123.5}$$

the number of magnetons may be derived; σ_{m_0} being the maximum value of the molecular magnetisation at the absolute zero, whereas 1123.5 indicates the average value of the so-called grammagneton [2]).

Since ferrous-salts, and ferrous sulfate in particular, are easily oxydated when exposed to the air and even in solutions, we soon carried out our measurements in a magnetical-indifferent atmosphere

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[1]) A. Piccard. Diss. 1913 Zürich.

[2]) P. Weiss. Physik. Zeitschrift 1911 S. 935.

of hydrogen, which at the same time simplified our calculations considerably.

Henceforth the solutions were prepared with boiled water.

They were analyzed as well by precipitating with ammonia as by reducing with potassiumpermanganate 1); in the first case we oxydated with nitric acid till the entire transformation into ferric-salt had taken place; whereas in the second case the permanganate was tested with oxalate; the second method proved sodium the most reliable (accuracy $4\,^0/_{00}$).

Save the ferrous sulfate of MERCK, all the material was provided by KAHLBAUM.

The ferrous ammoniumsulfate was the so-called "Manganfreie Morsche Salz". On account of the ferric-salts, examined till then 2), we could expect a dependence of the number of magnetons on the concentration with ferrous-salts as well.

However, our experiments showed an absolute constancy of this number as may be seen from the following tables:

TABLE I. Ferrous-sulfate.

$\chi \cdot 10^6$ solution	$\chi_a \cdot 10^4$ after correction	$n = \frac{\sigma_0}{1123.5}$	T	$^0/_0$ of salt
— 0.321	123.3	26.49	288°.6	0.488
— 0.319	122.9	26.48	288.6	0.492
— 0.306	121.9	26.46	290.7	0.512
— 0.0014	122.6	26.45	288.8	0.885
-- 0.0223	122.4	26.56	291.1	0.915
+ 0.2724	121.9	26.46	290.7	1.229
+ 1.256	122.0	26.45	290.3	2.445
+ 2.358	122.0	26.47	290.7	3.810
+ 6.140	121.1	26.52	294.1	8.560
+ 8.100	123.3	26.56	289.6	10.800
+ 9.010	121.4	26 57	294.2	12.100
+ 12.160	123.1	26.55	289.8	15.800
+ 12.420	122.8	26.56	290.9	16.170
+ 15.870	121.2	26.54	294.2	20.700

Average value of n — 26.51.

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1) TREADWELL, Quantitative Analyse.

2) B. CABRERA et E. MOLES, Mai 1913 Arch. des Sc. Ph. et N. Genève, whose results were on the whole confirmed by our own experiments (not published though).

TABLE 11. Ferrous-ammoniumsulfate.

$\chi \,.\, 10^6$ solution	$\chi_a \,.\, 10^4$ after correct.	$n = \frac{\sigma_0}{1123.5}$	T	$^0/_0$ of salt
— 0.609	121.5	26.49	293°.2	0.2503
— 0.606	121.6	26.49	292.2	0.2549
— 0.602	120.8	26.45	292.5	0.2639
— 0.512	120.6	26.47	294.4	0.485
— 0.407	121.3	26.47	292.3	0.726
— 0.397	121.2	26.49	293.0	0.751
— 0.057	123.1	26.54	289.3	1.520
+ 0.135	122.3	26.50	290.8	1.975
+ 0.152	122.7	26.48	289.2	2.007
+ 0.544	122.4	26.44	289.0	2.918
+ 0.563	121.2	26.44	292.0	2.980
+ 0.570	122.0	26.46	290.5	2.990
+ 0.587	121.9	26.45	290.5	3.030
+ 1.204	121.6	26.48	291.8	4.470
+ 1.179	121.2	26.44	291.8	4.430
+ 1.440	122.9	26.52	289.6	5.000
+ 1.877	122.0	26.50	291.2	6.020
+ 3.510	122.6	26.53	290.4	9.750
+ 3.580	121.7	26.44	290.9	9.980
+ 3.880	121.5	26.50	292.4	10.710
+ 4.740	122.9	26.57	290.8	12.570
+ 5.820	122.5	26.59	291.9	15.120
+ 6.890	123.3	26.59	290.4	17.450

Average value of n — 26.49.

However, in the lower concentrations, the state of things never seemed so simple — now the number of magnetons rose to 27 and higher, now it fell to 26.

The thought of traces of impurity suggested itself first; or perhaps the salt contained an excess of acid, however small it might be.

Yet, a great many experiments, where solutions were measured with widely different additions of sulphuric acid, showed again and again the independence of such influences — and as moreover it was evident from these experiments that solutions, thus prepared, were more constant and therefore more fit for experiment, we finally carried out our measurements of the lower concentrations on acid solutions only.

So here too the constancy of n showed itself.

To be able to calculate the results, special measurements were required on sulphuric acid and out of the following dates the average value for lower concentrations $\chi . 10^6 = -0.358$ is used.

The dates, marked * are taken from Cabrera [1]).

TABLE III. Sulphuric acid.

$\chi_m . 10^6$	%
−0.358	8.250
−0.336 *	9.282 *
− 0.350	24.110
−0.352	27.150
−0.364	43.500
−0.357	46.200
−0.379 *	60.300 *
−0.389	90.800
−0.392	90.800

Notwithstanding this, there still remained the first deviations in the strongly diluted solutions and the question was to which cause they ought to be attributed.

It was natural to consider the increased magnetisation as the effect of oxydation, the more so since Cabrera and we found higher values for the ferric sulfate.

However, a solution of 0.25 % with an excess of acid of 1.04 %, gave, after having been heated in boiling water and cooled again, exactly the same value.

This experiment might be considered as a disproof. At the same time it shows how the addition of an acid is an essential condition to the constancy of the solution, so that finally the chief cause seems to be the hydrolysis, which is checked by the acid.

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[1]) Cabrera, Arch. des Sc. Ph. et Nat. Dec. 1913 Genève.

If, on the other hand, we could further the hydrolysis, and thus accelerate the "transformation in time" which showed itself in many cases, a positive proof would be given.

Since, however, traces of NaOH already form a fine granular precipitate, such an experiment seems to be excluded from measurement.

The chemical complications, which in particular for iron-salts are so numerous, constantly impede the investigation of these salts.

Zürich Juli 1914. *Physikgebaüde des Eidgenössischen*
Polytechnikums.

Microbiology. — *"A microsaccharimeter".* By Miss. H. J. VAN LUTSENBURG MAAS and Prof. G. VAN ITERSON JR. (Communicated by Prof. M. W. BEIJERINCK.)

In the conscientious and extensive work of A. J. KLUYVER: "Biochemische suikerbepalingen" [1]) (Biochemical Sugaranalysis) a fermentation-saccharimeter is described, which enables us to quantitative fermentations under perfect sterile circumstances. The quantities of the different fermentable sugars, possibly at the same time present, are to be calculated from the quantities carbonic acid, produced in such an apparatus from a fixed volume liquid by different ferments.

The rich material, which KLUYVER published, shows in a convincing way, how this apparatus gives a most satisfactory and at the same time simple solution for the problem of quantitative sugar-determinations by means of the fermentation-method. Such a solution has in spite of the researches of many predecessors never been found.

The application of this method in studying biological questions, from which KLUYVER gives already some interesting examples, promises most important results.

By no means the fermentation-saccharimeter, whose description will follow, will be able to supersede the apparatus, used by KLUYVER. The latter will always be preferred when accuracy is required and a sufficient quantity of the sugars is to be had. The reason why, will be explained later, we only mention it here, because the applicability of the here described method is justified by the results, found with the apparatus of which KLUYVER gives the description.

In the first place some remarks may follow on this last apparatus and the limits of what can be attained will be indicated.

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[1]) Published by E. J. BRILL at Leiden, 1914.

In the current form the apparatus wants about 1 cc. liquid to ferment. By taking a smaller size this volume can be reduced to 0.5 cc., but the accuracy of the reading diminishes (influence of the convex mercury meniscus). For constructive and practical reasons it seems impossible to reduce the size more.

The quantity of fermentable sugar, used in the apparatus of ordinary size is about 40 mgr. (corresponding with 10 cc. CO_2) and should not be less than 4 mgr. The last limit is determined by the circumstance, that almost an equal volume of the carbonic acid as is produced from this quantity of sugar by the fermentation is soluble in 1 cc. of the sufficiently fermented liquid under average barometric pressure and at the temperature of the room. By applying a manipulation, viz. the addition of a known, small quantity fermentable sugar, it is possible to determine smaller quantities of sugar with this apparatus, but the analysis is not very accurate in that case. With the developing of small quantities of carbonic acid the influence of the factor, which is to be charged for the gas, dissolved in the fermented liquid, is comparatively very large, and just this factor is by the changing composition of that liquid always somewhat uncertain.

The inoculation-material for this apparatus is a small quantity of yeast, which is taken from a tube-culture with the aid of a thick platinum needle. That yeast quantity is so chosen by KLUYVER, in connection with a research of JODLBAUER, that the proportion yeast to sugar is about 1 : 2. The influence of the autofermentation is cancelled. With this yeast-concentration the fermentable sugars have usually completely disappeared after about 40 hours (when raffinose is present the time, necessary for the fermentation is much longer). This long fermentation makes it necessary to sterilize carefully the apparatus, the fermenting mixture and the mercury, shutting off the liquid.

For many biological researches a method for quantitative sugar-analysis would be desirable for quantities smaller than 1 cc. and often it will be necessary to estimate smaller portions than 4 mgr. with greater accuracy than is possible with the aid of the manipulation in the apparatus referred to. Therefore now an apparatus will be described with which this purpose can be reached. The quantities of sugar, which can be fermented are between 3.5 mgr. and 0.1 mgr. and a drop of 0.010 cc. will be sufficient to perform the analysis, though it is preferable to take a larger quantity of the liquid. Moreover it will be evident that with this new method the fermentation will be much sooner finished than with the old one, so that no sterile circumstances are necessary.

§ 1. *Description of the microsaccharimeter.*

The principal part of the microsaccharimeter (see the Plate , fig. 1) is made of a capillary tube of thick glass, with an inner diameter of about 2.8 mm. At a short distance from one of the ends this tube has been blown to a cylindric reservoir, the content of which is about 1 cc. and with a short neck. The other end of the tube has been enlarged to a funnel, of a content of about 1.5 cc. The length of the glass apparatus, measured from the point on the utmost right to the utmost left is about 35 cm. (in connect with the usual dimensions of the thermostats). The capillary tube has such a curve under the reservoir that the longest, straight part (see fig. 1) mounts to about half way the reservoir. This long straight part has been calibrated; the scale-division is in parts, each from 0.01 cc. The zero-point is as near as possible to the downward directed curve and the division continues till the upward bent. With the here mentioned dimensions this division will go to about 0.9 cc. and it is desirable, that it should not be much shorter. The dimensions are for the rest so chosen, that the content of the reservoir is a bit smaller than that of the bent and straight part of the capillary tube and the funnel together, a circumstance, which is to be observed by the constructor of the apparatus. The finishing of the neck of the small reservoir is to be done carefully. The opening of that neck is upward somewhat enlarged in a conical form, while also from the very short, narrow part of this opening downward a very regular conical transition must be (see fig. 3).

The glass apparatus is placed on a small stand (see fig. 2), made from a wooden platter (5.5×38 cm^2.), on which a wooden block has been fastened, that bears a cork clamp. This clamp is made from a conical cork of good quality (largest diameter 4 cm., high 3.5 cm.). This cork has on the short side a groove, which continues to some distance from the large side. The curved part of the capillary tube fits in this groove. The cork is further on at two sides filed parabolical (see fig. 2).

The glass apparatus is to be fixed in every desired stand by a brass pin with winged nut, fitting in the cork just above the curve of the capillary tube. By removing the brass pin the glass apparatus can be taken from the stand, which is necessary to clean it. To sterilize the apparatus is superfluous, but it should be dried carefully.

The two mercury levels, being after the fermentation in the reservoir and in the divided part of the capillary tube, can be placed on the same height by different simple ways. A rather good method

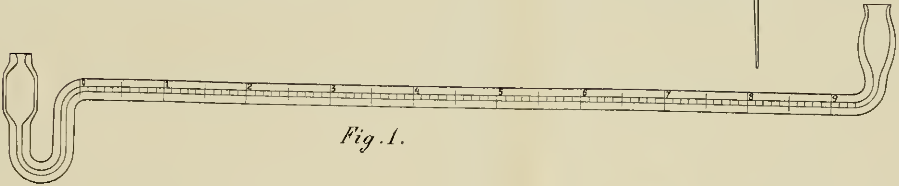

Fig. 1.

Fig. 3.

Fig. 4.

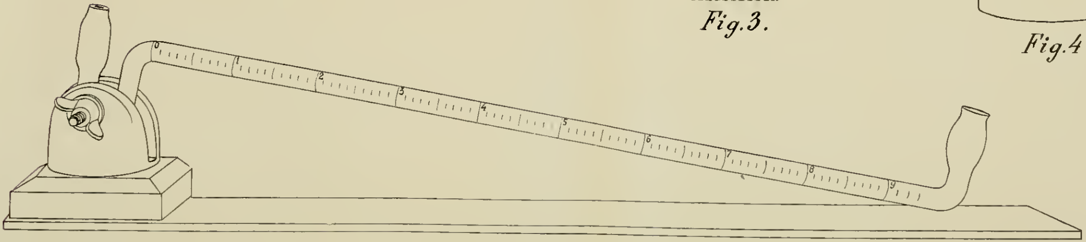

Fig. 2.

is by using an apparatus as shown in figure 4. This apparatus bears a pin, which can be moved over a vertical stand. The pin reaches before the microsaccharimeter, when the stand is placed behind it. To compare the mercury levels all is placed on an exactly horizontal table and by removing the apparatus over this table and changing the angle between the capillary tube and the platter, the two levels can be brought on exactly the same height.

For using this microsaccharimeter we want (besides different ferment-cultures): dried and cleaned mercury, paraffin with a melting-point of about 55° C., red sealing-wax of superior quality, some metal spatulas, a platinum spatula in a needle-holder, a number of dropping syringes, some capillary tubes (diameter 1 mm.), some small sterile glass tubes with cotton-wool stops and sterile main-water.[1])

§ 2. *Preparation of the yeasts.*

For a quantitative analysis with the microsaccharimeter the yeast is to be submitted to a very simple preparation. The yeast quantity, used in this apparatus is in proportion to the quantity of sugar rather large. So the volume of the carbonic acid, developed out of the glycogen present in the yeast can often be very important compared to the gas, produced by the fermentation of the sugar. This difficulty is to be prevented; before bringing the yeast in the apparatus, it is made free from glycogen by auto-fermentation.

The different ferments are the best cultivated in the ordinary culture-tubes on the surface of malt-gelatine. When tubes of a large size are used, one contains enough yeast to do at least six quantitative determinations with the microsaccharimeter. With the aid of a sterile platinum spatula the yeast is to be carefully taken from the gelatine-surface and divided in some cc. sterile main water in a glass tube stopped with cotton wool. Then the tubes with the different yeasts are placed in a thermostat at 30° C. With the aid of the iodine reaction it can be settled that under these circumstances all the glycogen has disappeared by auto-fermentation after four hours.

After this preparation the yeast has sunk to the bottom of the tube and the water, standing above, can easily be taken away with a dropping syringe. For this no sterile syringe is wanted, but for each other kind of yeast a new or cleaned one is to be used.

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[1]) The microsaccharimeter is to be had at J. C. Th. Marius, Lim., Utrecht the ferment cultures at the "Centralstelle für Pilzkulturen" at Amsterdam.

In the water above the yeast but little carbon dioxide is dissolved In the following calculation the water has been supposed to contain no carbonic acid, so a small, practically to be neglected, mistake is made. This mistake is completely to be avoided by refreshing the water above the sunken yeast, which too should be taken away with a dropping syringe. The sunken yeast is divided in the remaining water and brought into the saccharimeter with a capillary tube.

§ 3. *Method of using.*

In the first place the microsaccharimeter is to be filled with a certain quantity of dried, cleaned mercury.

The nut-wing is unscrewed and the glass apparatus placed as fig. 2 shows. The filling is done by the funnel, with a dropping syringe. When the funnel is full, it is carefully raised; the mercury streams to the reservoir *A* and remains partly in the capillary tube. The next lowering of the funnel makes the mercury stream partly back. By addition or removal of mercury the quantity can be taken so, that the reservoir with its neck and the capillary tube is filled as far as or just past the zero-point. To control this, the funnel is raised till the mercury reaches the border of the opening of the neck; the mercury will then be adjusted at zero, or between the first marks. After the apparatus has been filled with mercury, it is placed in the original position and with the aid of a metal spatula a bit of paraffin, melted on that spatula, is spread on the polished surface of the neck.

Only a thin cover is wanted, but it should reach the border of the opening; it is even to be preferred to cover the inner-wall of this neck over a short distance, but it is not necessary.

Now the nut-wing is fastened, but so, that the glass apparatus can still be moved in the cork and remains in every required position, when released. Then the apparatus is placed so that the tangentplane to the mercury level in the neck coincides with the paraffin cover. Therefore the eye is kept in the tangent-plane to this surface and the funnel is to be raised till the mercury meniscus can just be seen. In this phase the *first reading* of the mercury in the calibrated tube is made.

By the action of the capillarity in that calibrated tube a strongly convex meniscus is formed and the position of the utmost tangent-plane is to be read without difficulty with the naked eye up to in tenth parts of the calibration.

Next a drop of the fermenting liquid is brought on the mercury and on the surface of the neck with the aid of a dropping syringe. The size of this drop is to be regulated by the quantity of sugar to be fermented. This quantity ought not to surpass 3.5 mgr. and practically not to sink under 0,1 mgr. The concentration of the solution should be more than 0,4°/₀. Good results are to be had with a 3°/₀ sugar solution, from which it is best to take drops of 0,06—0,08 cc.

After this the funnel is carefully lowered; thereby the drop of liquid is drawn into the apparatus. This can be performed without any loss of liquid, if only the paraffin cover have been laid down in the right way on the neck of the reservoir. Should however any liquid be left behind, then this has to be removed with a small piece of filter-paper.

The meniscus of the solution in the upper part of the neck will be convex, especially when some paraffine had been brought along the inner side of the neck. This shape of the meniscus can be obtained in the best way by making the solution rise from a lower part of the neck up to the top, taking care however, not to have it lowered under the narrow part. In this way it is possible to bring the tangent-plane at the meniscus on the level of the upper surface of the neck. After fixing the apparatus in this position, the 2nd *reading* of the meniscus of the mercury in the straight capillary glass tube is made.

The difference between the two first readings gives: the volume of the sugar solution to an accuracy of 0,001 cc.

Now again the liquid is a bit lowered, but not so far as to reach the narrow part. Then, with a thin capillary glass tube, we add a drop of yeast-suspension, which has been prepared previously as already indicated. The drop is carefully thrown into the apparatus, until the meniscus, which again will be convex, reaches the same level as mentioned before. Now the 3rd *reading* is taken.

The difference between the 3rd. and the 2nd. reading gives: the volume of the added yeast-suspension. Care must be taken that to 1 part of sugar about from 5 to 8 parts of yeast be added (weighed in living state)[1]). With sugar concentrations of about 3 per cent and with suspensions of yeast, prepared in the described way, this can be done by taking the volume of the suspension nearly the same as that of the sugar solution.

After this 3rd. reading the liquid is allowed to go down to the narrow part of the neck; there the meniscus will be decidedly con-

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[1]) Just by the choice of these large quantities of yeast, the fermentation-time is much reduced, compared with the duration of the analysis, made by Kluyver.

cave. Then one melts some paraffine on a small metallic spatula and lets it flow along the inner side of the neck on the surface of the liquid. In this way it is possible to fill up the whole upper part of the neck with paraffin, without any difficulty and with a startling result. No air bubble ought to be present between the liquid and the paraffin, but no difficulties will arise, should a bubble be present, provided its volume is small compared with that of the carbon dioxide, evolved by the fermentation. Once the paraffin solidified, the 4th *reading* is made.

After this the apparatus can be sealed definitively, for which sealing-wax was used, as paraffine shrinks, when it solidifies and easily gets loose from the glass. The application of the sealing-wax is as follow. At the outer side of the round upper part of the neck, a ring of paraffin is taken away with a small knife. Care should be taken, not to damage the stop of paraffin, which seals off the liquid in the neck. Now on a small metallic spatula some sealing-wax is liquefied by heating and the melted wax is put on the part of the neck, from which the paraffin had been taken away. Not before the wax is well fixed on the glass, a drop of liquefied wax is put on the paraffin stop. Now the whole closure can be perfected by adding more sealing-wax.

This done, one puts the apparatus in the thermostat of 30° C., fixing it in the position of figure 2. The fermentation will be completely finished within 6 hours[1]). This time past, the apparatus is taken from the thermostat and fastened in such a position, that the mercury in the capillary tube and in the reservoir are on about the same level. Two hours are quite sufficient to have the apparatus cooled to the temperature of the air. The 5th *reading* is then made, but not before the mercury in the tube and in the reservoir is carefully placed on the same level. This can be done, as already indicated, by means of the small auxiliary apparatus, described in § 1. As the same time the temperature of the air and the barometer are read. Now all *data*, necessary for the calculation of the analysis are known.

In the experiments, dealed with in § 5 of this communication, the preparation of the yeast took place in the morning; the micro-saccharimeters were put into the thermostat at about 3 o'clock in the afternoon and were taken out of the thermostat in the evening of the same day. The last reading was made next morning.

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[1]) Till now, we did not yet study the fermentation of raffinose with this apparatus, it seems possible, that this sugar will ask a longer time to ferment completely.

§ 4. *How to calculate the results.*

The difference between the 5th and the 4th reading gives: the volume of the gaseous carbon dioxide, present in the apparatus at the end of the fermentation. Another portion of carbonic acid however is retained by the liquid and this portion too has to be taken into account. Now KLUYVER observed, that when sugar is fermented in yeast-extract at 15° C. and 760 mm., in 1 cc. of the liquid a quantity of carbonic acid is left behind which has a volume of 1.2 cc. at 0° C. and 760 mm. (provided that supersaturation of the liquid is avoided). By BOHR and BOCK however it was pointed out that at 15° C. and 760 mm. pure water retains a volume of carbonic acid, which after reduction to 0° C. and 760 mm. amounts to 1,019 cc. The fact that KLUYVER found more, can be explained by the special nature of his liquid.

Though in our experiments the carbon dioxide was not dissolved in pure water, as every fermented liquid retains alcohol, yet our liquid approaches more to pure water than yeast-extract. It is very probable, that under these circumstances the foresaid number falls between the two numbers, mentioned above. Moreover our readings were made at temperatures between 17° and 20° C. Now the solubility of carbon dioxide diminishes rather rapidly, when the temperature rises. After BOHR and BOCK the foresaid volume becomes 0,878 cc. at 20° C.

For these reasons we assume the forementioned volume, under the conditions of our experiments, to be I cc. This simplifies the calculation.

The total volume of carbon dioxide of 0° C. and 760 mm. now can be found by reducing at first the gaseous carbon dioxide to that temperature and pressure, which may be done quite efficiently by means of a table, published by KLUYVER[1]). This done, the volume of all the liquid is to be added (viz. the difference between the 3rd. and the 1th. reading).

KLUYVER made a large number of determinations of the volume of carbon dioxide (reduced to 0° C. and 760 mm.), obtainable with 6 different species of yeasts from 40 mgr. of 8 different sugars in the apparatus, used by him (see table XXVIII of his publication). Then also the number of milligrammes of sugar, equivalent to 1 cc. of CO_2 at that temperature and under normal pressure were known. We have limited our experiments for the

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[1]) l. c. p. 61.

yeasts to *Saccharomyces cerevisiae* (press-yeast), *Torula dattila* and *Torula monosa*, and for the sugars to glucose, fructose, saccharose and maltose. Especially the quantitative determination of these sugars, separately or as mixtures will be required in biological research work. Now these determinations are possible with the 3 yeasts mentioned, with this exception alone, that glucose and fructose are always found together. The first of the 3 yeasts is capable to ferment the 4 sugars, the second the monoses and saccharose and the last ferments only monoses.

Now Kluyver established, that out of the 4 mentioned sugars in his apparatus nearly the theoretical quantity of carbon dioxide is produced. Certainly in our microsaccharimeter we may expect no smaller quantity of this gas, as reproduction of yeast is practically impossible within the 6 hours of our experiments, whilst under the circumstances of Kluyver some reproduction may be expected. Therefore we took the theoretical value to make our calculations. This means, that we supposed a yield of 1 cc. of carbon dioxide (of 0° C. and 760 m.m.) to be equivalent to 4.05 mgr. of absolutely dried hexose (respectively to 4,45 mgr. hexose-hydrate, containing 1 H_2O) and to 3,85 mgr. of absolutely dried bihexose (respectively to 4,05 mgr. of bihexose-hydrate, containing 1 H_2O).

§ 5. *Numerical illustration.*

Here follow some examples of determinations, which we performed with the microsaccharimeter. We give only a small number of applications of this apparatus on the analysis of natural products, as we intend to publish a more detailed communication on this subject later on. Here we principally mention the results of fermentations with sugar solutions; we took the most pure sugars to be got. Thus, with the numbers published here, we intend to demonstrate the applicability of the method.

1. A 3 per cent. solution of glucosehydrate was fermented by *Torula monosa*. The readings were successively: 0,012; 0,070; 0,128; 0,133 and 0,436 cc. The last reading was made at 19° C. and under a pressure of 767 m.m.

The gaseous carbon dioxide, present in the apparatus after the fermention, was 0,303 cc. After reduction to 0° C. and 760 mm. this becomes 0,286 cc. The volume of the liquid in the apparatus is found to be 0,116 cc. Thus, the whole volume of carbon dioxide of 0° and 760 mm., obtained by the fermentation, may be supposed to be 0,402 cc.

This carbon dioxide is equivalent to 0,402 × 4,45 = 1,78 mgr. of glucosehydrate. Originally the apparatus received 0,058 cc. of liquid, corresponding to 1,74 mgr. of glucosehydrate.

2. With *T. monosa* we fermented a 1 per cent. solution of glucosehydrate. The successive readings were: 0,020; 0,030; 0,041; 0,053; 0,059 cc. The last reading was taken at 19° C. and 760 mm. The quantity of gaseous carbon dioxide in the apparatus after fermentation is found to be 0,006 cc.; after reduction to 0° C. and 760 mm. this volume remains the same. The volume of liquid was 0,021 cc. Consequently the total amount of carbonic acid of 0° and 760 mm. may be assumed to be 0,027 cc. This gives 0,027 × 4,45 = 0,12 mgr. glucosehydrate, whereas we took 0,10 mgr.

3. In a similar way we obtained the following results by fermenting other solutions of glucosehydrate with *T. monosa*. The two corresponding numbers are placed one beneath the other.

Taken:	1.89	1.77	1.41	1.35	1.59	1.59	1.83	1.74	1.89	mgr.
Found:	1.74	1.78	1.41	1.38	1.57	1.64	1.81	1.78	1.86	mgr.
Taken:	2.01	0.34	0.30	0.21	0.19	0.10	2.16	1.71	0.84	mgr.
Found:	1.99	0.38	0.29	0.26	0.22	0.12	2.20	1.65	0.93	mgr.

4. Solutions of glucosehydrate, fermented by *T. dattila* gave the following results:

Taken:	1.29	2.67	1.62	2.04	1.68	1.32	1.89	1.56	1.65	1.98	1.89	mgr.
Found:	1.54	2.65	1.74	1.94	1.62	1.34	1.93	1.60	1.78	1.93	1.65	mgr.

5. In the same way we found by fermenting solutions of glucosehydrate with *S. cerevisiae* (press-yeast):

Taken:	1.56	1.83	2.13	2.13	2.04	1.80	2.31	1.50	mgr.
Found:	1.62	1.90	2.18	2.14	2.20	2.16	2.38	1.82	mgr.

6. Quantitative determinations of fructose by fermenting with *T. monosa* gave us:

Taken:	1.65	1.68	1.26	2.01	2.25	mgr.
Found:	1.58	1.69	1.23	1.97	2.10	mgr.

7. From similar determinations of fructose, fermented by *T. dattila* resulted:

Taken:	1.47	1.62	0.99	1.44	1.89	1.50	mgr.
Found:	1.67	1.88	1.12	1.44	1.88	1.64	mgr.

8. The results of fermenting fructose with *S. cerevisiae* were these:

Taken:	1.56	1.68	1.80	1.56	1.41	1.68	mgr.
Found:	1.51	1.81	1.80	1.60	1.15	1.63	mgr.

9. Saccharose, fermented with *T. dattila* gave:

Taken : 1.65 1.80 1.68 2.49 2.19 2.31 2.25 0.78 2.13 1.31 1.59 mgr.
Found: 1.66 1.76 1.76 2.47 2.27 2.20 2.17 0.82 2.13 1.38 1.67 mgr.
Taken : 1.86 1.71 1.62 1.59 2.31 1.74 1.31 1.65 1.77 1.77 2.10 1.83 mgr.
Found: 1.97 1.73 1.68 1.58 2.21 1.80 1.38 1.64 1.81 1.83 2.17 1.95 mgr.

10. Solutions of saccharose with *S. cerevisiae* gave the following numbers:

Taken: 1.41 1.53 2.19 2.25 2.70 1.23 2.13 1.50 1.59 1.59 mgr.
Found: 1.72 1.62 2.25 2.35 2.53 1.34 2.16 1.70 1.62 1.75 mgr.
Taken: 1.65 1.80 1.47 mgr.
Found: 1.93 1.90 1.59 mgr.

11. Solutions of maltose, fermented with *S. cererisiae*:

Taken: 1.26 1.80 2.46 2.31 1.83 1.65 2.52 1.86 1.68 1.35 1.38 mgr.
Found: 1.38 1.72 2.32 2.32 1.72 1.52 2.42 1.66 1.55 1.30 1.51 mgr.

12. With a solution, containing 3 per cent. glucosehydrate, 3 per cent. saccharose and 3 per cent. maltosehydrate, we undertook three fermentations, viz. with *T. monosa*, *T. dattila* and *S. cerevisiae*. With *T. monosa* the carbonic acid obtained from 0,045 cc. of the solution was 0,326 cc., with *T. dattila* 0,633 cc. from 0,045 cc. and with *S. cerevisiae* 0,932 cc. from 0,043 cc.; all gasvolumes being reduced to 0° C, and 760 mm. From these numbers we calculate that of 1 cc. of the solution 7,1; 14,1 and 21,7 cc. of carbon dioxide will be obtained by each of the 3 yeasts. Consequently there were obtained 7,1 cc. from monoses (here from glucose-hydrate), 7,0 cc. from saccharose and 7,6 cc. from maltosehydrate. This means a composition of the solution of 3,1 per cent. of glucosehydrate, 2,7 per cent, of saccharose and 3,1 per cent. of maltosehydrate.

13. Other determinations with solutions of the same composition gave the following results:

2,85 °/₀ glucosehydraat; 3,2 °/₀ saccharose; 2,7 °/₀ maltosehydrate.
2,98 °/₀ ,, 3,19 °/₀ ,, 2,84 °/₀ ,,

The three last numbers were calculated from the results of analysis, made in triplo.

14. Juice, pressed from a slice of orange, was diluted with water to the threefold of the original volume and the diluted juice was fermented with the three different yeasts. One cc. of this liquid practically gave the same amount of carbon dioxide, when fermented with *T. dattila* and with *S. cerevisiae*, so that maltose was absent. The composition of the undiluted sap was calculated as to be: 2,6 per cent of monoses and 3,1 per cent. of saccharose.

15. Nectar from *Nicotiana affinis*, after dilution to about the threefold of the original volume, was fermented with *S. cerevisiae.* Two drops from the same flower were brought into two small platinum scales and herein the water was added. (The weighings were made with a torsion-balance, accurate to 0,1 mgr.). The two analyses, made separately gave as results: 33,9 and 34,4 per cent. of sugar in the undiluted nectar; the sugar being calculated as hexose.

In studying the numbers published here, one will see, that on the whole the results obtained with the microsaccharimeter, were quite satisfactory. Add to this, that sugar determinations by chemical analysis too are of no great accuracy, whilst here we took only a few milligrammes of sugar. For the study of a large number of biological problems the accuracy that was reached here, certainly will be quite sufficient.

Laboratory for Microscopical Anatomy of the
Technical Academy.

Delft, July 1915.

EXPLICATION OF PLATE.

Figure 1. Longitudinal section of the glass apparatus of the microsaccharimeter.

Figure 2. General view of the microsaccharimeter (the glass apparatus fixed in the cork clamp).

Figure 3. Longitudinal section of the neck (enlarged) of the microsaccharimeter, filled with mercury, as for the 1th. reading.

Figure 4. Auxiliary apparatus, which may be used to place the mercury in the tube and the reservoir on the same level.

Chemistry. — "*Investigations on the Temperature-Coefficients of the Free Molecular Surface-Energy of Liquids between* —80° *and* 1650° *C.*" **X**. *Measurements Relating to a Series of Aliphatic Compounds.* By Prof. F. M. Jaeger and Dr. Jul. Kahn.

§ 1. For the purpose of comparison of the variations, which occur in the values of the molecular surface-energy of several derivatives of the aliphatic series, when simple substitutions have been made in them, it appeared necessary also to investigate in detail the surface-tension and its temperature-coefficient of the following compounds: *Ethyl-iodide, Ethylene-chloride, Ethylidene-chloride, Acetylene-tetrachloride, Acetylene-tetrabromide, Epichlorohydrine, Carbonbisulphide, Methylalcohol, Formic Acid, Mono-, Di-* and *Trichloroacetic Acid, Levulinic Acid, Nitromethane, Bromonitromethane, Capronitrile, Dimethylsuccinate, Diethylbromoisosuccinate,* and *Acetylacetone.*

In the following we publish the results of the measurements with these derivatives.

The determination of the specific gravity was made either by means of the pycnometer, or by means of volumeters especially constructed for that purpose, and which were previously accurately calibrated. If both these methods could not be applied, the determinations were made by the aid of a hydrostatic method, which some time ago was developed by the first-named of us originally for the purpose of measuring the densities of molten salts and liquid magmata at very high temperatures, and which will be described in detail on a future suitable occasion. By preliminary experiments and by comparison of the results thus obtained with those collected by other methods, the applicability and reliability of the method were proved and the degree of accuracy established; the last appeared to be no less than that reached by the usual way of measuring.

§ 2.

I.

Ethyl-Iodide: C_2H_5J.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
−20°.5	1.427	1903.1	32.5	2.024	580.7
0	1.337	1782.7	30.4	1.979	551.4
20.4	1.238	1650.9	28.1	1.934	517.6
40.4	1.143	1524.8	25.9	1.895	483.6
64.8	1.023	1364.3	23.1	1.845	439.0

Molecular weight: **152.88**.

Radius of the Capillary tube: 0.03489 cm.
Depth: 0.1 mm.

This carefully purified liquid boils under a pressure of 760 mm. at 72°.5 C.; according to TIMMERMANS it solidifies at −110°.9 C. At the boilingpoint χ has the value: 22.3 Erg.

The temperature-coefficient of μ is between −20° and 0° C.: **1.43**; between 0° and 20°.4 C.: **1.65**; and between 20° and 65° C.: **1.84** Erg per degree: evidently therefore it gradually increases with rising temperature.

II.

Ethylene-chloride: $C_2H_4Cl_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm mercury of 0° C.	in Dynes			
*—20°	1.176	1567.8	37.2	1.311	664.4
* 0	1.080	1439.8	34.1	1.283	617.9
29.9	0.961	1281.2	30.1	1.239	558.2
48	0.880	1173.8	27.5	1.213	517.2
58.9	0.831	1107.7	25.9	1.197	491.5
86	0.733	977.2	22.7	1.158	440.4

Molecular weight: **98.95**. Radius of the Capillary tube: 0.04839 cm.; in the observations indicated by *, the radius was: 0.04867 cm. Depth: 0.1 mm.

Under a pressure of 770 mm. the liquid boils constantly at 86° C. In solid carbondioxide and alcohol it crystallizes and melts at —31° C. At the boilingpoint χ has the value: **23.6** Erg.

The density at 15° C. was: 1.2609; at 25° C.: 1.2463; at 50° C.: 1.2103. At t° C.: $d_{4^\circ} = 1.2826 - 0.001446\, t$.

The temperature-coefficient of μ has a mean value of: **2.16** Erg per degree.

III.

Ethylidene-chloride: $CH_3 \cdot CHCl_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—76°	1.144	1525.2	35.9	1.329	635.4
*—21	0.903	1203.9	28.3	1.240	524.5
* 0	0.819	1091.1	25.7	1.207	485.0
30.4	0.722	963.0	22.4	1.159	434.3
47.8	0.663	884.4	20.6	1.130	406 2
60.9	0.626	834.9	19.4	1.109	387.4

Molecular weight: **98.95**. Radius of the Capillary tube: 0.04839 cm.; in the observations indicated by *, the radius was: 0 04867 cm. Depth 0.1 mm.

The liquid boils at 60°.9 C. under a pressure of 770 mm. At —80° C. it becomes turbid, but does not crystallize. According to TIMMERMANS the substance melts at —96°.6 C. At the boiling-point the value of χ is **19.4** Erg. pro cm². The density at 15 C. was: 1.1830; at t° C.: $d_{4^\circ} = 1.2069 - 0.0016\, t + 0.00000015\, t^2$.

The temperature-coefficient of μ decreases gradually with rise of temperature: between —76° and —21° C. it is: **2.00**; between —21° and 0° C.: **1.88**; between 0° and 30°.4 C.: **1.66**; between 30°.4 C. and 47°.8 C.: **1.61**; and between 47°.8 and 60°.9 C.: **1.43** Erg. per degree. The μ-t-curve is therefore a concave one.

IV.

Acetylene-tetrachloride: $C_2H_2Cl_4$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
*—21°	1.254	1672.4	39.4	1.657	856.2
* 0	1.171	1561.5	36.7	1.620	809.6
29.9	1.054	1405.2	32.7	1.570	736.6
47.4	0.983	1310.2	30.5	1.544	694.7
58.3	0.936	1248.2	29.0	1.526	665.8
87.1	0.834	1111.8	25.7	1.488	600.0
103.2	0.784	1045.7	24.1	1.468	567.7
117.7	0.725	967.1	22.2	1.452	526.8
127.8	0.694	925.8	21.2	1.440	505.9

Molecular weight: **167.86**.

Radius of the Capillary tube: 0.04839 cm.; with the measurements indicated by *, the radius was: 0.04867 cm.
Depth: 0.1 mm.

The liquid boils at 146°.3 under 758 mm. mercury. In solid carbondioxide and alcohol it solidifies, and then melts at —50° C. At the boiling-point χ is about: 20.5 Erg. pro cm². The specific gravity at 25° C. is: 1.5779; at 50° C.: 1.5394; at 75 C.: 1.5042; at t°: $d_{4^\circ} = 1.6197 - 0.001738\,t + 0.00000264\,t^2$.

The temperature-coefficient of μ is fairly constant; its mean value is **2.36** Erg. per degree.

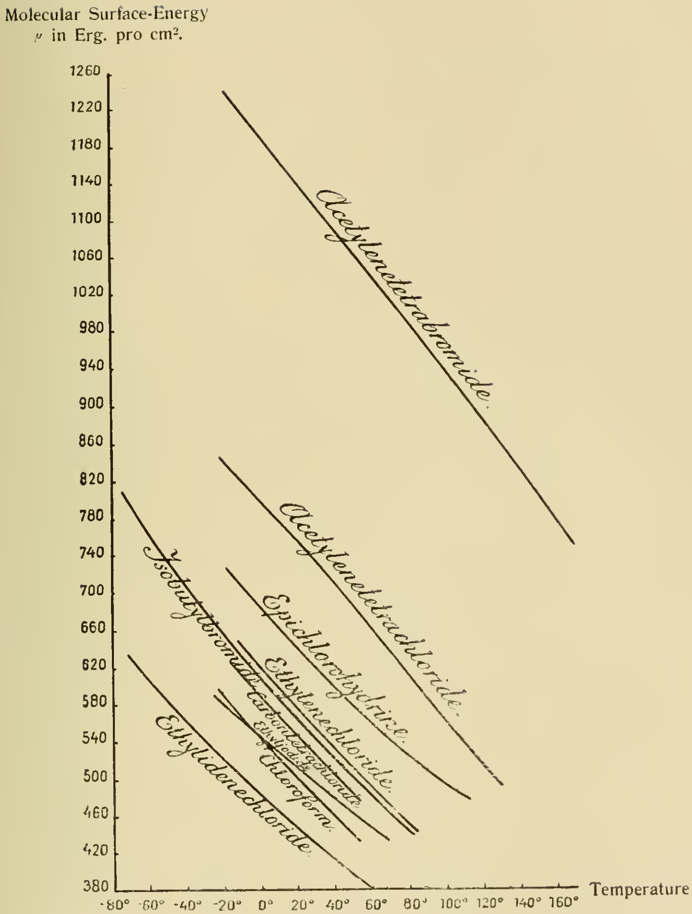

Molecular Surface-Energy
μ in Erg. pro cm².
1260
1220
1180
1140
1100
1060
1020
980
940
900
860
820
780
740
700
660
620
580
540
500
460
420
380
-80°
-60°
-40°
-20°
0°
20°
40°
60°
80°
100°
120°
140°
160°
Temperature
Acetylenetetrabromide.
Acetylenetetrachloride.
Epichlorohydrine.
Ethylenechloride.
Isobutylbromide.
Carbontetrachloride.
Ethyliodide.
Chloroform.
Ethylidenechloride.

Fig. 1.

V.

Acetylene-tetrabromide: $C_2H_2Br_4$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
*—21°	1.698	2264.2	53.1	3.039	1246.1
* 0	1.624	2165.6	50.7	2.996	1201.2
30.4	1.510	2012.8	46.7	2.934	1122.0
47.6	1.445	1926.0	44.6	2.897	1080.5
59.6	1.398	1864.0	43.1	2.871	1050.5
87.2	1.296	1727.6	39.8	2.814	983.1
102.1	1.240	1653.2	38.0	2.780	946.3
117.8	1.178	1570.6	36.0	2.747	903.6
127.3	1.144	1525.1	34.9	2.736	878.4
154.1	1.042	1388.7	31.6	2.669	808.6
175.5	0.964	1285.4	29.1	2.620	753.8

Molecular weight: **345.46.** Radius of the Capillary tube: 0.04839 cm.; in the observations indicated by *, it was : 0.04867 cm. Depth: 0.1 mm.

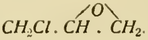
The bromide boils constantly at 132° under a pressure of 20 mm. In ice and salt it solidifies, after undercooling to —24° C., and melts at —3° C. On heating above 190° C. it is decomposed.

The density was at 50° C.: 2.8920; at 75° C.: 2.8390; at 100° C.: 2.7852. At t C. in general: $d_{4°} = 2.9956 \quad 0.00204\,t - 0.00000064\,t^2$.

The temperature-coefficient of μ is fairly constant; its mean value is: **2.51** Erg. per degree.

VI.

Epichlorohydrine:



$CH_2Cl . \overset{\diagup O \diagdown}{CH . CH_2}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
* -21°	1.288	1717.7	41.0	1.228	731.2
* 0	1.196	1594.5	38.0	1.205	686.4
30.3	1.079	1438.3	34.0	1.170	626.3
46.5	1.014	1351.5	31.9	1.147	595.5
59.8	0.958	1277.1	30.1	1.131	567.1
86.2	0.865	1153.1	27.1	1.095	521.7
102.8	0.815	1087.0	25.5	1.071	498.2
117.5	0.772	1029.1	24.1	1.049	477.5

Molecular weight: **92.50.** Radius of the Capillary tube: 0.04839 cm.; in the measurements, indicated by *, the radius was: 0.04867 cm. Depth: 0.1 mm.

Under a pressure of 758 mm., the liquid boils at 117° C.; in a bath of solid carbondioxide and alcohol it crystallises, and melts then at —48° C. At the boilingpoint χ is about: 24.1 Erg.

The density at 20° C. was: 1.1812; at 50° C.: 1.1436; at 75° C.: 1.1101. At $t°$ C.: $d_{4°} = 1{,}2046 - 0.00114\,t - 0.0000016\,t^2$.

The temperature-coefficient of μ is originally: **2.04** Erg; but from 86° C. upwards it decreases continually to **1.41** Erg per degree.

VII.

Carbonbisulphide: CS_2

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes.			
−72°	1.931	2574.4	44.3	1.398	636.5
−21	1.602	2146.0	36.8	1.323	548.6
0	1.483	1977.1	33.9	1.292	513.4
21.5	1.354	1805.1	30.9	1.262	475.3
40.9	1.245	1659.8	28.3	1.232	442.3

Molecular weight: **76.14.**

Radius of the Capillary tube: 0.03489 cm.
Depth: 0.1 mm.

The liquid was distilled several times, then shaken with mercury and again subjected to fractional distillation in an atmosphere of nitrogen after being completely dried. It boils at 46°.8 C. constantly; it solidifies (Timmermans) at − 111°.6 C. At the boiling-point χ has the value: 27.3 Erg. The specific gravity at 0° C. was: 1.2921; at 20° C.: 1.261; at 46° C.: 1.226. In general at t° C.: $d_{4^\circ} = 1.2921 - 0.00147\,t$.

The temperature-coefficient of μ is constant; its value is **1.75** Erg per degree.

VIII.

Methylalcohol: CH_3OH.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
−75°	1.246	1661.2	29.8	0.878	327.8
−20	1.043	1391.8	24.9	0.828	284.8
0	0.986	1314.6	23.5	0.810	272.8
20.8	0.924	1232.0	22.0	0.792	259.2
35.3	0.882	1177.0	21.0	0.778	250.4
50.1	0.841	1121.2	20.0	0.765	241.2
65	0.794	1058.6	18.8	0.752	229.3

Molecular weight: **32.03.**

Radius of Capillary tube: 0.03636 cm.
Depth: 0.1 mm.

The alcohol was obtained in an anhydrous state by boiling with dry calcium-oxide for several days; then it was carefully distilled. Under a pressure of 752 mm. it boils at from 65°.5 to 65°.8 C.; at this temperature the value of χ is: 18.7 Erg. It solidifies at −97°.1 C. (Timmermans). The specific gravity was calculated from the formula: $d_{4^\circ} = 0.8102 - 0.000905\,t - 0.000000085\,t^2$.

The temperature-coefficient of μ is very small: as a mean value about **0.67** Erg per degree.

IX.

Formic Acid: *HCO . OH.*

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm²
	in mm. mercury of 0° C.	in Dynes			
9°.2	1.596	2128.6	38.1	1.233	425.5
21.2	1.555	2073.7	37.2	1.218	418.8
35.3	1.510	2013.2	36.1	1.200	410.5
50.4	1.444	1925.1	34.5	1.181	396.5
64.8	1.386	1874.6	33.1	1.162	384.6
75.3	1.354	1787.6	32.0	1.149	374.6
90	1.263	1684.9	30.1	1.130	356.3
99.8	1.217	1622.5	29.0	1.117	346.0

Molecular weight: 46.02. Radius of the Capillary tube: 0.03636 cm.
Depth: 0.1 mm.

The acid solidifies below 0° C., and then melts again at + 6° C. It boils under a pressure of 762 mm. at 101° C.; at this temperature χ has the value: 28.8 Erg. The density was calculated from the equation: $d_{4^\circ} = 1.2441 - 0.001249\,t - 0.000000181\,t^2$.

The temperature-coefficient of μ is between 9° and 35°: **0.57** Erg.; between 35° and 75° C,: **0.90** Erg.; between 75° and 100° C.: **1.15** Erg. per degree.

X.

Monochloroacetic Acid: *CH_2Cl . COOH.*

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
80°.2	1.072	1429.2	33.3	1.352	565.0
92	1.042	1389.8	32.4	1.339	553.3
118.5	0.970	1293.8	30.1	1.305	522.9
*136.2	0.932	1242.0	28.1	1.285	493.2
*149.4	0.883	1175.3	26.6	1.260	473.0
*176.3	0.784	1045.0	23.5	1.235	423.5

Molecular weight: 94.49 Radius of the Capillary tube: 0.04792 cm.; the measurements indicated with * were made with a tube whose radius was 0.04670 cm.
Depth: 0.1 mm.

At a pressure of 20 mm. the acid boils constantly at 101° C. The melting-point was 62°.5 C. The density was at 75° C.: 1.3576; at 100° C.: 1.3261; at 125° C.: 1.2933. In general at t° C.: $d_{4^\circ} = 1.3878 \quad 0.001182\,(t-50^\circ) - 0.00000104\,(t-50^\circ)^2$.

The temperaturecoefficient of μ increases gradually with rise of temperature: between 80° and 92° C.: 0.96; between 92° and 118° C.: **1.14**; between 118° and 149° C.: **1.61**; and between 149° and 176° C.: **1.84** Erg per degree.

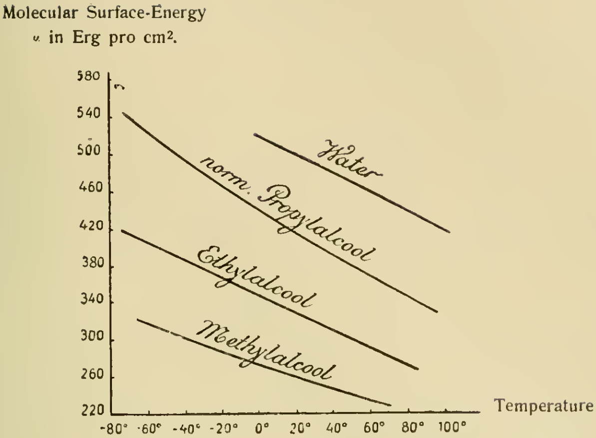

Molecular Surface-Energy
μ in Erg pro cm^2.
580
540
500
460
420
380
340
300
260
220
Water
norm. Propylalcool
Ethylalcool
Methylalcool
Temperature
-80°
-60°
-40°
-20°
0°
20°
40°
60°
80°
100°

Fig. 2.

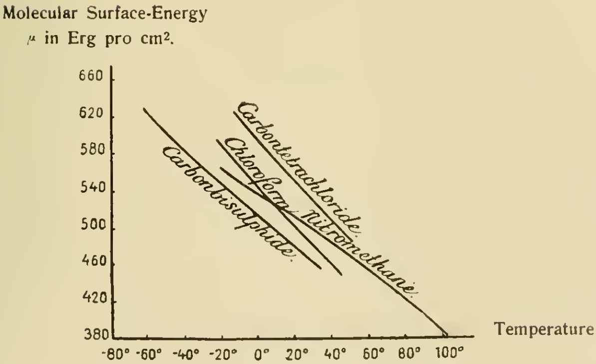

Molecular Surface-Energy
μ in Erg pro cm^2.
660
620
580
540
500
460
420
380
Carbontetrachloride
Chloroform
Carbonbisulphide
Nitromethane
Temperature
-80°
-60°
-40°
-20°
0°
20°
40°
60°
80°
100°

Fig. 3.

XI.

Dichloroacetic Acid: $CHCl_2 . COOH$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
0°	1.228	1637.2	38.1	1.592	796.5
25.7	1.143	1523.4	35.5	1.557	726.5
41	1.096	1460.6	34.0	1.535	691.8
55.9	1.052	1402.3	32.6	1.515	655.3
80.2	0.980	1306.4	30.3	1.488	605.3
92	0.945	1260.5	29.2	1.444	571.8
117	0.905	1206.2	27.9	1.431	539.8
*136.6	0.842	1122.1	25.1	1.405	481.4
*149.3	0.803	1070.7	24.0	1.387	456.0
*176.2	0.719	959.3	21.4	1.349	400.6

Molecular weight: **128.95**. Radius of the Capillary tube: 0.04792 cm.; in the observations indicated by *, this radius was: 0.04670 cm. Depth: 0.1 mm.

The acid boils at 192°.5 C. under a pressure of 763 mm.; on cooling it solidifies and melts again at +10° C.

The density at 12° C. was: 1.5759; at 75° C.: 1.4891; at 100° C. 1.4547; $t°$ C.: $d_{4°} = 1.5924 - 0.001378\, t$. The temperature-coefficients of μ oscillates beyond a mean value of about **2.30** Erg per degree.

XII.

Trichloroacetic Acid: $CCl_3 . COOH$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
80°.2	0.902	1202.0	27.8	1.575	613.8
92	0.876	1168.6	27.0	1.556	601.0
117.5	0.814	1085.2	25.1	1.515	568.7
*136.5	0.784	1045.0	23.4	1.484	537.6
*149.2	0.746	994.6	22.2	1.465	514.4
*176.1	0.665	886.5	19.7	1.415	467.1
*196	0.607	809.2	17.8	1.378	429.6

Molecular weight: **163.40**. Radius of the Capillary tube: 0.04792 cm.; in the observations marked by *, the radius was: 0.04670 cm. Depth: 0.1 mm.

Under a pressure of 765 mm. the acid boils at 195.°5 C.; under 21 mm. at 107 C. The melting-point was 57°·5 C.

The specific gravity at 75° C. was: 1.5829; at 100° C.: 1.5451; at 125° C.: 1.5082; at $t°$ C. $d_{4°} = 1.6216 - 0.001566\,(t - 50°) - 0.00000072\,(t\ \ 50\ )^2$.

The temperature-coefficient of μ originally increases with rise of temperature: between 80° and 92° C.: **1.09**; between 92° and 117° C.: **1.27**; between 117° and 136° C.: **1.63**; afterwards it remains fairly constant at **1.82** Erg per degree.

XIII.

Levulinic Acid: $CH_3.CO.CH_2.CH_2.COOH$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
25°.5	1.304	1738.2	39.7	1.135	868.1
41.1	1.268	1691.0	38.6	1.123	850.1
60.1	1.220	1626.6	37.1	1.109	823.9
81.5	1.166	1554.5	35.5	1.093	796.0
95.1	1.130	1506.4	34.4	1.083	776.1
115	1.082	1442.1	32.9	1.068	749.2

Molecular weight: **116.06**.

Radius of the Capillary tube: 0.04660 cm.
Depth: 0.1 mm.

Under atmospheric pressure the acid boils at 153°.5 C. Above 100° C. it is soon coloured yellowish and gets a special odour; the measurements were thus stopped because of the evident decomposition. The melting-point is 33° C. At 25° C. the density is: $d_{4°} = 1.1351$; at 50° C.: 1.1140; at 75° C.: 1.0924; at $t°$ in general: $d_{4°} = 1.1557 - 0.000814\,t - 0.0000004\,t^2$.

The temperature-coefficient of μ is almost constant and has the small mean value: **1.33** Erg per degree.

XIV.

Nitromethane: CH_3NO_2.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
*−21°.5	1.279	1705.4	40.6	1.199	557.6
* 0	1.202	1602.6	38.1	1.166	533.1
30.1	1.091	1454.8	34.3	1.123	492.1
46.3	1.026	1368.1	32.2	1.100	468.4
58.7	0.979	1306.0	30.8	1.086	451.9
86.2	0.868	1157.3	27.2	1.056	406.6
101.4	0.812	1082.9	25.4	1.040	383.6

Molecular weight: **61.03**.

Radius of the Capillary tube: 0.04839 cm.; in the observations indicated by *, the radius was: 0.04867 cm.
Depth: 0.1 mm.

The nitromethane boils at 102° C. under a pressure of 760 mm. On cooling below —24° C. it solidifies and melts at —17° C.; according to WALDEN the melting point is —26°.5 C. At the boiling-point χ has the value: 25.3 Erg pro cm.² The specific gravity at 15° C. is: $d_{4°} = 1.1437$ at 25°: 1.1297; 50° C.: 1.0970; in general: $d_{4°} = 1.1657 - 0.0015052\,t + 0.000002629\,t^2$.

The temperature-coefficient of μ evidently increases with rising temperature; between —21° and 0° it is: **1.14**; between 0° and 59°: **1.38**; between 59° and 101° C.: **1.58**; being thus appreciably under EÖTVÖS' normal-value of 2.2 Erg.

XV.

Bromonitromethane $CH_2(NO_2)Br$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes	
−18°.5	1.512	2015.9	48.3
0	1.431	1907.2	45.7
25.7	1.337	1782.1	42.7
40.5	1.280	1707.0	40.9
55.5	1.227	1636.1	39.2
80	1.139	1519.2	36.4
92.2	1.105	1473.2	35.3
116	1.002	1335.6	32.0
*135.8	0.919	1224.8	28.6

Molecular weight: 139.99. Radius of the Capillary tube: 0.04792 cm.; with the observations indicated by *, the radius was: R=0.04670 cm. Depth: 0.1 mm.

Under a pressure of 765 mm. the liquid boils at 152°.5 C.; in a bath of solid carbondioxide and alcohol it soon solidifies into a hard mass of crystals, melting at −28° C.

XVI.

Capronitrile: $C_5H_{11}CN$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
* −22°	0.903	1204.1	28.7	0.854	673.6
* 0	0.854	1138.3	27.1	0.835	645.6
29.9	0.781	1041.5	24.6	0.810	598.1
47.9	0.735	979.5	23.1	0.793	569.6
59.7	0.704	938.2	22.1	0.782	550.0
86	0.635	847.3	19.9	0.757	506.1
101.8	0.592	789.4	18.5	0.740	477.7
117.5	0.555	739.8	17.3	0.723	453.7
127.4	0.530	706.7	16.5	0.713	436.8
151.8	0.465	619.9	14.4	0.684	391.9

Molecular weight: **97.10**. Radius of the Capillary tube: 0.04839 cm.; in the measurements indicated by *, the radius was: 0.04867 cm. Depth: 0.1 mm.

This very ill-smelling liquid boils constantly at 157° C. under a pressure of 762 mm. In solid carbondioxide and alcohol, it solidifies and melts again at −45° C.

The density is at 24° C.: 0.8147; at 50° C.: 0.7914; at 75° C.: 0.7675. At t° C.: $d_{4^\circ} = 0.8347 - 0.000806\,t - 0.0000012\,t^2$.

The temperature-coefficient of μ has between 0° and 127° C. a mean value of about **1.63** Erg per degree, and above the last temperature a somewhat greater value: **1.84** Erg.

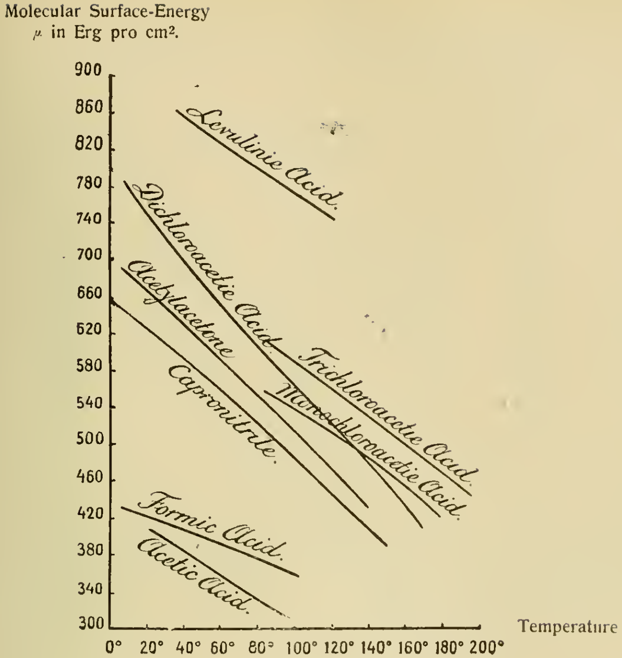


Fig. 4.

XVII.

Dimethyl-Succinate: $CH_3O \,.\, CO \,.\, CH_2 \,.\, CH_2 \,.\, CO \,.\, OCH_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
25°.2	1.123	1497.2	34.1	1.115	879.6
40.4	1.085	1446.5	33.1	1.097	863.1
54	1.015	1353.2	30.9	1.082	813.2
75.9	0.932	1242.5	28.3	1.058	756.0
95	0.870	1160.6	26.4	1.032	717.0
116	0.806	1069.5	24.3	1.014	667.8
135	0.745	993.6	22.5	0.995	626.2
150	0.694	925.0	20.9	0.980	587.6
176.2	0.585	779.9	17.5	0.955	500.5

Molecular weight: **146.08.**

Radius of the Capillary tube: 0,04670 cm.
Depth: 0.1 mm.

Under a pressure of 25 mm. the liquid boils at 103°.5 C.; the melting-point of the crystals is 18°.2 C. The specific gravity at 25° C. was: 1.1149; at 50° C.: 1.0865; at 75° C.: 1.0589; at t° in general: $d_{4^\circ} = 1.1441 - 0.001184\,t + 0.00000064\,t^2$.

The temperature-coefficient of μ is fairly constant up to 150° C. its mean value being: **2.32** Erg. per degree. Above 150° however it increases rapidly, perhaps caused by a beginning decomposition.

XVIII.

Diethyl-Bromoisosuccinate: $CH_3 . CBr (CO . OC_2H_5)_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
−21°	1.155	1539.8	35.0	1.377	1131.3
0	1.079	1439.0	32.7	1.350	1071.0
25.1	1.005	1340.5	30.4	1.318	1011.6
40.3	0.960	1280.5	29.0	1.300	974.0
52.8	0.918	1223.9	27.8	1.284	941.4
75.5	0.861	1147.7	26.0	1.257	893.0
95.4	0.809	1079.2	24.4	1.232	849.4
114	0.752	1002.6	22.6	1.211	795.8
134.1	0.698	930.6	20.9	1.189	745.0
152	0.652	869.4	19.5	1.169	703.0
176	0.581	775.1	17.3	1.144	632.7
197	0.499	665.3	14.7	1.121	544.9

Molecular weight: **253.03.** Radius of the Capillary tube: 0.04670 cm.
Depth: 0.1 mm.

Under a pressure of 13 mm. the liquid boils at 122° C. At −79° C. it becomes turbid and very viscous, but does not solidify. Above 176° a slow decomposition sets in, and the χ-t-curve then rapidly falls towards the t-axis. The specific gravity at 25° C. is: 1.3183; at 50° C.: 1.2875; at 75° C.: 1.2575. At t° in general it is calculated from: $d_{4^\circ} = 1.3499 - 0.00128\, t + 0.00000064\, t^2$.

The temperature-coefficient of μ is fairly constant up to 176°; its mean value is about: **2.54** Erg. per degree.

XIX.

Acetylacetone: $CH_3 . CO . CH_2 . CO . CH_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
−21°	1.124	1498.9	34.2	1.020	727.5
0	1.041	1387.7	31.6	0.998	681.9
25.2	0.956	1274.5	29.2	0.972	641.4
40.5	0.912	1216.3	27.7	0.957	614.8
54.5	0.867	1156.3	26.3	0.943	589.5
76.1	0.805	1073.3	24.4	0.923	554.8
94.8	0.752	1002.6	22.7	0.906	522.6
115	0.687	916.5	20.7	0.889	482.5
135	0.623	830.6	18.7	0.873	441.2

Molecular weight: **100.06.** Radius of the Capillary tube: 0.04670 cm.
Depth: 0.1 mm.

Under a pressure of 755 mm. the liquid boils at 137°.5 C. In a bath of solid carbondioxide and alcohol it crystallizes; the crystals melt at −30° C. At 25° C. the specific gravity is: 0.9721; at 50° C.: 0.9475; at 75° C.: 0.9241. At t° C.: $d_{4^\circ} = 0.9979 - 0.001056\, t + 0.00000096\, t^2$.

The μ-t curve has a peculiar shape, which is probably connected with the transformation of the keto $\rightleftarrows$ enol-equilibrium: between −21° and 0° $\frac{\partial \mu}{\partial t}$ is: 2.17 Erg., and decreases between 54° and 76° to **1.60**; afterwards it increases gradually to **2.06** Erg.

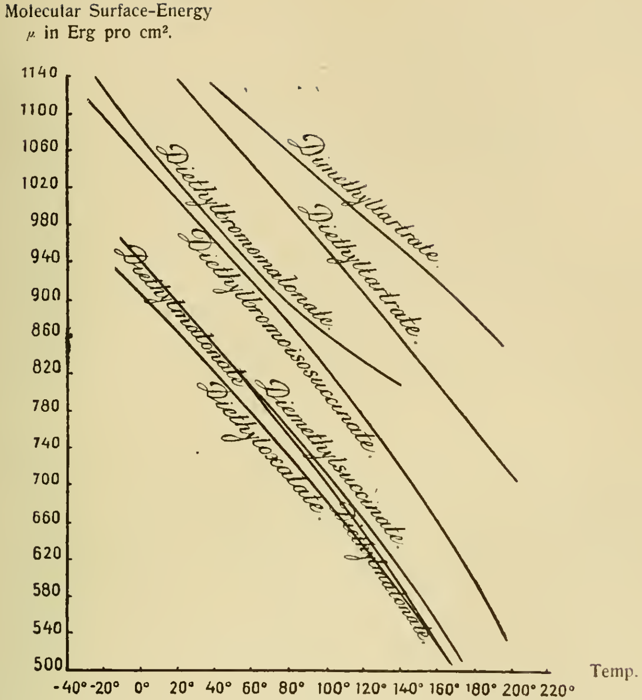


Fig. 5.

§ **3.** The results reviewed in Tables 1—19 and graphically reproduced in Fig. 1—5, give rise to the following general remarks.

In general the shape of the μ-t-curves, as determined by the values of the temperature-coefficients of μ, appears to be quite analogous in the case of derivatives of similar constitution: it is so in the case of all halogen-derivatives of the hydrocarbons (Fig. 1), in the case of the alcohols and water (Fig. 2), and in that of the neutral ethers of two-basic acids (Fig. 5).

In the case of *ethylene-*, and of *ethylidene-chloride* (Fig. 1), the different situation of the two chlorine-atoms in their molecules, appears in these cases to cause an appreciable difference of the values of μ at corresponding temperatures: thus such isomerides evidently do not possess the same surface-energy, as has been occasionally suspected by previous authors (Feustel). With the increase of the atomic weight of the halogen (cf. *acetylene-tetrabromide* and *-tetra-*

chloride) the surface-energy μ also increases. Substitution of hydrogen-atoms by the negative oxygen-atom has in the same way a magnifying influence on the original values of μ.

In the case of the *alcohols* (fig. 2) the values of μ, and also those of the temperature-coefficient of μ, increase regularly with the increase of the alkyl-radical; *water* however has evidently a special place.

In the case of *Acetic* and *Monochloro-*, and *Trichloroacetic Acids*, μ increases regularly with the content of halogen, while $\frac{\partial \mu}{\partial t}$ in these cases is quite analogous. *Dichloroacetic Acid* however shows a much larger temperature-coefficient, as a consequence of which the values of μ below 126° C. appear to be *greater*, above 126° however to be *smaller* than in the case of monochloroacetic acid. It must be mentioned also as a remarkable fact that the μ-t-curve for *Formic Acid* is entirely situated *above* that for Acetic Acid, while at the same time the value of $\frac{\partial \mu}{\partial t}$ for the formic acid appears to be unusually *small*. The special and diverging character of the formic acid shows itself in a most striking way in this fact too.

Diethylmalonate and *Dimethylsuccinate* (fig. 5) show within a rather considerable temperature-range, almost the same values of μ; furthermore a comparison of the μ-t-curves of *dimethylsuccinate* and *dimethyltartrate* clearly demonstrates the strongly magnifying power of the substitution of two hydrogen-atoms by the typically negative hydroxyl-groups. This increase of the molecular surface-energy by the substitution of *negative* elements of radicals into the original molecules, according to these data and those formerly published seems to be a quite *general* phenomenon.

With respect to the temperature-coefficients $\frac{\partial \mu}{\partial t}$ themselves, it may be remarked that in the case of the halogen-derivatives of the hydro-carbons they seem to be not unappreciably variable with the temperature in the case of *ethyliodide* and *ethylidenechloride*, and also in the case of *epichlorohydrine* from (1,43 to 1,88 Erg.). In the case of the *symmetrically* constituted compounds: *ethylenechloride*, and *tetrachloro-*, resp. *tetrabromo-acetylene*, they may be considered to be *constant*, while they furthermore appear to increase regularly with the augmenting content of the halogen:

For $C_2H_4Cl_2$: 2,16 Erg per degree.
For $C_2H_2Cl_4$: 2,36 Erg per degree.
For $C_2H_2Br_4$: 2,51 Erg per degree.

In the case of the *alcohols* and *water*, the values of $\frac{\partial\mu}{\partial t}$ are remarkably small; also in the case of the *alcohols* a regular increase with growing molecular weight is observable:

While in the case of *water* the value of $\frac{\partial\mu}{\partial t}$ is 1,0 Erg per degree,

it is for CH_3OH: 0,67 Erg per degree.
for C_2H_5OH: 0,94 Erg per degree.
and for C_3H_7OH: 1,10 Erg per degree.

On later occasions other regularities of this kind will be pointed out.

Groningen, Holland, June 1915.

Laboratory for Physical and Inorganic
Chemistry of the University.

Chemistry. — "*Investigations on the Temperature-Coefficients of the free Molecular Surface-Energy of Liquids between* — 80° *and* 1650° *C.*" **XI**. *The Surface-Tension of homologous Triglycerides of the fatty Acids*. By Prof. F. M. Jaeger and Dr. Jul. Kahn.

§ **1.** In the following we give the measurements made with the neutral ethers of glycerol and the fatty acids. The information about the surface-energy of the simple fats and its temperature-coefficient must be considered of high importance for practical reasons, because it allows conclusions to be made about the corresponding values for the natural fats, those being mixtures of the simple fats. The temperature-coefficient of μ appears furthermore to have very exceptional values for some of these derivatives which may be considered as a fact in many respects also of interest from a theoretical point of view.

Finally we give here again some measurements of the specific surface-energy χ and its temperature-coefficient, for natural butter and for margarine, which measurements were made with the purpose of finding out, if a reliable criterion could perhaps be obtained for the discrimination of pure natural butter from that which had been adulterated by vegetable fats. Although the temperature-coefficient of χ in the case of margarine evidently differs from that for natural butter, we think these differences too slight to found a reliable method upon these for the decision of the said questions.

§ **2.** The eleven compounds investigated are: *Glycerol, Glyceryltriformiate, Glyceryltriacetate, Glyceryltributyrate, Glyceryltricaproate, Glyceryltricaprylate, Glyceryltricaprinate, Glyceryltrilaurinate, Glyceryltripalmitate, Glyceryltristearate* and *Glyceryltrioleate.*

The butter and margarine used were both of the best kind; when molten, a heavier white precipitate is formed, consisting of salts and other components, mixed with water. Of course the measurements relating to such liquids can only have a relative value; but in any case they do not indicate any clearly evident difference between the two kinds of fats.

I.

Glycerol: $CH_2OH.CHOH.CH_2OH$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
0°	(ca. 3.1)	(ca. 4100)	(ca 88)	1.272	(ca. 1546)
13.5	(ca. 2.4)	(ca. 3200)	(ca. 69)	1.264	(ca. 1221)
26	2.297	3062.4	66.1	1.258	1156.5
35	2.182	2909.0	62.7	1.251	1101.0
50.2	2.085	2780.1	59.9	1.242	1057.0
65	2.023	2697.8	58.1	1.233	1030.2
74.5	2.010	2679.5	57.7	1.227	1026.5
90.8	1.975	2633.6	56.7	1.218	1013.5
104.1	1.941	2588.1	55.7	1.212	999.0
121	1.913	2551.4	54.9	1.200	991.2
130	1.886	2514.4	54.1	1.194	980.0
151	1.783	2378.1	51.1	1.182	931.9
171	1.708	2277.0	48.9	1.169	898.4
184.5	1.660	2213.0	47.5	1.162	876.2
202	1.585	2113.1	45.3	1.152	840.5

Molecular weight: **92.06.**

Radius of the Capillary tube: 0.04374 cm.
Depth: 0.1 mm.

The anhydrous compound melts at 19° C.; it can however be enormously undercooled; at —180° C. it becomes a glassy mass. The glycerol boils at 290° C., and under a pressure of 12 mm. at 180° C. The specific gravity at 20° C. is: 1.2604; at 50° C : 1.2420; at 100° C.: 1.1636. At t° in general: $d_{4^\circ} = 1.2720 - 0.000576\,t - 0.00000064\,t^2$. The temperature-coefficient of μ oscillates irregularly: in the beginning (from 13° to 50°) it is relatively great: **6.1** to **2.9** Erg.; then it decreases (between 50° and 200° C.) on: **1.8** to **1.5** Erg. per degree. The irregularities are undoubtedly connected with the embarrassing measurements in the case of this highly viscous liquid, especially at lower temperatures.

Glyceryltriformiate: $C_3H_5(O\,.\,COH)_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
*–20°	(1.972)	(2629.1)	(56.0)	1.352	(1438.7)
* 0	1.752	2335.8	49.6	1.332	1287.0
* 13.5	1.705	2273.1	48.3	1.318	1262.1
26	1.629	2171.9	46.7	1.305	1228.4
35	1.598	2130.7	45.8	1.296	1210.3
50.3	1.536	2048.4	44.0	1.281	1171.8
64.7	1.488	1983.6	42.6	1.266	1143.5
75.2	1.452	1934.1	41.5	1.256	1119.8
91.2	1.385	1847.2	39.6	1.240	1077.8
105	1.347	1797.0	38.5	1.225	1056.4
121	1.279	1705.5	36.5	1.210	1009.7
130.4	1.257	1671.8	35.8	1.200	995.9
151	1.182	1575.8	33.7	1.179	948.5
170	1.096	1461.2	31.1	1.159	885.4
184.8	1.015	1353.2	28.8	1.144	827.1

Molecular weight: **176.06**. Radius of the Capillary tube: 0.04374 cm.; in the determinations indicated by *, it was: 0.04320 cm. Depth: 0.1 mm.

The ether was prepared by Prof. Van Romburgh (Proc. Kon. Ak. v. Wet. Amsterdam 9, (109), (1907)) and kindly lent to me for the purpose of measurement. Under a pressure of 14 mm. it boils constantly at 147° C.; in a refrigerant mixture of alcohol and solid carbondioxide it crystallises slowly, and then melts at 18° C. At –20° C. the viscosity of the liquid is too great, to allow reliable measurements. Above 140° a slow decomposition sets in, acid vapours being evolved; the χ-t-curve therefore falls more rapidly to the t-axis. At the boilingpoint (266° C.) χ has a value of about 16.5 Erg.

The specific gravity at 50° C. was: 1.2812; at 75° C.: 1.2560; at 100° C.: 1.2305. At $t°$ C.: $d_{4^\circ} = 1.3319 - 0.001014\ t$.

The temperature-coefficient of μ is up to 150° C. fairly constant, and oscillates round a mean value of **2.20** Erg per degree; later on it increases, because of the reasons mentioned above, very rapidly to about **3.6** Erg per degree.

III.

Glyceryltriacetate: $C_3H_5(O.CO.CH_3)_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
—19°	1.580	2106.7	37.8	1.212	1204.9
0	1.543	2057.2	36.9	1.187	1192.6
21	1.488	1983.8	35.6	1.161	1167.8
35.2	1.456	1941.7	34.8	1.144	1152.8
50.2	1.419	1892.1	33.9	1.127	1134.2
65	1.382	1842.7	33.0	1.110	1115.3
75.2	1.349	1798.9	32.2	1.100	1092.4
90.2	1.300	1732.6	31.0	1.085	1063.8
99.8	1.262	1683.1	30.1	1.075	1039.3
115	1.200	1600.7	28.6	1.060	996.8
125	1.160	1546.5	27.6	1.051	967.4
139.8	1.089	1452.1	25.9	1.040	914.2
155	1.027	1369.6	24.4	1.028	868.0
169.2	0.977	1303.6	23.2	1.016	831.8
185.2	0.916	1221.1	21.7	1.007	782.6
200.3	0.862	1149.6	20.4	0.997	740.6

Molecular weight: **218.1**.

Radius of the Capillary tube: 0.03636 cm.
Depth: 0.1 mm.

At —78° C. the liquid gets glassy; at —20° it is again very viscous. Under a pressure of 40 mm. the liquid boils at 172°.5 C.; under atmospheric pressure at 260° C. The density at 25° C. is: 1.1562; at 50° C.: 1.1271; at 75° C.: 1.1001; at 100° C.: 1.0752. At $t°$ C.: $d_{4°} = 1.1874-0.00129\,t + 0.0000017\,t^2$.

The temperature-coefficient of μ increases gradually with rising temperature; between —19° and 0° C. it is: **0.64** Erg.; between 0° and 21° C.: **0.92** Erg.; between 21° and 35° C.: **1.05** Erg.; between 35° and 65° C.: **1.26** Erg.; between 65° and 100° C.: **2.20** Erg.; between 100° and 170° C.: **2.89** Erg.; and between 170° and 200° C. almost **3.0** Erg. per degree.

IV.

Glyceryltributyrate: $C_3H_5(O.CO.C_3H_7)_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_4	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
−20.5°	1.381	1841.1	33.0	1.080	1411.8
0	1.333	1776.7	31.8	1.060	1377.5
20.9	1.283	1710.7	30.6	1.040	1342.4
35.1	1.246	1661.2	29.7	1.024	1316.5
50.3	1.213	1617.2	28.9	1.011	1292.0
64.8	1.173	1561.7	27.9	1.005	1252.2
75.3	1.142	1523.7	27.2	0.998	1226.5
90.2	1.101	1467.8	26.2	0.979	1196.6
99.8	1.074	1431.8	25.5	0.966	1177.3
115.2	1.031	1375.2	24.5	0.954	1138.5
125.3	1.001	1333.3	23.7	0.948	1106.0
140	0.943	1259.1	22.4	0.939	1052.0
156	0.899	1199.2	21.3	0.924	1011.1
170.8	0.854	1138.5	20.2	0.911	968.0
184.5	0.817	1089.1	19.4	0.900	937.2
200.8	0.776	1034.0	18.3	0.890	890.7

Molecular weight: **302.2**.

Radius of the Capillary tube: 0.03636 cm.
Depth: 0.1 mm.

Under atmospheric pressure the liquid boils at 286° C. The density at 50° C. is: 1.0110; at 75° C.: 0.9982; at 100° C.: 0.9664. At t° C.: in general $d_{4°} = 1.0596 - 0.00101\, t + 0.0000008\, t^2$.

The temperature-coefficient of μ originally increases gradually from **1.70** Erg. between −20° and 50° C., and **2.42** Erg. between 50° and 115° C., to **3.44** Erg between 115° and 140° C. Afterwards it again decreases somewhat: between 140° and 201° C. its mean value is about **2.63** Erg per degree.

V.

Glyceryltricapronate: $C_3H_5(O.CO.C_5H_{11})_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
—20°	1.395	1859.2	33.4	1.028	1739.3
0	1.316	1754.8	31.5	1.011	1658.4
21	1.250	1666.6	29.9	0.993	1593.4
35.3	1.213	1617.2	29.0	0.982	1557.0
50.1	1.180	1573.2	28.2	0.970	1526.4
64.8	1.147	1529.2	27.4	0.958	1495.5
75.7	1.123	1496.3	26.8	0.949	1472.0
90	1.085	1446.7	25.9	0.938	1433.7
99.8	1.061	1414.5	25.3	0.931	1407.4
115.3	1.034	1376.5	24.6	0.919	1380.1
125	1.004	1338.5	23.9	0.905	1354.9
141	0.972	1295.9	23.0	0.900	1308.7
155.8	0.932	1243.1	22.2	0.890	1272.6
169.5	0.897	1190.6	21.3	0.880	1230.3
185	0.862	1149.7	20.5	0.871	1192.2
200	0.825	1100.1	19.6	0.860	1149.6

Molecular weight: **386.3**.

Radius of the Capillary tube: 0.03636 cm.
Depth: 0.1 mm.

In a refrigerant bath of solid carbondioxide and alcohol, the liquid gets very viscous, and then solidifies very slowly at —60° C. At 50° C. the density was: 0.9699; at 75° C.: 0.9501; at 100° C.: 0.9309. At $t°$ C.: $d_{4°} = 1.0113 - 0.000852\,t + 0.00000048\,t^2$.

The values of $\frac{\partial \mu}{\partial t}$ decrease with increasing temperature gradually from **4.04** Erg per degree at —20° C. to **2.54** Erg at 35° C. Afterwards they remain relatively constant, and oscillate somewhat round a mean value of **2.49** Erg per degree.

VI.

Glyceryltricaprylate: $C_3H_5(O.CO.C_7H_{15})_3$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
0°	1.258	1677.7	30.1	0.967	1861.8
21	1.218	1623.8	29.1	0.950	1821.3
35.1	1.194	1588.2	28.4	0.939	1791.4
50.3	1.156	1541.2	27.6	0.927	1756.0
65.3	1.126	1501.6	26.9	0.915	1726.3
75.7	1.106	1474.2	26.4	0.908	1702.9
90.3	1.073	1430.1	25.6	0.897	1664.8
99.8	1.052	1402.7	25.1	0.890	1640.8
115.5	1.015	1353.2	24.2	0.879	1595.2
125.2	0.994	1325.7	23.7	0.871	1571.7
140.2	0.961	1281.6	22.9	0.861	1530.5
154.8	0.924	1231.9	22.0	0.852	1480.6
170.5	0.902	1202.5	21.5	0.842	1458.4
185.8	0.863	1151.8	20.5	0.831	1402.8
200.2	0.826	1103.8	19.7	0.822	1357.9

Molecular weight: **470.4**.

Radius of the Capillary tube: 0.03636 cm.
Depth: 0.1 mm.

The compound solidifies at −22° C. slowly into a colourless crystal-aggregation; it melts again at +9° C.

The density at 50° C. is: 0.9273; at 75° C.: 0.9082; at 100° C.: 0.8897. At t° C.: $d_{4^\circ} = 0.9673 - 0.000824\,t + 0.00000048\,t^2$.

The temperature-coefficient of μ is between 0° and 76° C.: **2.12** Erg.; between 76° and 155° C. its mean value is about: **2.65** Erg; and between 155° and 200° C.: about **2.9** Erg per degree.

VII.

Glyceryltricaprinate: $C_3H_5(O.CO.C_9H_{19})_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
35°.4	0.956	1275.7	27.6	0.923	1965.0
50.2	0.940	1253.2	27.1	0.912	1944.9
65.3	0.915	1220.9	26.4	0.902	1908.6
74.6	0.902	1202.5	26.0	0.895	1889.5
90.5	0.867	1156.8	25.0	0.884	1831.9
104.1	0.834	1113.9	24.1	0.875	1778.0
121	0.803	1068.1	23.0	0.863	1712.6
130.3	0.779	1037.8	22.4	0.856	1677.0
151	0.740	985.1	21.3	0.842	1612.1
172	0.708	950.1	20.2	0.827	1547.4
184.9	0.681	913.8	19.5	0.818	1504.7
201.2	0.655	873 2	18.8	0.807	1463.9

Molecular weight: **554.49.**

Radius of the Capillary tube: 0.04374 cm.
Depth: 0.1 mm.

The substance melts at 31°.1 C. The density at 50° C. is: 0.9126; at 75° C.: 0.8950; at 100° C.: 0.8777. At $t°$ C.: $d_{4°} = 0.9475 - 0.000698\,t$.

The temperature-coefficient of μ has a mean value of about **3,09** Erg per degree.

VIII.

Glyceryltrilaurinate: $C_3H_5(O.CO.C_{11}H_{23})_3$.

Temperature in ° G.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
64°.7	1.209	1611.7	29.2	0.891	2338.5
75.1	1.180	1573.2	28.5	0.885	2293.1
90	1.147	1529.1	27.7	0 876	2343.7
99.8	1.122	1496.2	27.1	0.870	2205.1
114.8	1.093	1456.1	26.4	0.861	2161.5
126	1.064	1419.2	25.7	0.853	2118 9
139	1.040	1386.2	25.1	0.846	2080.9
156	0.997	1331.4	24.1	0.828	2026.8
170	0.978	1303.9	23.6	0.824	1991.1
185	0.949	1261.8	22.8	0.815	1937.8
200	0.916	1221.1	22.1	0.804	1895.4

Molecular weight: **638.59.**

Radius of the Capillary tube: 0.03636 cm.
Depth: 0.1 mm.

The compound melts at 46°.5 C. The specific gravity at 75° C. is: 0.8842; at 100° C.: 0.8676; at 125° C.: 0.8507. In general at $t°$ C.: $d_{4°} = 0.9005 - 0.00060\,(t-50°) - 0.00000024\,(t-50°)^2$.
The temperature-coefficient of μ oscillates somewhat round a mean value of: **3.33** Erg pro degree.

IX.

Glyceryltripalmitate: $C_3H_5(O.CO.C_{15}H_{31})_3$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
64°.3	1.287	1715.7	30.4	0.877	2863.4
75.3	1.257	1675.8	29.7	0.870	2812.5
90	1.206	1610.4	28.5	0.862	2715.5
99.8	1.182	1575.8	27.8	0.854	2665.3
115	1.139	1518.2	26.8	0.845	2587.7
125.5	1.124	1496.2	26.4	0.834	2571.4
140.2	1.077	1435.6	25.6	0.828	2505.6
154.8	1.060	1413.7	24.9	0.816	2460.9
170	1.031	1375.2	24.2	0.805	2413.4
184.8	1.000	1333.2	23.4	0.794	2355.2
200	0.963	1288.1	22.6	0.781	2299.8

Molecular weight **801.74.**

Radius of the Capillary tube: 0.03636 cm.
Depth: 0.1 mm.

The compound melts at 65°.1 C.; the metastable form melts at 46° C.
The specific gravity was at 75° C.: 0.8702; at 100° C.: 0.8544; at 125° C.: 0.8377. In general at t° C.: $d_{4^\circ} = 0.8851 \quad 0.000578(t-50^\circ) - 0.00000079(t-50^\circ)^2$.

The temperature-coefficient of μ is up to 90° C. about **5.55** Erg per degree; afterwards it decreases gradually from **5.10** Erg to **3.41** Erg per degree.

X.

Glyceryltristearate: $C_3H_5(O.CO.C_{17}H_{35})_3$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
121°	0.908	1210.5	26.0	0.840	2704.0
130	0.886	1181.2	25.3	0.834	2643.8
151	0.822	1095.9	23.5	0.820	2483.6
169	0.784	1045.2	22.3	0.807	2382.0
185	0.741	987.9	21.1	0.794	2278.3
201.2	0.725	966.6	19.8	0.782	2159.8

Molecular weight: **890.88**

Radius of the Capillary tube: 0.04374 cm.
Depth: 0.1 mm.

The ether melts at 71°.6 C.; its metastable form at 55° C. From 75° to 120° C. the value of χ changes only inconsiderably: from 26.9 Erg at 74°.6 C. to 26.5 Erg at 120° C. Above 120° C. the curve falls gradually; only this part of it is drawn in the diagram.
The density at 75° C. was: 0.8704; at 100° C.: 0.8542; at 125° C.: 0.8373. At t° C.: $d_{4^\circ} = 0.8859 \quad 0.000606(t-50^\circ) - 0.00000056(t-50^\circ)^2$.

The temperature-coefficient of μ oscillates round a mean value of **6.75** Erg per degree.

XI.

Glyceryltrioleate: $C_3H_5(O\,.\,CO\,.\,C_{17}H_{33})_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
—17°	1.656	2207.8	40.1	0.951	3822
0	1.535	2046.2	37.2	0.937	3580
21	1.436	1914.2	34.8	0.920	3391
35.3	1.375	1833.1	33.3	0.909	3271
50.1	1.335	1780.9	32.4	0.899	3206
65	1.304	1738.2	31.6	0.888	3153
75.8	1.273	1696.0	30.8	0.881	3089
90	1.233	1643.6	29.9	0.872	3019
99.8	1.209	1611.8	29.3	0.866	2972
114.8	1.180	1573.2	28.6	0.857	2922
125.2	1.159	1545.7	28.1	0.850	2886
141	1.131	1507.1	27.4	0.842	2832
154.8	1.106	1474.2	26.8	0.834	2788
170	1.081	1441.2	26.2	0.829	2736
185	1.056	1408.1	25.6	0.821	2691
200.6	1.031	1375.1	25.0	0.813	2645

Molecular weight: 884.82.

Radius of the Capillary tube: 0.03636 cm.
Depth: 0.1 m.m.

The liquid solidifies at about — 17° C. slowly, after becoming very viscous at that temperature.

The density at 50° C. was; 0.8992; at 75° C.: 0.8822; at 100° C.: 0.8665. At $t°$ C.: $d_{4°} = 0.9371 - 0.00081\,t + 0.00000104\,t^2$.

The temperature-coefficient of μ decreases gradually with rising temperature, and rather greatly from about 14 to 8.4 Erg. between — 17° and 21° C., to 4.7 Erg. between 21° and 90° C., and 3.25 Erg. between 90° and 200° C.

XII.

Butter.

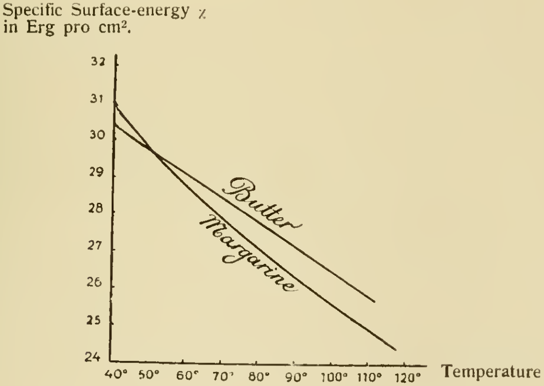
Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes	
40.2°	0.994	1325.2	30.5
54.1	0.953	1270.5	29.3
76.2	0.908	1210.5	27.9
94.8	0.879	1168.4	26.9
116.5	0.843	1123.9	25.8

Radius of the Capillary tube: 0.04667 cm.
Depth: 0.1 mm.

XIII.

Margarine.			
Temperature in ° C.	Maximum Pressure *H*		Surface-tension χ in Erg. pro cm²
	in mm. mercury of 0° C.	in Dynes	
40°.2	1.009	1345.6	31.0
54.1	0.952	1268.4	29.3
76.2	0.886	1181.2	27.2
94.8	0.829	1105.6	25.8
116.5	0.795	1060.1	24.4

Radius of the Capillary tube: 0.04667 cm.
Depth: 0.1 mm.



Specific Surface-energy of Butter and of Margarine.

§ **3.** The results here obtained lead to the following remarks. The absolute values of μ evidently increase in a regular and prominent way with augmenting carbon-content of the fatty acid; in the case of the ethers of the higher fatty acids they reach a magnitude quite comparable with that observed in the case of some molten inorganic salts. This fact certainly runs in some respects parallel with the strong increase of the molecular weight of these fats.

At the same time the temperature-coëfficients of μ regularly increase, with exception of the first term of the series, as can be seen from the following data:

Triformiate: 2,20—3,6
Triacetate: 1,05—1,26—2,20—2,89—3,0
Tributyrate: 1,70—2,42—2,60
Tricapronate: 2,49
Tricaprylate: 2,12—2,65—2,90
Tricaprinate: 3,09
Trilaurate: 3,33
Tripalmitate: 5,55—5,1—3,41
Tristearate: 6,75
Trioleate: 8,4—4,7—3,25

It will be remarked, that the μ-t-curve for *trioleate* is wholly situated *above* that for *tristearate*, which clearly demonstrates that in the case of the same number of carbon-atoms, the values of μ for the derivative of the *un*saturated acid will be greater than those for the derivative of the saturated acid with the same number of carbon-atoms.

Furthermore attention must be drawn to the fact that for the first five members of the series $\frac{\partial \mu}{\partial t}$ increases with rise of temperature; for tricaprinate, trilaurate and tristearate however it remains rather constant, while for tripalmitate, trioleate just as for glycerol [1]) itself, it decreases with rising temperature.

Most of the changes mentioned thus appear to occur in quite a regular way. It is at the moment hardly possible to give any probable explanation of the enormously great values of the temperature-coefficient of μ in the case of the higher members of this series.

With respect to the investigation of butter and margarine, we found for the butter studied here a value of $\frac{\partial \chi}{\partial t}$ of about: 0,055 Erg, and for the margarine of about: 0.087 Erg pro degree. The absolute values of χ however deviate only slightly for the two complex fats; at 50° C. both liquids must have about the same specific surface-energy of 29,8 Erg.

Laboratory for Physical and Inorganic
Chemistry of the University.

Groningen, June 1915.

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[1]) For *glycerol* $\frac{\partial \mu}{\partial t}$ varies between 1,8 and 1,5 Erg pro cm^2.

Chemistry. — "*Investigations on the Temperature-Coefficients of the free Molecular Surface-Energy of Liquids between* —80° *and* 1650° *C.*" **XII.** *The Surface-Energy of the Isotropous and Anisotropous Liquid Phases of some Aromatic Azoxy-Compounds and of Anisaldazine.* By Prof. F. M. JAEGER and Dr. JUL. KAHN.

§ **1.** With the purpose of elucidating better the significance of the temperature-coefficients of the free molecular surface-energy μ of liquids as a criterion for the degree to which these liquids are associated, we have now extended our measurements to some of these compounds which show more than one liquid phase and of which all, with the exception of the last, are optically anisotropous.

There can hardly be a doubt any longer that these anisotropous liquids should be considered really as quite *homogeneous* liquid phases of very peculiar molecular structure, while the mutual relations of these anisotropous phases to the isotropous phase on the one side and to the solid phase on the other, are quite analogous to those commonly observed in the cases of polymorphism.

The successive anisotropous liquids, which reveal themselves in the case of some of these substances and which in the case of *enantiotropic* transformations can exist within a proper, sharply limited temperature-range, may be distinguished according to the explanation given by the most probable hypothesis yet suggested, by a motion of the molecules in "swarms", which decrease in complexity after each higher transformation-temperature has been passed; these molecules themselves probably have moreover an atomistic structure, causing a general shape which is in one direction of space considerably more elongated than in the two directions perpendicular to the first.

By this hypothesis it thus becomes highly probable, that the *isotropous* liquid, which always appears at the *highest* transition-point, will possess a much less complex structure than the foregoing anisotropous liquids, — a supposition which will be found to agree entirely with our usual ideas about the progress of a dissociation occurring with increase of temperature.

If the hypothesis accepted till now was right, that a smaller value of $\frac{\partial \mu}{\partial t}$ than the normal of **2,2** erg stated by EÖTVÖS, indicates an association, but that a larger value than **2,2** Erg pro degree points to a dissociation of the liquid, — we may expect here that the mean value of the coefficient $\frac{\partial\mu}{\partial t}$ at temperatures *below* the transition-point of the anisotropous liquid will appear to be *smaller* than that of the isotropous liquid *above* the transformationpoint. The following measurements were made to verify this conclusion by means of experiments.

§ 2. The substances investigated here are in the first place the following compounds often studied already, which have been purified here with the utmost care:

para-Azoxy-Anisol: $CH_3O.C_6H_4.N_2O.C_6H_4.OCH_3$;
$t_1 = 114°$ C. and $t_2 = 138°$ C.
para-Azoxy-Phenetol: $C_2H_5O.C_6H_4.N_2O.C_6H_4.OC_2H_5$;
$t_1 = 138°$ C and $t_2 = 168°$ C.

and

para-Anisaldazine: $CH_3O.C_6H_4.CH:N.N:CH.C_6H_4.OCH_3$;
$t_1 = 169°$ C and $t_2 = 180°$ C.

The last mentioned substance was prepared from p-anisaldehyde and hydrazine-sulphate; it was purified by repeated crystallisation from boiling benzene.

Furthermore we choose: *Ethyl-para-Azoxybenzoate*: $C_2H_5O.CO.C_6H_4.N_2O.C_6H_4.CO.OC_2H_5$, which was purified by recrystallisation from a mixture of chloroform and benzene. The beautifully crystallized compound shows the transition-temperatures: $t_1 = 114°$ C. and $t_2 = 121°$ C. Finally we prepared, for other purposes also, a quantity of *Ethyl-para-Ethoxybenzalamino-α-Methylcinnamylate*: $C_2H_5O.C_6H_4.CH:N.C_6H_4.CH:C(CH_3).CO.OC_2H_5$ for the transitiontemperatures we found: $t_1 = 95°$ C. and $t_2 = 117°,8$ C., which numbers do not agree with those given in the literature on this compound.

The purity of the three first-named substances is above all doubt; as for the two last mentioned compounds the certainty is somewhat less, but it is very probable that the impurities possibly intermingled with them, are not of any considerable importance. Since the behaviour of the three first substances differs appreciably from that of the last two, the resp. μ-t-curves are placed in two different diagrams.

I.

para-Azoxy-Anisol: $C_3HO . C_6H_4 . N_2O . C_6H_4 . OCH_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
115°	1.136	1515.2	40.1	1.171	1463.3
120	1.104	1472.3	39.0	1.166	1427.3
126	1.067	1422.8	37.7	1.159	1385.2
129.5	1.034	1378.5	36.4	1.156	1339.8
133.5	1.072	1429.1	37.8	1.152	1394.6
138.1	1.077	1435.8	37.9	1.142	1406.4
144.5	1.056	1407.7	37.2	1.136	1385.2
155.2	1.025	1366.0	36.0	1.126	1348.5
160.5	1.003	1338.8	35.5	1.124	1331.3
174.5	0.977	1302.0	34.2	1.112	1292.0
190	0.940	1253.2	33.0	1.100	1255.5
211	0.897	1195.7	31.4	1.080	1209.4

Molecular weight: **258.14**.

Radius of the Capillary tube: 0.05425 cm.
Depth: 0.1 mm.

The compound was purified by repeated crystallisations. At 114° C. the solid phase begins to transform into an orange anisotropous liquid, which at 133°.5 C. is almost, at 138° completely, clear and transparent.

The temperature-coefficient of μ is remarkably great for the anisotropous liquid: between 115° and 126° C. about **7.1** Erg per degree, between 126° and 133° even **12.2** Erg per degree. For the isotropous liquid however it decreases gradually from the transition-temperature from **3.45** Erg to **2.20** Erg at 190° C.

para-Azoxyphenetol: $C_2H_5O.C_6H_4N_2O.C_6H_4OC_2H_5$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
142.5	0.882	1198.0	31.6	1.094	1292.5
147.5	0.875	1165.9	30.7	1.089	1259.5
151.8	0.854	1138.5	30.0	1.084	1234.6
159	0.827	1102.2	29.0	1.076	1199.4
164	0.813	1085.0	28.3	1.072	1173.3
168.5	0.835	1113.2	29.3	1.068	1217.6
174.5	0.814	1087.4	28.6	1.053	1200.0
190	0.779	1038.5	27.3	1.039	1155.7
205	0.742	990.8	26.2	1.026	1118.5
219	0.722	962.6	25.2	1.014	1084.2

Molecular weight: **286.17**. Radius of the Capillary tube: 0.05425 cm. Depth: 0.1 mm.

This beautifully crystallised compound is transformed into an anisotropous liquid at 138° C., which becomes transparent at 168° C. With this compound thus once more the fact is proved that the temperature-coefficient of μ for the anisotropous liquid is abnormally high: it decreases gradually from **6.60** Erg. at 143° C. to **4.89** Erg. between 159° and 164, and then increases suddenly under change of the algebraic sign, to **9.84** Erg. For the isotropous liquid it is nearly constant; its mean value is **2.6** Erg. per degree.

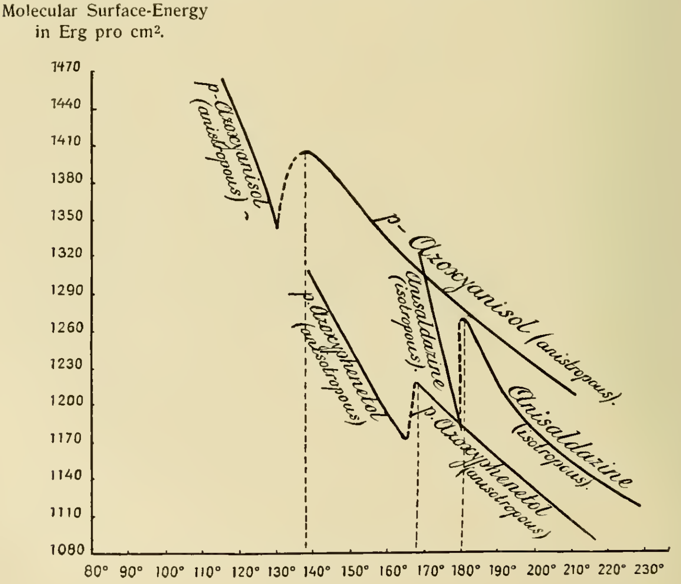

Fig. 1.

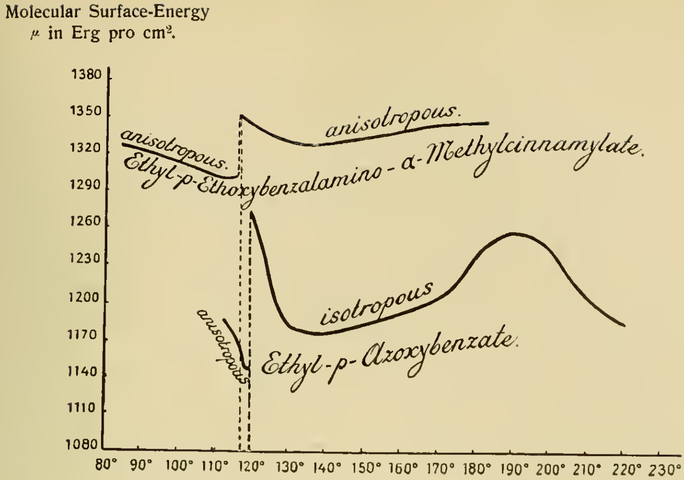

Fig. 2.

III.

Anisaldazine: $CH_3O.C_6H_4CH:N.N:CH.C_6H_4.OCH_3$.					
Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
171°	0.932	1242.5	32.1	1.051	1291.2
173.5	0.911	1214.0	31.4	1.049	1264.7
174.5	0.902	1203.5	31.1	1.048	1253.4
176.5	0.886	1181.2	30.5	1.046	1230.8
178	0 865	1154.8	29.9	1.044	1208.0
179	0.845	1128.4	29.4	1.043	1188.7
180.5	0.908	1210.5	31.2	1.035	1267.9
185	0.886	1181.2	30.4	1.031	1238.6
195	0.851	1134.5	29.2	1.023	1195.9
204.5	0.822	1096.4	28.3	1.015	1165.1
219	0.800	1067.1	27.4	1.002	1137.8
230.5	0.789	1044.7	26.8	0.993	1119.6

Molecular weight: **268.14.** Radius of the Capillary tube: 0.05301 cm.
Depth: 0.1 mm.

The compound was prepared from anisaldehyde and hydrazinesulphate in cold aqueous solution, and repeatedly crystallized from boiling benzene. The beautiful yellow crystals are at 169° C. transformed into an isotropous liquid, which at 180° C. gets clear and isotropous. The density of the isotropous liquid was: 1.0313 at 185° C.; at 205° C.: 1.0150; at 225° G.: 0.9977. At $t°$ C. in general: $d_{4°} = 1.0355-0.0007775\,(t-180\,)-0.00000125\,(t-180°)^2$.

For the anisotropous liquid the density at 173° C. was: 1.0486; at 180° C.: 1.0416; at $t°$ C: $d_{4°} = 1.0516-0.001\,(t-170\,)$. In this case also the temperature-coefficient of μ is for the anisotropous liquid exceptionally great: between 171° and 176° about: **11.0** Erg, afterwards **15.2** and even **19.3** Erg per degree. For the isotropous liquid it rapidly decreases with rise of temperature: At the transitionpoint: **6.5** Erg, then **4.27**; **3.25**; and finally **1.88** and **1.53** Erg per degree.

IV.

Ethyl-para-Azoxybenzoate: $C_2H_5O.CO.C_6H_4.N_2O.C_6H_4.CO.OC_2H_5$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
114°	0.789	1052.6	27.0	1.176	1185.6
116	0.788	1049.4	26.9	1.174	1182.5
118	0.776	1034.6	26.5	1.172	1166.3
119	0.764	1018.3	26.1	1.170	1150.0
120	0.762	1014.3	26.0	1.168	1146.9
121	0.832	1109.2	28.5	1.148	1271.7
124	0.809	1079.0	27.7	1.145	1238.1
125	0.779	1038.4	26.7	1.144	1194.2
130	0.774	1030.3	26.5	1.141	1187.3
140	0.768	1023.9	26.2	1.135	1178.0
150	0.770	1027.1	26.3	1.128	1187.4
160	0.771	1030.0	26.3	1.121	1192.3
170	0.770	1027.1	26.3	1.114	1197.3
180	0.799	1065.2	27.3	1.108	1247.3
190	0.804	1072.2	27.5	1.102	1261.0
200	0.793	1057.2	27.1	1.096	1247.2
210	0.762	1011.0	26.1	1.090	1205.6
220	0.757	1005.1	25.7	1.084	1191.2
230	0.741	987.9	25.3	1.079	1176.5

Molecular weight: **342.18**.

Radius of the Capillary tube: 0.05301 cm.
Depth: 0.1 mm.

The beautiful orange-coloured crystals are at 114° C. transformed into the anisotropous liquid, which at 121° C. is changed into the clear, amorphous one. All measurements were repeated after crystallisations of the substance used in mixtures of chloroform and benzene; as the peculiarities were observed again every time, they must be considered as essential features of the substance.

In this case also the temperature-coefficient of μ is abnormally high: irregularly oscillating, but with a mean value of about **7.2** Erg. per degree. Then μ increases suddenly with rise of temperature, and afterwards falls rapidly and irregularly in the isotropous liquid; then it increases again slowly to a maximum at about 190° C., to decrease afterwards slowly, and reach a final gradient of about **1.45** Erg. per degree. Very complicated reactions seem indeed to take place in this liquid.

V.

Ethyl-para-Ethoxybenzalamino-α-Methylcinnamate:
$C_2H_5O . C_6H_4 . CH : N . C_6H_4 . CH : C (CH_3) C . OOC_2H_5$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
85°	0.843	1123.7	28.7	1.075	1324.7
94.5	0.837	1112.9	28.5	1.068	1321.2
99	0.831	1108.0	28.3	1.064	1315.2
105.5	0.829	1104.7	28.1	1.058	1310.9
111	0.822	1095.8	27.9	1.053	1305.7
115.3	0.819	1090.9	27.8	1.049	1304.3
117.6	0.843	1123.7	28.7	1.045	1350.0
123.7	0.831	1107.8	28.3	1.040	1335.4
130.5	0.828	1101.9	28.1	1.034	1331.1
139	0.825	1099.9	28.0	1.027	1332.4
149	0.822	1095.8	27.9	1.018	1335.4
159	0.819	1091.9	27.8	1.010	1337.6
168.5	0.818	1089.8	27.8	1.002	1344.8
179	0.816	1085.8	27.7	0.993	1348.0

Molecular weight: 337.11.

Radius of the Capillary tube: 0.05265.
Depth: 0.1 mm.

The compound was prepared by the method described by W. Kasten (Dissertation, Halle, 1909 p. 41), and purified by repeated crystallisations. Contrary to the data given there, we found the transition-points to be: 95° C. into the anisotropous, greenishly opalescent liquid, and 117°.8 C. into the amorphous liquid. If every crystallisation-germ is excluded, the liquid can be undercooled to about 79°; it remains then only slightly viscous, and has a yellow colour. In this case also the temperature-coefficient of the surface-energy is extremely small; nor does the break in the curve at the transition-temperature seem to be of any considerable magnitude.

The density at 95° C. was: 1.0673; at 115° C. 1.0491. For the anisotropous liquid the density may thus be calculated from: $d_{4^\circ} = 1.0809 - 0.000905 (t - 80)$. For the isotropous liquid at 120° was found: 1.0428; at 140° C.: 1.0257; at 160° C.: 1.0086. In general at t C.: $d_{4^\circ} = 1.0599 - 0.000855 (t - 100^\circ)$. (Only to be used for temperatures from 117° upwards).

With the exception of the sudden increase of μ in the neighbourhood of 117° C., the temperature-coefficient of μ is here exceptionally small; for the isotropous liquid moreover it *increases* gradually with rise of temperature, and with a gradient of about 0.33 Erg per degree. The entire behaviour is very strange and enigmatic.

§ 3. If now we review in the first instance the results obtained with the three first-mentioned compounds, it will immediately attract attention that the corresponding μ-t-curves have all a *completely analogous* shape: this shows *two* branches, of which the first has regard to the anisotropous, the second to the isotropous liquid phase, and in all cases *without exception the first branch falls with increase of temperature more rapidly than the second.* The result is thus just opposite to what we should expect if we founded our opinion on the mentioned hypotheses about the molecular state of the two liquid phases; and with regard to the great probability of the correctness of these views, the fact observed may be considered as a rather strong argument *against* the opinion, that it is right to consider the smaller or greater values of $\frac{\partial \mu}{\partial t}$ as a somewhat sure criterion for the judgment of the degree of an occurring dissociation in the liquids.

It will be remarked further that the mutual position of the two branches of the curve always indicates *a sudden increase* of the value of μ at the transformation from the anisotropous-liquid into the isotropous-liquid condition. This discontinuity does not set in precisely at the transition-temperature; from the observations it seems rather probable, that it occurs in a *continuous* way, and already starts at temperatures below the transition-temperature.

In that case the two branches could perhaps be linked together in the way indicated in the diagrams by dotted lines (fig. 1).

Now although in the cases of both ethers *two* branches were also present in the μ-t-curves (fig. 2), and here too μ seems to increase suddenly at the transformation into the isotropous-liquid state, another remarkable peculiarity reveals itself here in so far, as the values of μ for the isotropous-liquid phase fall in the beginning with increase of temperature and then increase again to a flatter or steeper maximum in the curve. It can hardly be doubted that these phenomena are *real* ones; in these isotropous liquids we were therefore forced to see the first instances of liquids, whose free surface-energy increases with a rise of temperature. The explanation of such an abnormal phenomenon must be found in the algebraic sign of the heat-effect which accompanies the eventually isothermical enlargement of the surface-layer of the liquid. What peculiarities of the molecular structure of these isotropous liquids could be the cause of such abnormal heat-effect, is for the moment incomprehensible and very difficult to imagine. In any case the said phenomena indicate the presence of molecular conditions in these liquids, differing of course very much from those, which are intrinsic for most of the common isotropous liquids.

Laboratory for Inorganic and Physical
Chemistry of the University.

Groningen, June 1915.

Botany. – *"Crystallised Starch"*. By Prof. Dr. M. W. Beijerinck.

The fact that starch crystallises easily is not generally known. It is true that Arthur Meyer supported the view that the starch grain is a sphero-crystal, ¹) but convincing figures he does not give; his considerations are hypothetical and not decisive as he did not make any microscopical examination on soluble starch. Moreover, the highest temperature used by him was but 145° C., and he continued the heating not long enough.

Most species of starch, such as that of potato, wheat, barley, rye, rice, maize, behave as follows.

When a 10°/₀ solution, after previous boiling and gelatinising in distilled water, is heated during fifteen minutes or half an hour at 150° to 160° C., the grains dissolve to a perfectly clear, transparent liquid, in which, at slow cooling, a crystalline deposit sets off, consisting of very fine needles, which are either isolated or united in groups of various shapes, not seldom resembling natural starch, and which must undoubtedly be considered as crystallised starch on account of their behaviour towards diastase and chemical reagents.

The free needles, measuring but few microns or parts of microns, make the impression of an amorphous sediment. The groups, formed by longer needles have the shape of corn-sheaves or bundles of arrows (bolidesms); or of discs (bolidiscs), reminding in size and form of the red blood-cells; or they are more or less regular globules (spherites or sphero-crystals), from whose surface, however, here and there project the crystal needles.

Potato starch is very well apt to produce bolidesms and sphero-crystals; it is sufficient to heat to 150° C., during a quarter of an hour, a 10°/₀ solution in distilled water, previously boiled and gelatinised. After being kept 24 hours in a cold room loose needles, bolidesms or sphero-crystals are precipitated, and their crystalline nature is easily observable. What circumstances determine the union of the needles to bundles is not yet well known, but certainly slowness of crystallisation favours it, and the concentration has also some influence. Not seldom the whole deposit consists of a magnificent mass of sphero-crystals (Fig. 1). The discs, to which I shall return presently, are formed from potato starch at a somewhat lower temperature than the needles mentioned here.

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¹) Untersuchungen über Stärkekörner, Jena, 1895 Beiträge zur Kenntnis der Stärkegallerten, Kolloidchemische Beihefte Bd. 5, Pag. 1. 1913. The observations and opinions of Bütschli, Untersuchungen über Strukturen, Pag 283, Leipzig 1898, are obscure.

The two constituents of the starch grain, which I described earlier, [1]) namely the amylopectose, non-soluble at boiling, which forms the wall of the starch grain, and the granulose (amylose), which does dissolve at boiling and forms the inner part, change both at 150° C. into crystallisable starch.

It is not difficult to convert 40°/₀ of the original starch into needles or sphero-crystals. With a lower temperature or a shorter time of heating the quantity of starch, which crystallises increases, but at the same time the needles become shorter and less distinct. When heated at 110° to 120° C. the solution, at first perfectly clear, quite coagulates at cooling and becomes white as porcelain. This coagulated substance or gel, must also be considered as consisting of crystals, but the needles are nearly, or in fact ultramicroscopic. They do not show any orientation.

As the temperature is taken higher, the quantity of dextrine, which does not crystallise, increases. The iodine reaction shows that this dextrine contains much erythrodextrine at lower temperatures, and at higher consists only of leukodextrine, colouring light brown. At temperatures of from 160° to 170° C. the 10°/₀ potato starch quite changes into dextrine in from half an hour to three quarters of an hour; besides, the presence of sugar, susceptible to alcoholic fermentation, may then already be observed.

The sphero-crystals and needles of the starch dissolve, when heated in water, more slowly than soluble starch, which I ascribe to the greater size of the artificial needles, compared with that of the needles composing the natural and soluble starch. These needles consist in my opinion of a substance (granulose) impermeable to water, so that the dissolving must begin at the outside and will be the slower as the needles are thicker.

At 70° C. the solubility becomes very great, without any sign of production of paste or of gelatinising. With iodine the colour of the solution is pure blue. The effect of diastase on the granulose needles is as usual: erythrodiastase extracted from crude barley-flower, forms erythrodextrine and maltose, whilst leukodiastase prepared from malt, produces leukodextrine and maltose.

Of crystallisable dextrine and amylodextrine, so much discussed in literature, I perceived nothing in my experiments; the latter substance is evidently crystallised starch, with so much erythro- or leukodextrine between the needles, that the pure blue iodine colour of the granulose is modified to violet or reddish brown. When the

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[1]) Proceedings of the Academy of Sciences. Amsterdam, 11 April, 1912.

crystalline mass, which in fact sometimes colours red with iodine, is washed out with much water, the dextrine, and with it the "amylodextrine reaction" quite disappears, to make place for pure blue.

The crystals may also be obtained from soluble potato starch. Such starch is prepared by keeping raw starch during 10 days under 10 %-ic cold hydrochloric acid.

Crystal discs (bolidiscs) result very easily from wheat starch. The heating must be somewhat longer and the temperature higher than for potato starch. Besides, it is more difficult to obtain a perfectly clear solution from wheat paste.

Fig. 3 shows, 230 times magnified, the discs formed in a beakerglass of 100 cm^3, in which wheat starch, previously boiled in distilled water, is heated to 160° C. The discs are thinnest in the middle and from this centre the needles radiate. The discs resemble natural wheat starch as well in shape as in size. With polarised light I could not, however, perceive anything of the axial cross, which is so very obvious in natural starch. I suppose that it does exist, but is too feeble to be observed. It is, namely, a fact that the structure of the spherites and discs is much looser than that of natural starch, so that in a volume unit of the latter many more needles occur than in the discs and spherites. If now the double refraction of the separate needles be not great, their united power in the discs need not necessarily show the same as is seen in the natural grains.

That the double refraction of the common starch grains reposes on their crystalline nature and not on tangential and radial tensions, may be concluded from the fact, that the axial cross is in the usual way perceptible in soluble starch. As this substance is prepared with strong hydrochloric acid, whereby from 10 to 16 % of the dry substance is extracted, it must be concluded that all tensions, originally present in the grain, disappear.

That the discs may also be obtained from potato starch is demonstrated in Fig. 3, where 10% potato starch, after boiling and gelatinising in distilled water, in a 100 cm^3 beakerglass, heated to 125° C. during 3$^1/_2$ hour, and after 24 hours of crystallisation in a room of about 16° C., is figured 600 times magnified.

By moving the coverglass on the slide, many discs may be observed laterally, as is clearly seen in the photo. In the preparation of wheat starch used for fig. 3, all the grains are lying on their broad side.

The crystal discs of the starch are now and then referred to in literature as "Jacquelain discs", but without any allusion to their crystalline structure. JACQUELAIN himself, who first mentioned these grains, called them "granules de fécule". [1])

After having become acquainted with the described facts and found them confirmed for other species of starch, I convinced myself that the natural starch grain also is built up of crystal needles radiating from the dot or hilum. This may best be seen in soluble potato starch, very cautiously heated in the microscopic preparation on the slide under the coverglass, when all the stages of the dissolving in hot water can be followed. The tiny radiating crystal needles then become visible in a ring-shaped arrangement, such as might be expected from the structure of the starch grain itself. It seems that the length of the needles corresponds with the thickness of the rings.

From the preceding I conclude, that the formation of the starch grain takes place in the following way. The amyloplast produces granulose, which in the interior crystallises to small spherites, just as in a solution. But this granulose production occurs periodically, and so the process of crystallisation gives rise to the formation of the layers of the grain.

To explain the great difference existing between starch gelatinised at 100° C. and that heated to 150° and 160° C. it must be accepted that in the starch grain, beside the granulose, an incrustating substance exists, functioning as a "protecting colloid", whose presence makes the needles remain short, the shorter the more of the colloid is present. It remains active unto about 100° C., but above this temperature it slowly decomposes, quite to vanish at about 150° C.

The hypothesis that this protecting colloid might be a phosphoric ester of granulose; is contrary to the properties of soluble starch, for this behaves at crystallisation of the solutions, prepared between 100° and 150° C., precisely in the same manner as natural starch so that the protecting colloid is still present in this substance, whereas it might be expected that an ester would be decomposed by the strong, $10^0/_0$-ic hydrochloric acid used for its preparation.

Perhaps the colloid is the amyloplast itself, which, at the formation of the starch grain, remains partly enclosed between the fine granulose needles. Its greatest accumulation would then occur in the amylopectose wall of the grain, which does not yet dissolve at boiling.

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[1]) J. A. JACQUELAIN, Mémoire sur la fécule. Annales de Chimie et de Physique. T. 63, Pag. 173, Paris 1840. Much in this treatise is incorrect and obscure, else the discs would certainly already earlier have drawn general attention.

M. W. BEIJERINCK: „Crystallised Starch."

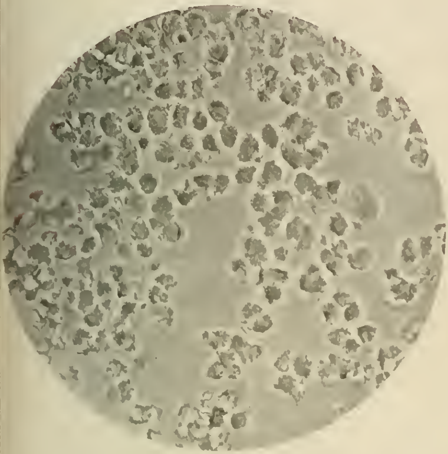
Fig. 1 (600).

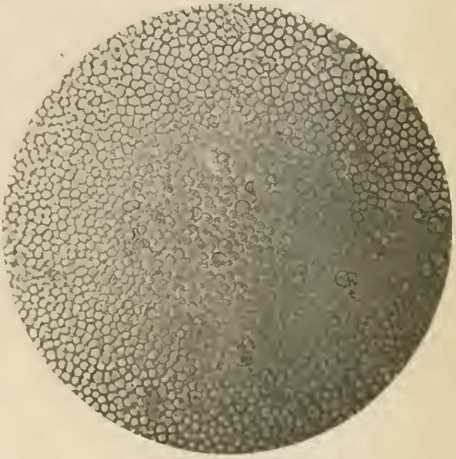
Fig. 3 (230).

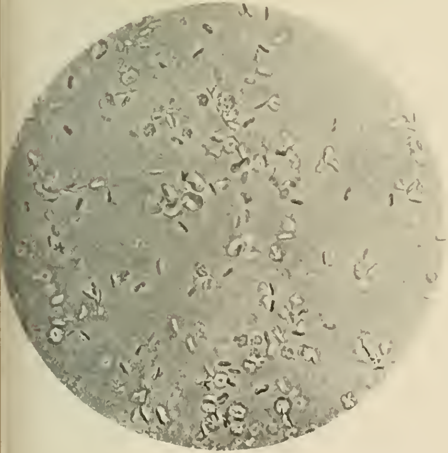
Fig. 2 (600).

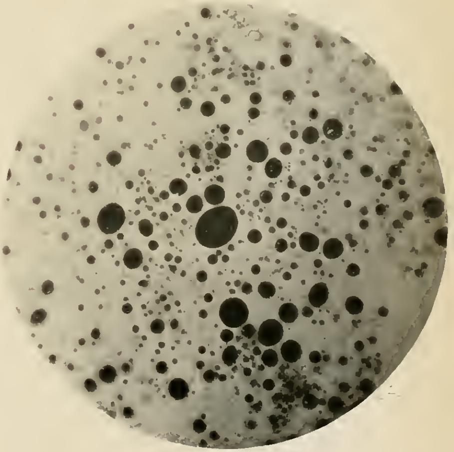
Fig. 4 (200)

That no difference could be found in the rate of nitrogen between the granulose and the amylopectose of the starch grain, to which circumstance I directed attention in my communication of 11 April 1912, I ascribe to the extremely small absolute rate of nitrogen in both constituents; but I think that the relative difference is considerable.

I will not omit to draw attention to the existence of starch species, which after heating, do not crystallise in the usual way. To these belongs arrowroot. If a 10 °/₀ paste of arrowroot is precisely treated as above described, it becomes after cooling, as usually, turbid and precipitates; but instead of a crystalline deposit we find in the microscopic preparation drops of various sizes, and homogeneous structure (Fig. 4), which later, however, become turbid and granulous. With iodine these drops turn deep blue and evidently consist of granulose like the crystal needles of the other starch species. The liquid between the drops is also a granulose solution, but less concentrated. The drops remind of a heavy oil, but they differ from it by such a small surface tension that notwithstanding their liquid state many may be pear- or egg shaped, and even pointed. Double refraction I could not perceive, but, nevertheless, I think it probable that they must be reckoned to the liquid crystals. That after some time the drops become turbid can be explained by the growing in length and thickness of the ultra-microscopic needles, which constitute the liquid crystal drops, hence, by the same process of crystallisation by which the needles originate.

The facts here briefly described deserve further attention from a physico-chemical view.

EXPLANATION OF THE FIGURES.

Fig. 1 (600). Sphero-crystals of 10 °/₀ potato starch, half an hour at 150° C.

Fig. 2 (600). Bolidiscs or JACQUELAIN discs of potato starch, half an hour at 125° C.

Fig. 3 (230). Bolidiscs or JACQUELAIN discs of wheat starch, three quarters of an hour at 160° C.

Fig. 4 (200). Drops or liquid crystals of 10°/₀ arrowroot, three quarters of an hour at 140° C., coloured with iodine.

Meteorology. — "*On the relation between meteorological conditions in the Netherlands and some circumjacent places. Atmospheric Pressure.*" By Dr. J. P. van der Stok.

(Communicated in the meeting of May 29, 1915).

1. For the knowledge of the climate of a country as also for the forecasting of the weather, it is of importance to investigate in how far a relation exists between the meteorological conditions within a limited region and in circumjacent places, chosen for this purpose, and to what degree local influences are felt.

Statistical methods, leading to empirical, numerical relations, involve the objection that many peculiarities, especially secondary phenomena, disappear by the collective treatment, but by their means existing relations may become more prominent, which necessarily remain unobserved by those who, for many years, have made a special study of the individual phenomena and, if no new relations are brought to light, quantitative rules are substituted for qualitative knowledge. As the most simple and principal problem, the question will be examined, what relation exists between the oscillations of the atmospheric pressure at de Bilt and the oscillations at a few surrounding places.

The isobars for different months and the corresponding average values of the wind show that this relation can hardly be the same in different seasons. We come to the same conclusion by investigating the relation existing between barometric oscillations within the region of high pressure near the Azores and of low pressure near Iceland, by which the climate of Western Europe is considerably affected.

Each factor indicates that the observations made during the months of January, February, and December are the fittest material for this inquiry which, therefore, is restricted to the wintermonths.

2. The method followed is simple, but necessarily laborious.

If the deviations from the average barometric height at a central point and the circumjacent stations be denoted by $x_1, x_2 \ldots x_n$, then, the quantities under consideration being small, a linear relation may be assumed to exist

$$x_1 = b_{12}x_2 + b_{13}x_3 \;\ldots\; b_{1n}x_n = F_1 , \quad . \quad . \quad . \quad . \quad (1)$$

and the coefficients b can be calculated by means of the method of least squares from the n—1 equations formed by multiplying the equations (1) successively by $x_2, x_3 \ldots x_n$ and addition of the total number of equations.

Putting

$$\frac{\Sigma x_i^2}{n} = \sigma_i^2 \qquad r_{pq} = \frac{\Sigma x_p x_q}{n\sigma_p\sigma_q} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where n denotes the number of equations, σ the standard deviation and r_{pq} the correlation-coefficient (c.c.) between x_p and x_q, the $n-1$ equations deduced from (1) can be substituted by the equivalent set of equations:

$$\left.\begin{array}{l} r_{12} = a_2 + a_3 r_{23} + a_4 r_{24} + \ldots a_n r_{2n} \\ r_{13} = a_2 r_{23} + a_3 + a_4 r_{34} + \ldots a_n r_{3n} \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ r_{1n} = a_2 r_{2n} + a_3 r_{3n} + a_4 r_{4n} + \ldots a_n \end{array}\right\} \quad . \quad . \quad . \quad . \quad (3)$$

By the quantities a thus calculated, the quantities b become

$$b_{12} = \frac{\sigma_1}{\sigma_2} a_2 \quad , \quad b_{13} = \frac{\sigma_1}{\sigma_3} a_3 \ldots b_{1n} = \frac{\sigma_1}{\sigma_n} a_n \ .$$

Obviously the equation (1) holds good only to a limited degree because the data are necessarily incomplete; a measure of the completeness is obtained by putting

$$R_1 x_1 = F_1$$

from which

$$R_1^2 = \frac{\Sigma F_1^2}{\Sigma x_1^2}$$

or, by substitution of the values (2):

$$\begin{array}{l} R_1^2 = a_2^2 + a_3^2 + a_4^2 \ldots a_n^2 \\ \quad + 2a_2 a_3 r_{23} + 2a_2 a_4 r_{24} \ldots 2a_2 a_n r_{2n} \\ \quad + 2a_3 a_4 r_{34} + 2a_3 a_5 r_{35} \ldots 2a_3 a_n r_{3n} \\ \quad \ldots\ldots\ldots\ldots\ldots\ldots \\ \quad + 2a_{n-1} a_n r_{n-1\,.\,n} \end{array}$$

The quantity R represents the general c.c. of equations (1) and the probable error of one determination of x_1 becomes

$$w = a\sigma_1 \sqrt{1-R^2} \qquad a = 0.67449$$

The partial c.c., defined as the c.c. between x_p and x_q when all other values x are zero, is calculated by solving also the equations

$$x_2 = F_2 \quad , \quad x_3 = F_3 \ldots x_n = F_n$$

and is given by the expression

$$\varrho_{pq} = \sqrt{b_{pq}\, b_{qp}}\ .$$

the sign of ϱ being that of the quantities b.

For the probable error of the c.c., Pearson gives the formula

$$f = {}^2/_3 \frac{1-r^2}{\sqrt{n}} .$$

It holds good for the case of normal distribution of deviations and the c.c. is considered to be reliable when f is considerably smaller than the c.c. itself; in the following tables

$$q = {}^r/_f .$$

3. The monthly mean values of barometric height in Iceland and the region of the Azores are compiled from Danish and Portuguese annals for the 36 years 1875—1910.

The Iceland values are obtained by taking the average of three stations namely: Berufjord, Grimsey and Stykkisholm.

From the Portuguese observations average values were calculated for two stations: Punta Delgada (Azores) and Funchal (Madeira); for the years 1906—1910 Horta was substituted for Funchal.

The monthly means thus obtained and considered as normal values, are shown in Table I; they are uncorrected for height above sealevel, this correction being unnecessary for the calculation of deviations, and given only to show the correspondence existing between the annual variation of the differences of pressure and the c.c. of table II.

TABLE I.

Monthly means of atmospheric pressure 1875—1910, 700 mm. +

	Azores	Iceland	Δ		Azores	Iceland	Δ
January	65.0	48.3	+16.7	July	65.7	56.4	+ 9.3
February	64.2	50.6	13.6	August	64.4	56.0	8.4
March	63.3	53.0	10.3	September	63.9	53.6	10.3
April	63.6	56.6	7.0	October	62.4	53.8	8.6
May	63.7	59.3	4.4	November	63.0	52.5	10.5
June	65.3	57.7	7.6	December	64.3	48.5	15.8

It appears from these data that the differences of atmospheric pressure are greatest in the winter months and smallest in May. Table II shows the results of the calculation relating to the deviations from the normal values of table I.

TABLE II.

Standard deviations and correlation coefficients Iceland = 1, Azores = 2.

	σ_1	σ_2	r	q	b_{12}	b_{21}
January	6.31 mm.	2.86 mm.	— 0.527	6.5	— 1.164	— 0.239
February	7.00	3.97	— 0.595	8.2	— 1.048	— 0.337
March	5.30	3.07	— 0.620	9.0	— 1.071	— 0.359
April	3.83	2.24	— 0.484	5.6	— 0.827	— 0.283
May	2.96	1.51	— 0.365	3.7	— 0.717	— 0.186
June	3.32	1.39	— 0.396	4.2	— 0.946	— 0.166
July	2.64	1.25	— 0.345	3.5	— 0.727	— 0.164
August	3.01	1.21	— 0.376	3.9	— 0.933	— 0.152
September	3.56	1.18	— 0.485	5.7	— 1.459	— 0.162
October	4.36	2.31	— 0.469	5.3	— 0.885	— 0.249
November	5.52	2.87	— 0.421	4.5	— 0.810	— 0.219
December	5.04	2.97	— 0.541	6.8	— 0.919	— 0.318

These results show, with a certainty much greater than can be obtained by graphic representations that the antagonism between the barometric oscillations in the region of the Azores and the northern parts of the Atlantic Ocean is evident in every month. From the regular course of the values of r, in the summer months as well as in winter, the conclusion may be drawn that a value of $q = 3.5$ indicates a reliable result, for, if the four months: May—August were taken together, the same value $r = 0.37$ would be obtained, but now with a factor of accuracy twice as great, or $q = 7.5$.

In his extensive investigation of correlations between monthly oscillations of atmospheric pressure and temperature at 49 stations in the northern hemisphere during the three winter months of the years 1897—1906, EXNER[1]) gives the value $r = -0.479$ ($q = 5.0$) for the c.c. between Stykkisholm and Punta Delgada which correspond well with the data of table II, and the fact that, by using a number of observations four times as great, a *greater* value is found may be considered as proof of the reliability of the results obtained.

4. For an investigation of the relation between oscillations of atmospheric pressure at different places, the "Dekadenbericht" edited

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[1]) F. M. EXNER, Ueber monatliche Witterungsanomalien auf der nördlichen Erdhälfte im Winter. Sitz. Ber. Akad. d. W. Wien **122**, 1913 (1105—1240).

by the "Deutsche Seewarte" contains valuable data: commencing in 1900, this publication gives ten-day means of barometric heights, in such a way that three average values are always formed for each month. At the same time normal values are given so that deviations from the normals can be formed at once for the purpose of further treatment. In accordance with the results of Table II, the inquiry is restricted to the winter months from December 1900 to February 1914 as being the most disturbed; the number of observations therefore amounts to 126.

From the stations in this publication the following places were chosen, in the equations represented by their rank-number; the values σ are the standard deviations.

1. Helder $\sigma_1 = 6.96$ mm.
2. Valencia (W. coast Ireland) $\sigma_2 = 8.70$ „
3. Clermont (S. France) $\sigma_3 = 5.98$ „
4. Milan (N. Italy) $\sigma_4 = 5.82$ „
5. Neufahrwasser (Baltic Sea coast, Prussia) $\sigma_5 = 6.30$ „
6. Christiansund (W. coast Norway) $\sigma_6 = 8.45$ „

TABLE III.

Correlation-coefficiënts r, factors of precision q and distances D.

Helder—Valencia	$r_{12} = 0.770$	$q = 30.8$	$D =$ 9°.2
Helder—Clermont	$r_{13} = 0.727$	25.7	7°.25
Helder—Milan	$r_{14} = 0.511$	11.5	8°.0
Helder—Neufahrwasser . .	$r_{15} = 0.633$	17.6	8°.35
Helder—Christiansund . .	$r_{16} = 0.609$	16.1	10°.3
Valencia—Clermont . . .	$r_{23} = 0.704$	23.2	10°.7
Valencia—Milan	$r_{24} = 0.380$	7.4	14°.3
Valencia—Neufahrwasser .	$r_{25} = 0.247$	4.4	17°.4
Valencia Christiansund. .	$r_{26} = 0.310$	5.7	14°.7
Clermont Milan	$r_{34} = 0.645$	18.4	4°.2
Clermont—Neufahrwasser .	$r_{35} = 0.246$	4.4	13°.15
Clermont—Christiansund .	$r_{36} = 0.058$	1.0	17°.5
Milan—Neufahrwasser . .	$r_{45} = 0.370$	7.1	10°.8
Milan—Christiansund . .	$r_{46} = 0.095$	1.6	17°.7
Neufahrw.—Christiansund .	$r_{56} = 0.746$	28.0	10°.4

In Table III (p. 314) the different correlation coefficients are given and the distances between the stations expressed in degrees of the great circle corresponding to about 111 k.m.

For ascertaining meteorological conditions, the regression-equations (preferably called meteorological condition equations) are of greater importance than these general, interdependent correlation coefficients.

$$\left.\begin{array}{ll}
 & R \\
x_1 = 0.238\, x_2 + 0.520\, x_3 + 0.011\, x_4 + 0.201\, x_5 + 0.292\, x_6 & 0.943 \\
x_2 = 0.928\, x_1 + 0.416\, x_3 - 0.096\, x_4 - 0.485\, x_5 - 0.112\, x_6 & 0.830 \\
x_3 = 0\ 680\, x_1 + 0.109\, x_2 + 0.242\, x_4 - 0.026\, x_5 - 0.336\, x_6 & 0.908 \\
x_4 = 0.038\, x_1 - 0.076\, x_2 + 0\ 594\, x_3 + 0.353\, x_5 - 0.150\, x_6 & 0.672 \\
x_5 = 0.457\, x_1 - 0.259\, x_2 - 0.054\, x_3 + 0.250\, x_4 + 0.396\, x_6 & 0.843 \\
x_6 = 0.929\, x_1 + 0.063\, x_2 - 0.822\, x_3 - 0.150\, x_4 + 0.573\, x_5 & 0.873
\end{array}\right\} \quad (4)$$

The partial c.c. calculated from the coefficients of these equations are given in Table IV, arranged according to their magnitude.

TABLE IV. Partial correlation-coefficients.

Helder—Clermont	0.594	Valencia—Christiansund. .	0.084
Helder—Christiansund . .	0.521	Helder—Milan	0.020
Neufahrw. - Christiansund .	0.476	Clermont - Neufahrwasser .	– 0.037
Helder—Valencia	0.470	Valencia—Milan	—0.085
Milan—Clermont	0.379	Milan—Christansund . .	—0.150
Helder—Neufahrwasser . .	0.303	Valencia - Neufahrwasser .	– 0.355
Milan - Neufahrwasser . .	0.297	Clermont—Christiansund .	—0.526
Valencia—Clermont . . .	0.213		

From these results it appears that the choice of the stations was good, except Milan which, although at about the same distance from Helder as Clermont, still exercises a much smaller influence.

Clermont and Milan being at a mutual distance of only 4°.2. it is possible that this result is due to purely arithmetical reasons; the method followed involves that two stations near to each other must be considered as one, because it depends on incalculable factors how the common effect is distributed over either point, this being of no importance for the result.

If this were the case, however, the partial c.c. between Clermont and Milan ought to be nearly equal to unity, which is contradicted by the c.c.: 0.379.

It appears, therefore, that Milan is situated out of the circle of influence, which from a meteorological point of view is perfectly clear because here the influence of the Alpine montain chains and the Mediterranean prevails, the equations (4) are, therefore, actually based upon only four points, situated round Helder and the first equation proves that these are sufficient to account for the barometric oscillations in the central point to an extent of 94 %.

As it may be assumed that this percentage would increase by augmenting the number of stations, it appears from this equation that local disturbances have only a subordinate influence. Whether this statement is also applicable to the summer months can only be proved by experiment.

Another result is that the meteorological field cannot be considered as uniform in different directions, the influence of Clermont being twice as great as that of Valencia at a slightly greater distance from Helder.

It may be, further, remarked that the central point, without exception, plays a more important part in the equations for the surrounding stations than, inversely, the latter for Helder; which is easily understood because the central point represents the meteorological conditions common to the whole field of disturbance. In the partial c.c. this asymmetry disappears and for these quantities the question arises whether and to what degree the relations are dependent on the distance.

Assuming that this relation can be taken as linear so that

$$\varrho = 1 - kD$$

where D denotes the distance, expressed in degrees and k a constant, we find for Valencia, Clermont and Christiansund for k respectively:

0.0576 0.0560 0.0465

for Neufahrwasser the somewhat different value: 0.0834.

According to this relation the partial c.c. at equal distances of 5° would be

$$\varrho_{12} = 0.711 \qquad \varrho_{13} = 0.720 \qquad \varrho_{15} = 0.583 \qquad \varrho_{16} = 0.767.$$

Finally the remarkable fact may be noticed that the same negative correlation, observed between the region of the Azores and Iceland at a distance of about 35°, appears to exist, and with the same magnitude, between the stations Clermont and Christiansund at about half the distance.

5. In order to come to a conclusion concerning the results obtained,

it seemed desirable to institute a similar inquiry based upon other data and partly other stations.

For this purpose daily observations made at 7 a. m. as published in different weather bulletins and inscribed in registers at de Bilt, were chosen.

A first group of stations is: 1. de Bilt, 2. Ile d'Aix (W. coast France), 3. Dresden, 4. Lerwick (Shetland Isles). The distances between de Bilt and the surrounding stations are:

$$7^\circ.38 \quad 5^\circ.42 \ , \ 8^\circ.80 \ ,$$

the azimuths:

$$N\,217^\circ 11'\,E \ , \ N\,97^\circ 44'\,E \ , \ N\,338^\circ 59'\,E \ ,$$

the mutual angular distance, therefore, about 120°.

The data are observations made during the winter months of January, February, December 1912, January, February, December 1913 and January, February 1914, in total 240 observations.

The standard deviations are:

$$\sigma_1 = 8.25 \ , \ \sigma_2 = 7.79 \ , \ \sigma_3 = 7.96 \ , \ \sigma_4 = 10.72 \ mm.$$

The correlation coefficients:

$$\begin{array}{lll} r_{12} = 0.709 \ , & r_{13} = 0.868 \ , & r_{14} = 0.579 \\ r_{23} = 0.532 \ , & r_{24} = 0.1475 \ , & r_{34} = 0.402 \end{array}$$

The criterion $q = {}^{r}/_{f}$ for the reliability of the c.c. calculated, mentioned above, cannot be applied in this case (as it was for ten day and monthly means) because daily observations are by no means to be considered as independent data.

The condition-equations calculated from these values are as follows:

$$\left.\begin{array}{ll} x_1 = 0.395\,x_2 + 0.568\,x_3 + 0.234\,x_4 & R_1 = 0.957 \\ x_2 = 1.370\,x_1 - 0.525\,x_3 - 0.346\,x_4 & R_2 = 0.821 \\ x_3 = 1.207\,x_1 - 0.321\,x_2 - 0.205\,x_4 & R_3 = 0.905 \\ x_4 = 2.042\,x_1 - 0.873\,x_2 - 0.842\,x_3 & R_4 = 0.751 \end{array}\right\} \quad . \ . \ (5)$$

The partial c.c., the mutual distances, the variation k of the partial c.c. per degree of distance and the partial c.c. for equal distances of 5° from the centre are:

$$\begin{array}{lll} & & k = 5 \\ \varrho_{12} = 0.735 & k_{12} = 0.0358 & \varrho_{12} = 0.821 \\ \varrho_{13} = 0.828 & k_{13} = 0.0318 & \varrho_{13} = 0.841 \\ \varrho_{14} = 0.691 & k_{14} = 0.0351 & \varrho_{14} = 0.824 \\ \hline & \text{Mean } 0.0342 & \text{Mean } 0.829 \end{array}$$

$$\begin{array}{ll} \varrho_{23} = -\,0.411 & D_{23} = 11^\circ.10 \\ \varrho_{24} = 0.550 & D_{24} = 14^\circ.12 \\ \varrho_{34} = -\,0.415 & D_{34} = 12^\circ.50 \end{array}$$

6. A second set of four stations is:

1. De Bilt, 2. Valencia, 3. Mülhausen i. E. and 4. Sylt (W. coast Schleswig Holstein).

The distances from de Bilt to the surrounding stations are respectively:

$$9^\circ.48, \qquad 4^\circ.57, \qquad 3^\circ.39$$

the azimuths:

$$N\ 32^\circ\ 40'\ E. \qquad N\ 161^\circ\ 32'\ E, \qquad N\ 275^\circ\ 13'\ E.$$

For these places the angular distance is likewise about 120°, and they differ 60° with the stations mentioned sub 5.

The standard deviations are

$$\sigma_1 = 8.25, \ \sigma_2 = 10.82, \ \sigma_3 = 7.30, \ \sigma_4 = 8.96 \text{ mm.}$$

The correlation coefficients:

$$\begin{array}{lll} r_{12} = 0.633 \ , & r_{13} = 0.818 \ , & r_{14} = 0.864 \\ r_{23} = 0.480 \ , & r_{24} = 0.433 \ , & r_{34} = 0.528 \end{array}$$

from which the following condition-equations derive:

$$\left.\begin{array}{ll} x_1 = 0.140\, x_2 + 0.494\, x_3 + 0.510\, x_4 & R_1 = 0.976 \\ x_2 = 2.417\, x_1 - 0.852\, x_3 - 1.034\, x_4 & R_2 = 0.722 \\ x_3 = 1.457\, x_1 - 0.146\, x_2 - 0.653\, x_4 & R_3 = 0.905 \\ x_4 = 1.595\, x_1 - 0.188\, x_2 - 0.693\, x_3 & R_4 = 0.934 \end{array}\right\} \quad . \ . \ (6)$$

For the partial c.c., the distances not yet mentioned, the variation k for one degree distance and the c.c. for equal distances of 5°, we find:

$$\begin{array}{lll} & & k = 5 \\ \varrho_{12} = 0.583 & k_{12} = 0.0441 & \varrho_{12} = 0.780 \\ \varrho_{13} = 0.848 & k_{13} = 0.0332 & \varrho_{13} = 0.834 \\ \varrho_{14} = 0.902 & k_{14} = 0.0290 & \varrho_{14} = 0.855 \\ \hline & \text{Mean } 0.0354 & \text{Mean } 0.823 \end{array}$$

$$\begin{array}{ll} \varrho_{23} = -\ 0.352 & D_{23} = 12^\circ\ 03 \\ \varrho_{24} = -\ 0.440 & D_{24} = 11^\circ.45 \\ \varrho_{34} = -\ 0.672 & D_{34} = \ 7^\circ.17 \end{array}$$

Either group proves that barometric oscillations in a central point may be determined with great accuracy from only three well chosen stations; the condition-equations for de Bilt (x_1) show even a greater value of R than the corresponding equations (4) and the equations for the three easterly stations: Dresden, Mülhausen and Sylt all show a value greater than 0.9. As one would perhaps be inclined to overrate the value of such a c.c. for an actual calculation, it seems not superfluous to remark that if — as in this case — the standard deviation is relatively great, a large value of c.c. may leave a pretty large margin of uncertainty. According to the formula given in § 2 the probable errors of a determination from (5) and (6) for de Bilt with $R = 0.957$ and 0.976 resp. are 1.62 and 1.21 m.m.; they prove however, as well as equ. (4) that local influences play an unimportant part.

In the same manner as from (4), it appears from (5) and (6) that the influence of the eastern stations Mülhausen, Dresden and Sylt is considerably greater than that of the western stations: Valencia, Ile d'Aix and Lerwick.

For the partial c.c. between Helder and Valencia we have found 0.470 (Table IV) whereas for that between de Bilt and Valencia, as deduced from (6), we find 0.583, an agreement which can be considered fairly satisfactory if we take into account that the data used in computing these values are totally different.

As mentioned in § 3, for the first series general normal values have been used, given in the "Berichte" so that it is possible that in this case the sum of the deviations for each station is not exactly equal to zero which, of course, would influence the value of the c.c.

It is, however, more probable that the cause of this disagreement must be ascribed to an insufficiency of the number of observations used in § 5 and § 6, because the values of k found in the first investigation (§ 4) are all greater than those derived from the groups treated in § 5 and § 6, from which a generally smaller value of the c.c. would follow. Owing to the mutual dependence a number of 240 daily observations cannot be considered as equivalent to 126 tenday means and it is a general law in statistical investigations that the computed relations show a tendency to give smaller limiting values as the data increase in number.

7. Finally the question may be put, what will the condition equation become when the two groups of three surrounding stations are taken together so that the deviation of atmospheric pressure in the central point is determined by 6 circumjacent stations within angular distance of about 60°.

The numeration of the stations then becomes:

1. de Bilt
2. Valencia
3. Ile d'Aix
4. Mülhausen
5. Dresden
6. Sylt
7. Lerwick

The c.c. computed in § 5 and § 6 and all products can be used for this purpose so that the labour entailed for this calculation was relatively small.

The values not yet given are:

$r_{23} = 0.670$ $\quad r_{36} = 0.359$ $\quad r_{67} = 0.744$

$r_{25} = 0.360$ $\quad r_{45} = 0.781$

$r_{27} = 0.543$ $\quad r_{47} = 0.134$

$r_{34} = 0.888$ $\quad r_{56} = 0.848$

And the condition equation becomes:

$$x_1 = 0.140\ x_2 - 0.069\ x_3 + 0.624\ x_4 - 0.101\ x_5 + \\ + 0.538\ x_6 + 0.015\ x_7 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (7)$$

It appears from (7) that the methods of computation followed in this inquiry fails in this case in so far that, owing to the insufficient distances between successive stations, negative coefficients now appear in the equations. Obviously they are due to a mutual distribution of common influence which must be considered as unreal and as a mere arithmetical result.

Equation (7), therefore, shows a great resemblance to the first of the equations (6); the coefficients are alternatively small or even negative and if we reduce the equation to one with three terms by an equal distribution of the odd over the even coefficients so that for example:

$$coëff.\ x_2 = 0.624 - \frac{0.069 + 0.101}{2} = 0.539,$$

we find the following equation little different from (6)

$$x_1 = 0.113\ x_2 + 0.539\ x_3 + 0.495\ x_4$$

In equation (7) the prevailing influence of the stations Mülhausen and Sylt is still more conspicuous than in the results of other groups.

A calculation of the remaining equation and of partial c.c. would in this case have no meaning.

Taken as a whole equation (7) is to be considered as an improvement because the general correlation-coefficient is very large namely

$$R = 0.9953$$

from which follows, for the calculation of one value, the probable error:

$$w = 0.539\ mm.$$

Meteorology. — *"On the relation between meteorological conditions in the Netherlands and some circumjacent places. Difference of atmospheric pressure and wind."* By Dr. J. P. VAN DER STOK.

1. In previous communications it was proved that the relation between direction and magnitude of the gradient of atmospheric pressure on the one hand, and force and angle of deviation (between wind and gradient) of the wind on the other hand is not a constant quantity, but varies with the azimuth of the gradient [1]) and with increase and decrease of pressure difference [2]).

If we select from the gradients, as calculated for the Netherlands and published in the weather charts, those pointing to eight points of the compass, then, for the period 1904—1910, the wind at De Bilt and the whole year, we find the following results:

TABLE I. Average values of angle of deviation α and force of the wind (Beaufort scale) for different directions of unity gradient.

Direction-gradient	Number of observations $\alpha =$ 45°	67°.5	90°	Sum	Average force $\alpha =$ 45°	67°.5	90°	Aver. force for grad. = 1	Average deviation
N	208	165	66	439	1.9	1.8	2.0	1.86	60°
NE	44	123	112	279	1.8	1.9	2.0	1.93	73
E	17	44	59	120	3.0	2.8	3.2	2.97	79
SE	14	54	42	110	3.4	2.9	3.2	3.06	73
S	69	71	39	179	2.2	2.0	2.0	2.05	64
SW	38	92	51	181	1.9	2.1	2.6	2.17	69
W	75	73	28	176	2.1	2.3	2.3	2.14	62
NW	180	122	29	331	1.9	2.0	2.3	1.95	57
Total	645	744	426	1815	Aver. 1.94	2.03	2.30	2.05	64.8

Various objections against the method followed in this inquiry may be raised.

Angles of deviation smaller than 45° are left out of consideration

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[1]) On the angle of deviation between gradient of atmospheric pressure and air motion. Amsterdam. Proc. Sci. K. Akad. Wet. 14, 1912 (865—875).

[2]) The relation between changes of the weather and local phenomena. Ibid. 14, 1912 (856—865).

because these are usually associated with feeble wind forces, so that the direction becomes uncertain.

It appears however from the large frequencies for $\alpha = 45^\circ$ and N and NW directions of the gradient (208 and 180), greater than any other, that the omission of smaller values of α in these cases certainly gives too great a value for the average angle of deviation, whereas for E and SE directions of the gradient the influence of smaller values than 45° are compensated by those greater than 90°. The results of this inquiry are therefore to be considered as doubtful, not only in an absolute but also in a relative sense.

A more serious objection against this method is that it appears from table I that the meteorological field is by no means to be taken as uniform: easterly and south-easterly gradients are generally associated with wind forces and angles of deviation considerably greater than northerly and north-westerly directed gradients. The frequencies indicate that a gradient of a given magnitude and direction may be accompanied by different forces and angles of deviation so that the gradient, calculated as a *resultant* difference of pressure in a central point and four circumjacent stations cannot be considered as a reliable measure of the wind. A positive difference in a given direction does not exercise the same influence as a negative difference in the opposite direction. If, therefore, we wish to investigate this relation, the computation of a resultant must be avoided and each direction is to be taken into account with its proper coefficient of influence.

2. To this purpose *differences* of atmospheric pressure between Flushing on the one hand and Valencia, Biarritz, Munich, Neufahrwasser and Lerwick in the other hand are associated with the wind at the first named station, as published in the annals of the K. N. M. Institute for each day of the eight months: January, February, December 1912 and 1913, and January, February 1914. The average differences for the whole period are:

1.	Flushing—Valencia	+ 5.8 mm.
2.	,, —Biarritz	— 1.9
3.	,, —Munich	— 4.3
4.	,, —Neufahrwasser	+ 0.4
5.	,, —Lerwick	+ 7.9.

The average wind at Flushing during the same period is:

3.70 m.p.s. S 25°36′ W

$W_n = -3.34$ N component

$W_e = -1.60$ E component.

The length D and the azimuth A of the arcs joining Flushing and the other stations are:

1.	$D = 8°34'$	$A =$ N 278°41′ E
2.	8°40′	205°31′
3.	6°8′	119°39′
4.	9°23′	66°4′
5.	9°8′	345°4′

Denoting the deviations from the average values of the pressure differences by x_1, $x_2 \ldots x_5$, and those of the north- and east components of the wind, by x_6 and x_7, and further assuming that a linear relation is justified we can put:

$$x_6 = b_{61}x_1 + b_{62}x_2 + \ldots + b_{65}x_5$$
$$x_7 = b_{71}x_1 + b_{72}x_2 + \ldots + b_{75}x_5\,.$$

The treatment was the same as explained in a previous paper and the following results were obtained:

$r_{12} = +0.383$
$r_{13} = -0.185$
$r_{14} = -0.354$
$r_{15} = +0.297$
$r_{23} = +0.576$
$r_{24} = -0.116$
$r_{25} = -0.201$
$r_{34} = +0.290$
$r_{35} = -0.491$
$r_{45} = +0.197$

$r_{16} = -0.456$
$r_{26} = +0.256$
$r_{36} = +0.737$
$r_{46} = +0.300$
$r_{56} = -0.561$
$r_{17} = +0.313$
$r_{27} = +0.765$
$r_{37} = +0.522$
$r_{47} = -0.375$
$r_{57} = -0.463$

$\sigma_1 = 8.47$ mm.
$\sigma_2 = 7.15$,,
$\sigma_3 = 4.57$,,
$\sigma_4 = 7.72$,,
$\sigma_5 = 8.97$,,
$\sigma_6 = 4.55$ m.p.s.
$\sigma_7 = 6.01$,,

The condition equations then become:

$$\left.\begin{aligned} x_6 &= -0.134\,x_1 + 0.002\,x_2 + 0.537\,x_3 + 0.061\,x_4 - 0.123\,x_5 \\ x_7 &= +0.089\,x_1 + 0.426\,x_2 + 0.293\,x_3 - 0.227\,x_4 - 0.155\,x_5 \end{aligned}\right\} \qquad (1)$$

The general correlation coefficient of the first equation (N. component) is $R = 0.825$, of the second equation (E. component) $R = 0.870$. It follows from these results that the actual pressure differences, deduced from observations made at 5 circumjacent stations enable us to account for the wind blowing in the centre to a degree of $85^{0}/_{0}$ or, in other words, the expected deviation from the mean value with an average uncertainty of $\sigma_6 = \pm 4.55$ and $\sigma_7 = \pm 6.01$ as a first, rough approximation of the wind components is improved by equation (1) with

$$(1 - \sqrt{1 - R^2}) \times 100 \left\{ \begin{aligned} &= 43^5 \\ &= 50^5 \end{aligned} \right. \text{per cent.}$$

It appears from equ. (1) that a positive gradient in the direction of Valencia produces a SE wind, in the direction of Biarritz an E, of Munich a NE, of Neufahrwasser a NW, and of Lerwick a SW wind and further, that, although the distance from Flushing is about the same, Biarritz exercises a much stronger influence than Valencia. These results are in accordance with the experience afforded by the study of the weather charts, but they give quantitative relations by means of which a calculation of the resulting wind becomes possible.

With the help of equ. (1) it is possible to demonstrate in a more conspicuous manner the influence of the gradient direction on the velocity of the wind and the angle of deviation by putting the question: which wind will be caused by or, rather, will be associated with a fictitious distribution where the pressure difference in the whole field is uniform and represented by isobars, successively drawn in the directions of eight principal points of the compass, and at distances from each other equal to unity (1 mm. per degree of latitude).

Denoting the distance of a station from Flushing by D, the azimuth of the joining arc by A, the azimuth of the gradient by α and the average difference of pressure by β, then

$$x_i = D \cos (A_i - \alpha) - \beta_i$$

where i is to be given successively the values 1 to 5.

The components of the wind then follow from the values computed from (1):

$$W_n = w_n + x_6 \qquad W_e = w + x_7.$$

The results of this calculation are given in table II.

TABLE II.

Direction gradient	Wind velocity for grad. = 1 m. p. s.	Direction of wind	Angle of deviation
N	5.43	N 248° E	68°
NE	5.29	294	69
E	5.53	349	79
SE	7.21	35	80
S	8.35	67	67
SW	7.55	97	52
W	5.56	139	49
NW	4.90	198	63

According to the expectation formulated in § 1, by this improved method a smaller minimum value is found for the angle of deviation than in table I; at the same time the positions of the maxima and minima are somewhat shifted.

It may be noticed that for the correlation between Munich and Lerwick for pressure *differences* a negative value, $r_{35} = -0.491$ has been found of the same order of magnitude as the *partial* correlation of deviations from pressure between Clermont and Christiansund viz. -0.536, and between the region of the Azores and Iceland.

The laborious calculations of partial corr. coeff. may, therefore, often be avoided by forming *differences*, by which process large common influences are eliminated.

3. For a third investigation the average wind for the Netherlands has been calculated (for the same period as mentioned in § 2 and 7 a.m.) from the stations De Bilt, Flushing, Helder, and Groningen and this average wind has been associated with pressure differences between De Bilt on the one hand and Sylt, Dresden, Mülhausen, Ile d'Aix, Valencia, and Lerwick on the other hand; the azimuths of these stations differ about 60° C.

The ranknumbers, average values and standard deviations now become:

	Pressure differences	Average differences	Standard deviation
1.	De Bilt—Sylt	+ 1.58 mm.	$\sigma_1 = 4.96$ mm.
2.	,, —Dresden	— 1.99	$\sigma_2 = 4.16$
3.	,, —Mülhausen	— 3.71	$\sigma_3 = 4.74$
4.	,, —Ile d'Aix	— 1.48	$\sigma_4 = 6.38$
5.	,, —Valencia	+ 5.31	$\sigma_5 = 8.47$
6.	,, —Lerwick	+ 7.95	$\sigma_6 = 8.97$
	Wind		
7.	North-component	— 2.63 m.p.s.	$\sigma_7 = 3.61$ m.p.s.
8.	East-component	— 0.95	$\sigma_8 = 4.52$

The correlation-coefficients are:

$r_{12} = +0.366$
$r_{13} = -0.446$
$r_{14} = -0.520$
$r_{15} = -0.253$
$r_{16} = +0.546$

$r_{25} = -0.411$
$r_{26} = -0.271$
$r_{27} = +0.663$
$r_{28} = -0.246$

$r_{45} = +0.420$
$r_{46} = -0.289$
$r_{47} = +0.243$
$r_{48} = +0.763$

$r_{17} = -0.168 \qquad r_{34} = +0.782 \qquad r_{56} = +0.300$

$r_{18} = -0.820 \qquad r_{35} = +0.014 \qquad r_{57} = -0.398$

$\qquad\qquad\qquad\quad r_{36} = -0.508 \qquad r_{58} = +0.323$

$r_{23} = +0.354 \qquad r_{37} = +0.624 \qquad r_{67} = -0.635$

$r_{24} = -0.061 \qquad r_{38} = +0.687 \qquad r_{68} = -0.535$

The condition equations reduced from these values are:

$$\left.\begin{array}{l} x_7 = -0.085x_1 + 0.396x_2 + 0.255x_3 - 0.038x_4 - 0.060x_5 - 0.103x_6 \\ x_8 = -0.239x_1 - 0.346x_2 + 0.454x_3 + 0.068x_4 + 0.083x_5 - 0.129x_6 \end{array}\right\} \quad (2)$$

with the general correlation-coefficients:

$$R_7 = 0.856\,, \quad R_8 = 0.938$$

With respect to a first expectation with the average uncertainty σ_7 and σ_8 the expectation has been, therefore, improved respectively 48 and 65 per cent, and the computation with the help of 6 stations affords an improvement with respect to the use of 5 stations with only 5°/₀ for the north-component, but with 15°/₀ for the east-component. The probable uncertainty becomes ± 1.24 and ± 1.05 m.p.s.

TABLE III.

Direction gradient	Direction wind	Wind-velocity	Angle of deviation
N	N 231° E	3.43 m.p.s.	51°
NNE	258	3.39	56
NE	285	3.35	60
ENE	309	3.56	62
E	338	3.76	68
ESE	3	4.11	70
SE	25	4.44	70
SSE	45	4.96	67
S	62	5.28	62
SSW	80	5.46	57
SW	96	5.39	51
WSW	114	5.14	47
W	133	4.73	43
WNW	154	4.27	42
NW	178	3.86	43
NNW	204	3.58	47

Table III (p. 326) shows the values of the wind velocity, the direction of the wind and the angle of deviation as calculated from equation (2) for 16 different directions of the gradient and a uniform field of 1 mm. difference of pressure per degree of latitude.

A comparison of these results with those of table II shows that the use of an average wind for the whole country has induced a more regular course in the numbers, but also that considerable differences are due to this method. The wind velocity and the angles of deviation have become smaller as also the azimuths and wind directions. From this result we may conclude that the northerly stations behave differently in many respects from Flushing and that a combination as made in this inquiry is not desirable.

Physics. — "*On a General Electromagnetic Thesis and its Application to the Magnetic State of a Twisted Iron Bar*". By Dr. G. J. Elias. (Communicated by Prof. H. A. Lorentz).

(Communicated in the meeting of May 29, 1915).

Wiedemann has already observed that in a longitudinally resp. circularly magnetized iron bar a circular resp. longitudinal magnetisation arises in consequence of torsion. Moreover he discovered that a bar which is at the same time longitudinally and circularly magnetized, is twisted. These observations formed the starting point of the following considerations.

In a magnetic field, in which the magnetic induction can be an arbitrary vector function of the magnetic force variable from point to point, whereas the media in the field can be anisotropic also with respect to the conductivity, but in which no phenomena of hysteresis occur, the equation

$$T = \frac{1}{c}\int \Sigma\, i\, dM \text{ [1]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

holds for the magnetic field energy.

In this i means the current in a circuit M, the induction flux passing through this circuit, c representing the ratio of the electromagnetic to the electrostatic unity of electricity. The summation extends over all the circuits, the integration covering a range from M for $i = 0$ to the final value which M assumes.

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[1] In this and following formulae Lorentz's system of unities is used.

1. Let us now consider two linear conductors (circuits), in which currents i_1 and i_2 run. Let M_1 be the induction flux passing through the first, M_2 that through the second wire. If M_1 and M_2 change infinitely little, then follows from (1)

$$d\,T = \frac{1}{c}\,(i_1 dM_1 + i_2\, dM_2),$$

for which we may put:

$$dT = \frac{1}{c}\, d\,(i_1\, M_1 + i_2\, M_2) - \frac{1}{c}\, M_1\, di_1 - \frac{1}{c}\, M_2\, di_2.$$

The first member of this equation is a total differential, as T is perfectly determined by i_1 and i_2, hence

$$M_1\, di_1 + M_2\, di_2$$

must also be a total differential, from which follows:

$$\frac{\partial M_1}{\partial i_2} = \frac{\partial M_2}{\partial i_1}\,{}^{1}), \quad \ldots \ldots \ldots \quad (2)$$

i.e. the increase of the induction flux passing through the first circuit, caused by an infinitely small current variation in the second, is equal to the increase of induction flux passing through the second circuit, caused by an equal change of current in the first.

An increase of the induction flux dM will give rise to an electrical impulse, in which through every section of the circuit the quantity of electricity

$$de = -\frac{1}{c}\frac{dM}{w}$$

passes, if w represents the resistance of the circuit. The negative sign means that the direction of the current, is in lefthand cyclical order with the increase of the induction flux.

If now the current i_1 increases by the infinitely small amount of di_1, the induction flux through the second circuit will increase by:

$$dM_2 = \frac{\partial M_2}{\partial\, i_1} di_1.$$

Hence for a short time an induction current will pass through the second conductor. If after the lapse of this time the current in this conductor has again the same value as before, then the "integral current", i.e. the total quantity of electricity set in motion by the induction current amounts to:

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[1]) For so far as I have been able to ascertain, this relation, as well as those following later (3), (8), (15) and (17) is new.

$$de_2 = -\frac{1}{c} \cdot \frac{dM_2}{w_2} = -\frac{1}{c \cdot w_2} \frac{\partial M_2}{\partial i_1} di_1 .$$

In the same way for an infinitesimal change of i_2 the integral current in the first conductor will amount to

$$de_1 = -\frac{1}{c \cdot w_1} \frac{\partial M_1}{\partial i_2} di_2 .$$

If $di_1 = di_2$, it follows from this by the aid of (2)

$$w_1 de_1 = w_2 de_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3')$$

If by $\frac{\partial e_1}{\partial i_2}$ resp. $\frac{\partial e_2}{\partial i_1}$ we denote the quotient of the integral current in the first resp. second conductor and the change of current in the second resp. first conductor, we may also write:

$$w_1 \frac{\partial e_1}{\partial i_2} = w_2 \frac{\partial e_2}{\partial i_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In case the permeability is independent of the intensity of the field, so that $\mathfrak{B}$ in general is a linear vector function of $\mathfrak{H}$, both $\mathfrak{H}$ and $\mathfrak{B}$ are linear functions of i_1 and i_2, hence M_1 and M_2 too. Then we may write:

$$\left. \begin{aligned} M_1 &= L_{11} i_1 + L_{12} i_2 \\ M_2 &= L_{21} i_1 + L_{22} i_2 \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From (2) then follows the known thesis:

$$L_{12} = L_{21} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

i.e. with equal currents in the two circuits the first sends as many induction lines through the second as the second through the first. For this case the magnetic field energy becomes according to (1):

$$T = \frac{1}{2c} L_{11} i_1^2 + \frac{1}{c} L_{12} i_1 i_2 + \frac{1}{2c} L_{22} i_2^2 \quad . \quad . \quad . \quad . \quad (6)$$

If the current in the first circuit increases by di_1, then the integral current in the second amounts to:

$$de_2 = -\frac{dM_2}{c \cdot w_2} = -\frac{L_{21} \cdot di_1}{c \cdot w_2} .$$

On increase of the current in the second conductor by di_2 the integral current:

$$de_1 = -\frac{L_{12} \cdot di_2}{c \cdot w_1} .$$

flows through the first.

Both expressions can be integrated. If e_1 resp. e_2 represent the integral currents, which pass through the first resp. second circuit on increase of the current in the second resp. first circuit to the same amount i, the relation

$$e_1 w_1 = e_2 w_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

exists between these quantities.

2. We shall now consider the case that the function which represents the relation between $\mathfrak{B}$ and $\mathfrak{H}$ is variable in some parts of the field. This variability is meant in very general sense: we may e. g. imagine it as a dependence of volume, pressure, temperature etc. or as variations in consequence of elastic deformations, while also motions of the particles of the medium may be understood by it. We except, however, such changes which are attended with motions of the current conductors or parts of them. Let the variability be expressed by means of the general coordinate a. Then the induction flux through the circuits will in general depend on a. With a variation of a the relation (2) holds both before and after the change, so that we get:

$$\frac{\partial}{\partial a}\frac{\partial M_1}{\partial i_2} = \frac{\partial}{\partial a}\frac{\partial M_2}{\partial i_1},$$

for which we may write, seeing that

$$\frac{1}{c}\,dM_1 = -\,w_1 de_1 \qquad \frac{1}{c}\,dM_2 = -\,w_2 de_2$$

$$\frac{\partial}{\partial a}\left(w_1\frac{\partial e_1}{\partial i_2}\right) = \frac{\partial}{\partial a}\left(w_2\frac{\partial e_2}{\partial i_1}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

when we attach analogous signification to the partial differential quotients $\frac{\partial e_1}{\partial i_2}$ and $\frac{\partial e_2}{\partial i_1}$ as above for (3). If the resistances are not dependent on a, we get:

$$w_1\frac{\partial}{\partial i_2}\frac{\partial e_1}{\partial a} = w_2\frac{\partial}{\partial i_1}\frac{\partial e_2}{\partial a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8')$$

We may express this relation in the following words: Successively we measure four quantities of electricity: 1. the integral current $(de_1)_{i_1, i_2}$ in the first conductor, which is the result of the change da, whilst the currents i_1 and i_2 run through the two conductors; 2. the integral current $(de_2)_{i_1, i_2}$, which flows in the second conductor under the same circumstances; 3. the integral current $(de_1)_{i_1, i_2+di}$ in the first conductor, which is the result of the same change as under 1, with this difference however, that the current in the second conductor is $i_2 + di$; 4. the integral current $(de_2)_{i_1+di, i_2}$ in the second conductor, which is the consequence of the same change as under

2, with this difference, however, that the current in the first conductor is $i_i + di$.

Now according to (8′) the difference of $(de_1)_{i_1, i_2}$ and $(de_1)_{i_1, i_2 + di}$, multiplied by the resistance of the first conductor must be equal to the difference of $(de_2)_{i_1, i_2}$ and $(de_2)_{i_1 + di, i_2}$, multiplied by the resistance of the second conductor.

If the relation between $\mathfrak{B}$ and $\mathfrak{H}$ is linear, then on change of a the relation (7) will hold, both before and after the change, so that we have quite generally

$$\frac{\partial}{\partial a}(w_1 e_1) = \frac{\partial}{\partial a}(w_2 e_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If the resistances are not dependent on a we have

$$w_1 \frac{\partial e_1}{\partial a} = w_2 \frac{\partial e_2}{\partial a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9')$$

i.e. when in the first circuit there runs a current i, the second being without current, and the change da is accompanied with an integral current de_2 in the second conductor, then the product of de_2 with the resistance of the second circuit will be equal to the product of the resistance of the first circuit with the integral current de_1, which flows through the first circuit in consequence of the change da, when the current i now exists in the second conductor, the first being currentless.

3. Up to now we only considered linear conductors. In order to be able to apply the above derived relations to three-dimensional conductors, we shall first prove a general thesis.

We imagine an arbitrary conductor in which certain electrical forces are active. Let the conductor be an anisotropic body, of such a symmetry, however, that there are three main directions which are vertical with respect to each other, in which the current coincides with the electrical force. In this case:

$$\left.\begin{aligned} \mathfrak{J}_x &= \sigma_{11}\,\mathfrak{E}_x + \sigma_{12}\,\mathfrak{E}_y + \sigma_{13}\,\mathfrak{E}_z \\ \mathfrak{J}_y &= \sigma_{21}\,\mathfrak{E}_x + \sigma_{22}\,\mathfrak{E}_y + \sigma_{23}\,\mathfrak{E}_z \\ \mathfrak{J}_z &= \sigma_{31}\,\mathfrak{E}_x + \sigma_{32}\,\mathfrak{E}_y + \sigma_{33}\,\mathfrak{E}_z \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

in which

$$\sigma_{12} = \sigma_{21} \qquad \sigma_{23} = \sigma_{32} \qquad \sigma_{31} = \sigma_{13}.$$

Now let a system of electrical forces $\mathfrak{E}^{(1)}$ give rise to a current $\mathfrak{J}^{(1)}$, the system $\mathfrak{E}^{(2)}$ giving rise to a current $\mathfrak{J}^{(2)}$. Then the following equation will hold for every volume element, as is easy to see by the aid of (10):

$$(\mathfrak{E}^{(1)} . \mathfrak{J}^{(2)}) = (\mathfrak{E}^{(2)} . \mathfrak{J}^{(1)}).$$

Integrated with respect to an arbitrary volume of the conductor this yields:

$$\int(\mathfrak{E}^{(1)} . \mathfrak{J}^{(2)}) . dS = \int(\mathfrak{E}^{(2)} . \mathfrak{J}^{(1)}) . dS \quad . \quad . \quad . \quad . \quad . \quad (11)$$

This we apply to a conductor consisting of two parts, one of which, A, is a three-dimensional body, whereas the other, B, which is to be considered as linear, is in contact with the three-dimensional part in its initial point P and its final point Q. Let us suppose in the linear part a galvanometer G, which we use to measure the current I in the linear part. The case that arbitrary electrical forces are active in this system, e.g. originating from induction actions which can vary from moment to moment, we shall denote by (1). In case (2) on the other hand we imagine a constant electromotive force to act in the linear part. Then there will exist a potential difference $\varphi_Q - \varphi_P$ between the points Q and P.

In both cases we divide the three-dimensional part A into the circuits that compose the current. Let us call the current in each circuit i and let us denote an element of the circuit by ds, then the relation (11) gives:

$$\Sigma\int\mathfrak{E}^{(1)}_{(2)} . i^{(2)} ds^{(2)} = \Sigma\int\mathfrak{E}^{(2)}_{s(1)} . i^{(1)} . ds^{(1)}.$$

In this the integration takes place along the circuits, the summation extending over all the circuits. In the lefthand member we may write $i^{(2)} = \frac{1}{w^{(2)}}(\varphi_Q - \varphi_P)$, when $w^{(2)}$ denotes the resistance of a circuit in case (2). For every circuit this current is multiplied by the linear integral of the electrical force in case (1) along the circuit. In the righthand member we shall have to distinguish between circuits which are closed in themselves inside the part A, and circuits which start in Q and terminate in P. For the first kind:

$$\int\mathfrak{E}^{(2)}_{s(1)} ds_{(1)} = 0,$$

seeing that

$$\mathfrak{E}^{(2)} = -\nabla\varphi.$$

For the second kind:

$$\int\mathfrak{E}^{(2)}_{s(1)} ds^{(1)} = \varphi_Q - \varphi_P,$$

further holding for this:

$$\Sigma i^{(1)} = I,$$

when I is the current measured by the aid of the galvanometer G. If we divide both parts by $\varphi_Q - \varphi_P$, we get finally:

$$I = \Sigma \frac{1}{w^{(2)}} \int^{(1)} \mathfrak{E}_{s^{(2)}} \, ds^{(2)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

or expressed in words: the total current flowing through the linear part B is obtained by division of the part A into those circuits which are the consequence of the presence of a constant electromotive force in the linear part B, by integration of the electric force $\mathfrak{E}$ along every circuit, by division every time of these line integrals by the resistance of the circuit, and by taking finally the sum of all these quotients.

If we now call an element of a circuit in case (2) briefly ds, we can, with the omission of the indices, also write:

$$I = \Sigma \frac{1}{w} \int \mathfrak{E}_s \, ds.$$

Hence we may assign an imaginary current to every circuit

$$i = \frac{1}{w} \, . \int_Q^P \mathfrak{E}_s \, ds,$$

from which follows:

$$i \, . \, w = \int_Q^P \mathfrak{E}_s \, ds.$$

On the other hand:

$$I \, . \, W_0 = \int_P^Q \mathfrak{E}_s \, ds$$

holds according to the law of Ohm for the linear part, when W_0 represents the resistance of this.

By adding the two last relations we get:

$$iw + I \, W_0 = \int \mathfrak{E}_s \, ds,$$

in which the integration is extended all along the circuit. If we put:

$$\int \mathfrak{E}_s \, ds = E,$$

we get:

$$i = \frac{E}{w} - \frac{I \, W_0}{w}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and further by summation over all the circuits and introduction of:

$$\Sigma i = I \qquad \Sigma \frac{1}{w} = \frac{1}{W_1},$$

if W_1 is the resistance of the part A,

$$I = \frac{W_1}{W_1 + W_0} \Sigma \frac{E}{w} = \frac{W_1}{W} \Sigma \frac{E}{w},$$

if W is the resistance of the whole system.

If now by w we represent a resistance which is $\frac{W}{W_1}$ times as great as that of the circuit between Q and P, we get:

$$I = \Sigma \frac{E}{w} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The resistance w introduced here is practically the resistance of a circuit closed in itself, to which the circuits of case (2) discussed above can be supplemented by continuation into the linear part of the conductor. The summation is extended here over all the circuits of the case indicated above by (2).

5. We shall now consider the case of two current conductors of the kind considered just now, so each consisting of a three-dimensional and a linear part. When currents pass through these conductors, either in one of them or in both, and we want to examine the induction action which is the consequence of a change, either of the current in these conductors or of the properties of the surrounding field, then we may, therefore, according to what was derived just now, divide these conductors into the circuits which are the consequence of the presence of a constant electromotive force in the linear part of these conductors, examine the induction action in each of these circuits and take the sum of these.

Let the resistances of the conductors be W_1 and W_2, the currents, measured in the linear part, I_1 and I_2. We shall examine the influence of a change of these currents. We can now divide the first conductor into m circuits, each with a current i_1, the second into n circuits, each with a current i_2, so that we shall have:

$$I_1 = mi_1 \qquad I_2 = ni_2.$$

The resistance of each circuit of the first conductor amounts to $m \, . \, W_1$, of the second conductor to $n \, . \, W_2$, as the electromotive force must be taken the same for all of them on division into circuits. If we increase the current in every circuit of the second conductor by di_2, then the total induction flux through the p^{th} circuit of the first conductor will be increased by:

$$dM_{1,p} = \sum_n \frac{\partial M_{1,p}}{\partial i_{2,q}} \cdot di_2.$$

As the resistance of every circuit amounts to $m \cdot W_1$ we get for the integral current, which flows through the linear part of the first conductor:

$$de_1 = - \frac{di_2}{c\, m.\, W_1} \sum_m \sum_n \frac{\partial M_{1,p}}{\partial i_{2,q}}$$

For this may also be written:

$$de_1 = - \frac{dI_2}{c.m.n.\, W_1} \sum_m \sum_n \frac{\partial M_{1,p}}{\partial i_{2,q}}.$$

In the same way the integral current

$$de_2 = - \frac{dI_1}{c\, m.n.\, W_2} \sum_m \sum_n \frac{\partial M_{2.q}}{\partial i_{1.p}}$$

flows through the linear part of the second conductor on a change dI_1 of the current in the first conductor.

If

$$dI_1 = dI_2,$$

then follows, when (2) is used:

$$W_1 \cdot de_1 = W_2 \cdot de_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (15')$$

In general:

$$W_1 \frac{\partial e_1}{\partial I_2} = W_2 \frac{\partial e_2}{\partial I_1} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

in which the meaning of the differential quotients is analagous to that which was attached to them above in (3).

This relation is analagous to (3). It holds quite generally, so long as $\mathfrak{B}$ is a univalent function of $\mathfrak{H}$, which, however, can be quite arbitrary for the rest.

If the permeability is independent of the strength of the field, so that there exists a linear relation between $\mathfrak{B}$ and $\mathfrak{H}$, we shall be able to integrate equation (15). So we get:

$$W_1 \cdot e_1 = W_2 \cdot e_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

analogous to relation (7). Here just as there e_1 resp. e_2 will mean the integral currents which flow through the linear part of the first resp. second conductor, when the current in the second resp. first conductor increases from zero to the same value I, the other conductor being without current.

5. Just as we did before in the case of two circuits we can also

now consider the case of an infinitely small change of the function which indicates the relation between $\mathfrak{B}$ and $\mathfrak{H}$, in some parts of the field, as result of an infinitely small change of a general coordinate a.

In general (15) will be valid both before and after the change of a, so that analogous to (8) we get from this:

$$\frac{\partial}{\partial a}\left(W_1 \frac{\partial e_1}{\partial I_2}\right)=\frac{\partial}{\partial a}\left(W_2 \frac{\partial e_2}{\partial I_1}\right) \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If the resistances remain unchanged we get analogous to (8'):

$$W_1 \frac{\partial}{\partial I_2} \frac{\partial e_1}{\partial a} = W_2 \frac{\partial}{\partial I_1} \frac{\partial e_2}{\partial a} \,, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17')$$

which relation is also open to analogous interpretation.

In the special case of a linear relation between $\mathfrak{B}$ and $\mathfrak{H}$ we shall get in the same way analogous to (9):

$$\frac{\partial}{\partial a}(W_1 e_1) = \frac{\partial}{\partial a}(W_2 e_2) \,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

which becomes for invariable resistances:

$$W_1 \frac{\partial e_1}{\partial a} = W_2 \frac{\partial e_2}{\partial a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18')$$

Here e_1 and e_2 have the same signification as above in (16).

6. We now inquire into the work of the ponderomotive forces, being accompanied with a modification in the magnetic field, which is the consequence of the infinitely small change da. We assume that at the change da the external electromotive forces remain unchanged, and likewise the coefficients σ, which in the most general case determine the relation between the electrical force and the current.

If $\mathfrak{E}$ represents the electric force, and $\mathfrak{E}^e$ the external electromotive force, then the quantity of energy

$$\{(\mathfrak{E} + \mathfrak{E}^e) \,.\, \mathfrak{J}\} \,.\, dS \,.\, dt.$$

will be consumed as Joule heat in the volume element dS in the time dt.

On the other hand the energy supplied by the current generators in the time dt is:

$$(\mathfrak{E}^e \,.\, \mathfrak{J}) \,.\, dS \,.\, dt.$$

The difference of these two expressions:

$$-(\mathfrak{E} \,.\, \mathfrak{J}) \,.\, dS \,.\, dt$$

passes into other modes of energy. Integrated with respect to all the conductors this becomes:

$$\int (\mathfrak{E} . \mathfrak{J}) . dS . dt.$$

If we introduce

$$\mathfrak{J} = c\, curl\, \mathfrak{H},$$

and if we make use of the known thesis of the vector calculus that the following equation holds generally:

$$div\, [\mathfrak{A}\, \mathfrak{B}] = \mathfrak{B}\, curl\, \mathfrak{A} - \mathfrak{A}\, curl\, \mathfrak{B}$$

then we get for the above expression:

$$- c \int (curl\, \mathfrak{E}, \mathfrak{H})\, dS . dt + c \int div\, [\mathfrak{E}, \mathfrak{H}]\, dS . dt.$$

Introducing further:

$$curl\, \mathfrak{E} = - \frac{1}{c} \frac{d\mathfrak{B}}{dt}$$

and making use of Gauss's theorem, we get:

$$\int \left(\frac{d\mathfrak{B}}{dt}, \mathfrak{H}\right) dS . dt + c \int [\mathfrak{E}, \mathfrak{H}]_{\nu}\, d\sigma . dt.$$

The second term vanishes, as on the surfaces of the current conductors the normal component of $[\mathfrak{E}, \mathfrak{H}]$ is continuous, and the integral amounts to zero over the plane in infinity. Accordingly the first term only remains. This will have to be equal to the increase of the energy of the magnetic field and the work of the ponderomotive forces. Hence we get:

$$dT + dA = \int \left(\frac{d\mathfrak{B}}{dt}, \mathfrak{H}\right) dS . dt.$$

Per volume and time unity:

$$dT + dA = \left(\frac{d\mathfrak{B}}{dt}, \mathfrak{H}\right) dt.$$

For the energy of the magnetic field per volume unity the expression:

$$T = \int_0^{\mathfrak{H}} (\mathfrak{H}, d\mathfrak{B}).$$

holds generally.

With the change *da* we shall get:

$$dT = \int_0^{\mathfrak{H} + d\mathfrak{H}} (\mathfrak{H}, d\mathfrak{B}') - . \int_0^{\mathfrak{H}} (\mathfrak{H}, d\mathfrak{B}),$$

in which $d\mathfrak{H}$ represents the change of the final value of $\mathfrak{H}$, and $\mathfrak{B}'$ the value of $\mathfrak{B}$ corresponding to $\mathfrak{H}$ in the changed state. Now we get:

$$-dA = \int\limits_0^{\mathfrak{H}+d\mathfrak{H}} (\mathfrak{H}, d\mathfrak{B}') - \int\limits_0^{\mathfrak{H}} (\mathfrak{H}, d\mathfrak{B}) - (d\mathfrak{B}, \mathfrak{H}),$$

from which easily follows:

$$dA = \frac{\partial}{\partial a} \int\limits_0^{\mathfrak{H}} (\mathfrak{B}, d\mathfrak{H}) \, . \, da$$

Integrated with respect to the whole field this becomes:

$$dA = \frac{\partial}{\partial a} \int dS \int \mathfrak{B} \, . \, d\,\mathfrak{H} . \, da \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

We can always split up the vector $\mathfrak{H}$ into two parts, $\mathfrak{H}^0$, for which holds $div\ \mathfrak{H}^0 = 0$, and $\mathfrak{H}^1$, for which holds $curl\ \mathfrak{H}^1 = 0$ [1]). Taking into consideration that generally

$$\int dS \, (\mathfrak{A} \, . \, \mathfrak{B}) = 0$$

on integration over the whole space, when

$$div\ \mathfrak{A} = 0, \quad curl\ \mathfrak{B} = 0,$$

we get:

$$dA = \frac{\partial}{\partial a} \int dS \int \mathfrak{B} \, . \, d\mathfrak{H}^0$$

Making use of the equation:

$$\mathfrak{B} = \mathfrak{H} + \mathfrak{M},$$

we get:

$$dA = \frac{\partial}{\partial a} \left\{ \int dS \int \mathfrak{H} d\mathfrak{H}^0 + \int dS \int \mathfrak{M} d\mathfrak{H}^0 \right\} . \, da.$$

As in the first term we can again split up $\mathfrak{H}$ into $\mathfrak{H}^0$ and $\mathfrak{H}^1$, in which $\mathfrak{H}^0$ is independent of a — $\mathfrak{H}^0$ being determined by the current $\mathfrak{J}$ — and as the product $\mathfrak{H}^1 \, d\, \mathfrak{H}^0$ integrated over the whole field yields zero, this term will vanish, so that there remains:

$$dA = \int dS \int \frac{\partial \mathfrak{M}}{\partial a} \, d\mathfrak{H}^0 \, . \, da \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

In this $\dfrac{\partial \mathfrak{M}}{\partial a}$ denotes the change of the magnetisation in consequence of a change da, in which the external electromotive forces and also the coefficients determining the conductivity, remain unchanged.

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[1]) In general we shall understand by $\mathfrak{H}^0$ the intensity of the field as it would be without the presence of the iron, $\mathfrak{H}$ representing the real strength of the field. The difference is $\mathfrak{H}^1$.

7. We shall now consider a special case. Let us imagine a system of two currents, one passing through a vertical cylindrical iron bar, the other through a vertical solenoid which is concentric with the iron bar. We suppose the iron bar, whose length is assumed to be large with respect to the diameter, to be in the middle part of the solenoid, and that the latter on both sides projects far beyond the bar. For the present we assume for simplicity's sake that the permeability of the iron has a constant value.

The first current I_1 gives rise to a circular magnetisation in the iron, the second I_2 to a longitudinal magnetisation. If I_1 and I_2 are in righthand cyclical order the corresponding strengths of the field $\mathfrak{H}_1{}^0$ and $\mathfrak{H}_2{}^0$ are so too.

The resistances of the conductors are called W_1 and W_2.

We can now twist the iron bar, I_1 being $= I$ and $I_2 = 0$; in consequence of this three main directions will arise in the iron with different permeability, which will also cause a longitudinal magnetisation in the bar, which is accompanied with an impulse of current in the second conductor. Likewise we may twist the bar when $I_1 = 0$ and $I_2 = I$, which gives rise to a circular magnetisation of the bar, and accompanying this an impulse of current in the first conductor. We shall compute for both cases the quantities of electricity which pass through every section in consequence of the impulses of current.

If the radius of the iron bar is R, then

$$\mathfrak{H}^0{}_1 = \frac{r I_1}{2\pi . R^2 . c}\,.$$

holds for the intensity of te field $\mathfrak{H}^0{}_1$ inside the iron at the distance r from the axis of the cylinder.

If the solenoid has m windings per unity of length, the intensity of the field in the middle part in which the iron bar is found, is:

$$\mathfrak{H}^0{}_2 = \frac{1}{c} . m . I_2\,.$$

We shall assume the bar, which has a length l, to be twisted over an angle $\varphi = l.\alpha$, and this in such a way that while one extremity, where the current I_1 enters, is held fast, the other extremity is twisted over an angle φ in the sense of the current I_2. In consequence of this an originally square surface element with sides of a length one of a cylinder surface concentric with the axis of the bar, with radius r, will assume a rhombic shape.

In this the angle which the sides of the rhomb, which were originally parallel to the axis, form with the direction of the axis, becomes equal to $r\,\alpha$, so long as the second and higher powers of α are neglected. The diagonals of the rhomb become resp.:

$$\sqrt{2}\,(1+\tfrac{1}{2}\,r\,\alpha) \qquad \text{and} \qquad \sqrt{2}\,(1-\tfrac{1}{2}\,r\,\alpha),$$

hence the ratio between this and the original length resp.

$$1+\tfrac{1}{2}\,r\,\alpha \qquad \text{and} \qquad 1-\tfrac{1}{2}\,r\,\alpha.$$

We call the direction of the strength of the field $\mathfrak{H}^0_1$ x, that of the strength of the field $\mathfrak{H}^0_2$ y.

In consequence of the twisting the considered surface element has obtained two main directions, which coincide with the diagonals of the rhomb[1]. We call the direction of the diagonal which falls between the positive x-direction and the positive y-direction, u, that of the other diagonal v. In the direction u the iron is elongated, in the direction v compressed. The elongation resp. compression amounts to $\frac{1}{2}\,r\,\alpha$ per unity of length. Let $k\,.\,\lambda$ be the increase of the permeability in a certain direction, when the elongation per unity of length amounts to λ in that direction, the compression per unity of length normal to that direction being of the same value. Then

$$\mu_u = \mu + \tfrac{1}{2}\,k\,r\,\alpha \qquad\qquad \mu_v = \mu - \tfrac{1}{2}\,k\,r\,\alpha.$$

We assume k to be independent of the strength of the field.

If we further assume the angles which the directions u and v form with x and y to amount to 45°, which is permissible so long as we confine ourselves to quantities of the first order in α, we get:

$$\mathfrak{H}_u = \tfrac{1}{2}\sqrt{2}\,(\mathfrak{H}_x + \mathfrak{H}_y)$$
$$\mathfrak{H}_v = \tfrac{1}{2}\sqrt{2}\,(-\,\mathfrak{H}_x + \mathfrak{H}_y),$$

and further, as:

$$\mathfrak{B}_u = \mu_u\,.\,\mathfrak{H}_u \qquad\qquad \mathfrak{B}_v = \mu_v\,.\,\mathfrak{H}_v,$$

$$\mathfrak{B}_u = \frac{\mu}{2}\sqrt{2}\,(\mathfrak{H}_x + \mathfrak{H}_y) + \tfrac{1}{4}\,k\,r\,\alpha\sqrt{2}\,(\mathfrak{H}_x + \mathfrak{H}_y)$$

$$\mathfrak{B}_v = \frac{\mu}{2}\sqrt{2}\,(-\,\mathfrak{H}_x + \mathfrak{H}_y) + \tfrac{1}{4}\,k\,r\,\alpha\sqrt{2}\,(-\,\mathfrak{H}_x + \mathfrak{H}_y),$$

from which follows:

$$\mathfrak{B}_x = \mu\,\mathfrak{H}_x + \tfrac{1}{2}\,k\,r\,\alpha\,\mathfrak{H}_y$$
$$\mathfrak{B}_y = \mu\,\mathfrak{H}_y + \tfrac{1}{2}\,k\,r\,\alpha\,\mathfrak{H}_x.$$

We see that here the relation $\mu_{12} = \mu_{21}$ holding universally for anisotropic media with three mutually normal main directions is satisfied.

In the twisted bar $\mathfrak{H}_x$ has everywhere the same value at a certain distance from the axis, when we move along a circle normal to the axis, as there is radial symmetry with respect to this axis. The

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[1] The third radially directed main direction may be left out of consideration, as no change takes place in that direction.

line integral of $\mathfrak{H}_x$ along this circle amounts therefore to $2\pi r \,.\, \mathfrak{H}_x$; this line integral also amounts to $2\pi r \,.\, \mathfrak{H}_1{}^0$, so that we get:

$$\mathfrak{H}_x = {}_1\mathfrak{H}^0.$$

We shall further assume the length of the bar to be large with respect to its diameter, in which case the influence of the magnetisation at the extremities in the determination of the field intensity inside the bar in case of longitudinal magnetisation will be small, so that we may assume

$$\mathfrak{H}_y = \mathfrak{H}_2{}^0.$$

Inside the bar the following equations hold

$$\mathfrak{B}_x = \mu \mathfrak{H}_1{}^0 + \tfrac{1}{2}\, kra\, \mathfrak{H}_2{}^0$$
$$\mathfrak{B}_y = \mu \mathfrak{H}_2{}^0 + \tfrac{1}{2}\, kra\, \mathfrak{H}_1{}^0$$

The change of the magnetic induction within the bar in consequence of the twisting amounts to

$$\Delta \mathfrak{B}_x = \tfrac{1}{2}\, kra\, \mathfrak{H}_2{}^0$$
$$\Delta \mathfrak{B}_y = \tfrac{1}{2}\, kra\, \mathfrak{H}_1{}^0$$

In the same way we have for the magnetisation:

$$\mathfrak{M}_x = \varkappa \,.\, \mathfrak{H}_1{}^0 + \tfrac{1}{2}\, kra\, \mathfrak{H}_2{}^0$$
$$\mathfrak{M}_y = \varkappa \,.\, \mathfrak{H}_2{}^0 + \tfrac{1}{2}\, kra\, \mathfrak{H}_1{}^0$$

Also outside the magnetic induction changes in consequence of the twisting. On account of the change of $\mathfrak{B}_y$ the quantity of magnetism will namely change at the extremities of the bar which will give rise to a change of strength of the field outside the bar. If there was no iron inside the solenoid, and if this was infinitely long, the change of the magnetism at the extremities would not give rise to an induction current at all, because every quantity of magnetism sends its induction lines through the windings lying on either side, and the sense of rotation of the induced electric force is directed for the windings on one side opposite to that on the other side. We commit an error on account of the presence of the iron inside the solenoid in as much as the magnetic induction inside the iron does not change in the same way as that outside it. As we have, however, assumed that as far as the magnetic induction inside the iron is concerned, we may disregard the magnetism at the extremities, we may also leave this error out of account.

In order to calculate the induction impulse, we must therefore integrate the just mentioned amounts of $\Delta \mathfrak{B}_x$ and $\Delta \mathfrak{B}_y$ inside the bar over the surface which is surrounded by every circuit, and then sum up over all the circuits.

We explicitly excepted (§ 2 above) movements of the current conductors. Here, however, such movements occur in consequence of the twisting. Now in case of longitudinal magnetisation of the bar the movement of matter, which is the consequence of the torsion, will give rise to an induction impulse in radial direction, which has no influence on the induction impulse in longitudinal direction. In the case of circular magnetisation on the other hand no induction lines will be cut by the matter on twisting, so that no induction impulse takes place. The movement of the substance will, therefore, have no influence in these cases on the induction impulses, which are accordingly exclusively the consequence of the change of the properties of the substance.

A. If we now first suppose $I_1 = I, I_2 = 0$, hence the case of circular magnetisation, then:

$$\mathfrak{H}_1^0 = \frac{rI}{2\pi R^2 . c} \qquad \mathfrak{H}_2^0 = 0$$

$$\triangle \mathfrak{B}_y = \frac{kIar^3}{4\pi R^2 . c} \qquad \triangle \mathfrak{B}_x = 0.$$

Now $\triangle \mathfrak{B}_y$ must be integrated over all the surface elements which are normal to the direction y, so over all the windings of the solenoid. The increase of the flux of induction through one winding amounts to:

$$\triangle M_y = 2\pi \int_0^R \triangle \mathfrak{B}_y . rdr = \frac{kIaR^2}{8c}$$

As there are $m.l.$ windings to the length l of the bar, the total increase of the induction flux will be $m.l. \triangle M_y$ and the electricity set in motion:

$$e_2 = - \frac{ml . kIaR^2}{8 W_2 . c^2}.$$

If we introduce the angle of twisting $\varphi = l . a$, we get:

$$e_2 = - \frac{m\varphi kIR^2}{8 W_2 . c^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

With a positive value of k we come to the conclusion that for the considered twisting the sense in which the impulse takes place, is in lefthand cyclical order with the current I.

In the other circuit the impulse is zero, as $\triangle \mathfrak{B}_y = 0$.

B. Let us now suppose $I_1 = 0$, $I_2 = I$, hence the case of longitudinal magnetisation; then:

$$\mathfrak{H}_1^0 = 0 \qquad \mathfrak{H}_2^0 = \frac{mI}{c}$$

$$\Delta\mathfrak{B}_x = \frac{1}{2c}\, mkraI \qquad \Delta\mathfrak{B}_y = 0.$$

In order to calculate the impulse in the first circuit, we shall divide the first conductor into conducting tubes, which each of them again consists of circuits. Let the conducting tubes, which are concentric and cylindrical in the iron, have a radius r there and a thickness dr. When we then give them dimensions proportional to this in the other parts of the conductor, the resistance of such a tube will be:

$$w = \frac{R^2}{2r\; dr} \,.\, W_1$$

The increase of the induction flux through the surface surrounded by every circuit belonging to the conducting tube, amounts to:

$$\Delta M_r = l\int_r^R dr \,.\, \Delta\mathfrak{B}_x = \frac{1}{4c}\, mlkIa\,(R^2 - r^2).$$

The quantity of electricity set in motion in the conductor, now becomes, when we make use of the mode of calculation explained in § 3, which finds expression in (14):

$$e_1 = -\Sigma\frac{\Delta M_r}{c.w} = -\frac{mlkIa}{2R^2 W_1 c^2}\int_0^R (R^2 - r^2)\, r\, dr = -\frac{mlkIaR^2}{8W_1c^2}\,.$$

With introduction of the angle of twisting φ this becomes:

$$e_1 = -\frac{m\varphi kIR^2}{8W_1c^2} \quad \ldots\ldots\ldots \quad (22)$$

Hence from (21) and (22) we find really

$$e_1 W_1 = e_2 W_2$$

in agreement with (18′).

If k is positive, then the sense in which the impulse takes place, is in lefthand cyclical order with the current I.

As $\Delta\mathfrak{B}_y = 0$, the impulse in the second conductor is zero.

We may assume that the circuits run parallel to the axis over the greater part of the length. The direction of the current can, however, be different for different circuits. In this case we shall be allowed to use the formula (13) for the real current. It follows from this that the circuits where the motion of electricity is zero, will lie on a cylinder surface, the radius r of which is given by the equation:

$$\frac{1}{c}\,\Delta M_r = -e_1 \,.\, W_{01},$$

in which W_{01} is the resistance of the linear part of the circuit. From this we get:

$$r = R\sqrt{\frac{2W_1 - W_{01}}{2W_1}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (23)$$

When W_{01} is small compared with W_1, r will differ little from R. As a rule, however, the reverse will be the case, from which ensues that r approaches the value $\frac{1}{2}R\sqrt{2}$. We can calculate the current through the central part of the bar by means of the relation (13). For this we get:

$$e_1^{(c)} = -\frac{mqkI.R^2}{32c^2(W_1 - W_{01})}\left(\frac{2W_1 - W_{01}}{W_1}\right)^2 . \quad . \; . \; . \; . \quad (24)$$

When $W_1 - W_{01}$ is small with respect to W_1 this quantity of electricity will become much larger than e_1; it can become arbitrarily large with respect to e_1 when $W_1 - W_{01}$ is made small enough with respect to W_1. On the other hand when W_{01} was small with respect to W_1, $e_1^{(c)}$ would differ only little from e_1.

Let us now suppose that a current I_1 runs in the first conductor, a current I_2 in the second. We assume that then the state of equilibrium is characterized by this that the bar is twisted over an angle α per unity of length. The torsion couple amounting to $KR^4 . \alpha$, the elastic energy of the bar is $\frac{1}{2}KR^4 . \alpha^2 . l$ in the twisted state. We make this state undergo an infinitesimal change so that α increases by the amount $d\alpha$. Then the elastic energy increases by the amount $KR^4\,\alpha\, l\, d\alpha$, the work of the ponderomotive forces being found from (20) for the considered change, which formula, after introduction of $\mathfrak{M}_x$ and $\mathfrak{M}_y$, produces

$$dA = \tfrac{1}{2}\,k \,.\, d\alpha \int r \,.\, \mathfrak{H}_1^0\, \mathfrak{H}_2^0 \,.\, dS = \frac{1}{8c^2}\, mlk\, I_1 I_2 R^2 \,.\, d\alpha.$$

In case of equilibrium this work must be equal to the increase of the elastic energy, from which we find for the angle α:

$$\alpha = \frac{kmI_1I_2}{8c^2KR^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (25)$$

The whole torsion becomes:

$$\varphi = \frac{kmlI_1I_2}{8c^2KR^2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (25')$$

If k is positive, then with the given current directions of I_1 and I_2 the bar will be twisted so that when the extremity where I_1 enters, is kept in fixed position, the other extremity is rotated in the sense of the current I_2, hence counter clockwise, when we look towards this extremity. Of course the sense of the rotation changes on reversal of one of the currents.

Hence the bar assumes the shape of a righthand screw, when the currents I_1 and I_2 are in righthand cyclical order. Further the angle over which the bar is twisted, is proportional to the total number of windings of the solenoid, which falls on the length of the bar, to the intensities of the currents, and in inverse ratio to the square of the radius.

Above we found an expression for the work of the ponderomotive forces dA on the increase of the torsion $d\alpha$. If the torsion amounts to α, we can integrate this expression, through which we get:

$$A = \frac{1}{8c^2}\, m\, k\, q\, I_1\, I_2\, R^2$$

We find this work back in the first place in the elastic energy U of the bar. If into the expression for this $\frac{1}{2} K R^4 \alpha q$, we introduce the above found expression for α, we get for this:

$$U = \frac{1}{16c^2}\, m\, k\, q\, I_1\, I_2\, R^2.$$

The rest, which is of the same amount as U, is converted into kinetic energy, or when we make the motion take place infinitely slowly by means of external couples, into external work.

Let us now inquire into the increase of magnetic field energy. For this purpose we make use of the expression:

$$T = \int d\, S \int \mathfrak{H}\, d\, \mathfrak{B},$$

which can be easily derived from (1).

Here we introduce:

$$\mathfrak{H}_x = \frac{r I_1}{2\pi c R^2} \qquad \mathfrak{H}_y = \frac{m}{c}\, I_2$$

$$\Delta\, \mathfrak{B}_x = \frac{1}{2c}\, m\, k\, r\, \alpha\, I_2 \qquad \Delta\, \mathfrak{B}_y = -\frac{k r^2 \alpha I_1}{R^2}$$

We get then:

$$\Delta T = \int d\, S \int (\mathfrak{H}_x\, d\, \Delta\, \mathfrak{B}_x + \mathfrak{H}_y\, d\, \Delta\, \mathfrak{B}_y) = \frac{1}{8c^2}\, m\, q\, k\, I_1\, I_2\, R^2$$

Hence

$$A + \Delta T = \frac{1}{4c^2}\, m q k\, I_1 I_2 R^2.$$

On the other hand on account of the torsion the quantity of electricity

$$e_1 = -\frac{mqkI_2R^2}{8\,W_1c^2}$$

is circulated in the first conductor. The electromotive force in that conductor amounts to $E_1 = I_1 \,.\, W_1$. In consequence of the circulation of the quantity of electricity e_1, the generator of the current yields, besides the JOULE heat, the quantity of energy $-E_1e_1$, which amounts to:

$$-E_1e_1 = \frac{mqkI_1I_2R^2}{8c^2}.$$

We find in the same way that after subtraction of the JOULE heat, an equal amount of energy is yielded by the second generator of current. Together the total quantity of energy yielded by the generator of current, amounts therefore to:

$$\frac{1}{4c^2}\,mqk\,I_1I_2R^2,$$

which corresponds with the value $A + \Delta T$, required for the work of the ponderomotive forces and the increase of the magnetic energy.

Chemistry. — "*Molecular-Allotropy and Phase-Allotropy in Organic Chemistry.*" By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

1. *Survey of organic pseudo-systems.*

I have indicated the appearance of a substance in two or more similar phases by the name *phase-allotropy*, and the occurrence of different kinds of molecules of the same substance by the name of *molecular-allotropy*. It may be assumed as known that one of the conclusions to which the theory of allotropy leads, is this that phase-allotropy is based on molecular-allotropy.

The region in which the existence of molecular allotropy is easiest to demonstrate is the region of organic chemistry, and I think that I have to attribute this fact to this that the velocity of conversion between the different kinds of molecules which present the phenomenon of isomery or polymery, is on the whole much smaller in organic chemistry than in anorganic chemistry; in organic substances it seems even not perceptible in many cases. The substances, for which this is, however, the case, and which were formerly called tautomers, are comparatively few as yet, but undoubtedly their number will increase as the experiment is made more refined.

It is obvious that a test of the just mentioned conclusion from the theory of allotropy will be most easily carried out in the region of organic chemistry, but on the other hand a test in the region of anorganic chemistry will be, especially for elements, of greater scientific interest.

Accordingly the research is continued both in anorganic and organic domain, and the purpose of this communication is to draw attention to the gigantic field of research which is opened up for us in organic region for a study in this direction.

Bancroft [1]) was the first to take into account the influence of the time in the study of systems of organic substances which can occur in two different forms. In this consideration he came to *three* cases.

1. The time element vanishes in consequence of the practically immediate setting in of the (internal) equilibrium.

2. The setting in of the (internal) equilibrium takes place so slowly that so-called "false equilibria" occur, for which case Bakhuis Roozeboom [2]) derived different T, X-figures.

3. The (internal) equilibrium sets in with such a velocity that the system behaves as a binary one in case of rapid working, as a unary one in case of slow working.

The substances belonging to the latter group, and their number is undoubtedly enormously great especially in the domain of organic chemistry, yield very satisfactory material of research.

Bancroft was the first who discovered a pseudo binary system in *dichlorostilbene* examined by Zincke [3]) and explained its behaviour. Zincke had discovered that when the form with the highest melting point was kept in molten condition for a long time (200°), there took place a lowering of the point of solidification from 192° to 160°, which was to be attributed, as Bancroft stated, to this that the substance had assumed (internal) equilibrium at 200°, in which the molecules of one form had been partially converted to those of the other form.

Among the organic substances which can occur in different isomer forms, variations of the melting point are met with in very many cases according to the literature, which variations must be attributed to a conversion in the direction of the internal equilibrium or to a retardation of the setting in of the internal equilibrium.

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[1]) Journ phys. Chem. **2**. 143 (1898).

[2]) Z. f. phys. Chem. **28**. 289 (1899).

[3]) Lieb. Ann. **198**. 115 (1879).

Specially the group of the *oximes* furnishes several examples. In this respect we may mention in the first place *acetaldoxim* studied by DUNSTAN and DYMOND[1]), and later more closely examined by CARVETH[2]).

Further may be mentioned *benzaldoxim*, for which the first data have been given by BECKMANN[3]), the discoverer of the isomeric conversions of these substances. This substance was more closely investigated by CAMERON[4]), whose results were later tested and improved by SCHOEVERS's study[5]). CARVETH[6]) investigated also another *oxim*, viz. *anisoldoxim*, of which BECKMANN[7]) had also found two isomers.

A very interesting substance is the *benzilorthocarbonic acid*, of which GRAEBE and JUILLARD[8]) found two distinctly different crystallized products, one white, the other yellow.

While enantiotropy is a very frequently occurring phenomenon in anorganic chemistry, we find this phenomenon only exceedingly rarely mentioned in the organic literature. We should undoubtedly be mistaken if we supposed that it must be inferred from this that the phenomenon of enantiotropy in organic region is met with only by great exception. In the first place this circumstance is much sooner to be ascribed to this that on account of the slight velocity of conversion between the different kinds of molecules of organic substances, the phenomenon of enantiotropy manifests itself much less easily, and in the second place to the absolute absence of an accurate systematic investigation in this direction.

It is, however, known of *benzilorthocarbonic acid* that it is enantiotropic. SOCH[9]) has namely demonstrated this with certainty, and considerably extended GRAEBE's[10]) investigation.

We have further a very important group of allotropic substances with distinct transformation in the *keto-* and *enol compounds*.

WOLF[11]) devoted an investigation to *formylphenyl acetic ester*, of

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[1]) Journ. chem. Soc. **61**, 470 (1892); **65**, 206 (1894).

[2]) Journ. phys. chem. **2**, 159 (1898).

[3]) Ber. **20**, 2768 (1887); **37**, 3042 (1902).

[4]) Journ. phys. chem. **2**, 409 (1898).

[5]) Dissertatie 43.

[6]) Journ. phys. chem. **3**, 437 (1899).

[7]) Ber. **23**, 2103 (1890).

[8]) Ber. **21**. 2003 (1888).

[9]) Journ. phys. chem. **2**, 364 (1898).

[10]) Ber. **23**, 1344 (1890).

[11]) Journ. phys. chem. **4**, 123 (1900).

which WISLICENUS[1]) had discovered two modifications a few years before, viz. the solid *keto* and the liquid *enol* compound.

Of late a number of investigations on other substances with intermolecular transformation have been published by DIMROTH[2]). These very interesting publications treat molecular conversions in derivatives of triazol, in different solvents.

One of the isomers is always an acid which can be determined titrimetrically, which may be called a very favourable circumstance for the study of the phenomena of conversion.

Another substance whose peculiar behaviour has already induced many investigators to occupy themselves with it, is the *hydrazon of acetaldehyde*, of which FISCHER[3]) discovered two modifications.

BAMBERGER and PEMSEL[4]) undertook a further investigation, a few years later also LOCKEMANN and LIESCHE[5]), and six years later LAWS and SIDGWICK[6]), but none of these investigators has succeeded in unravelling the behaviour of this peculiar substance.

P. nitrobenzal-phenyl-methyl-hydrazon, investigated by BACKER[7]) is another hydrazon which shows great resemblance with the former. Also this substance possesses two modifications, a red and a yellow one, but it is not known as yet, in what relation these forms are to each other.

The system *ureum-ammoniumcyanate*, further examined by WALKER and HAMBLY[8]), just as the system *sulpho-ureum-ammoniumsulphocyanate* studied by VOLHARD[9]) WADDELL[10]), REYNOLDS and WERNER[11]), FINDLAY[12]), and finally by SMITS and KETTNER[13]), likewise belong to the organic pseudo-systems, just as *cyanogen-paracyanogen* investigated by TERWEN[14]) and *cyanogenichydrogenic acid, cyaniric acid* and *cyamelide* investigated by TROOST and HAUTEFEUILLE[15]).

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[1]) Ber. **20**, 2933 (1887); **28**, 767 (1895).

[2]) Ber. **35**, 4041 (1902); Lieb. Ann **335**, 1 (1904); **338**, 143 (1905), **364**, 183 (1909); **373**, 336 (1910), **377**, 127 (1910).

[3]) Ber. **29**, 795 (1896).

[4]) Ber. **36**, 85 (1903)

[5]) Lieb. Ann. **342**, 14 (1905).

[6]) Journ. Chem. Soc. **99**, 2085 (1911).

[7]) Dissertation, Leiden 1911.

[8]) Journ. chem. Soc. **67**, 746 (1895).

[9]) Ber. **7**, 92 (1874).

[10]) Journ. phys. chem. **2**, 525 (1898).

[11]) Journ. chem. Soc: **83**, 1 (1903).

[12]) Journ. chem. Soc. **85**, 403 (1904).

[13]) These Proc. Vol. **15**, p. 683 (1912).

[14]) Dissertation Amsterdam 1913.

[15]) Compt. rend **66**, 795; **67**, 1345.

Among the organic nitro compounds there are some that belong to the group of the pseudo acids, as was found by HANTSCH[1]) and HOLLEMAN[2]) in the investigation of *brominephenylnitromethane* and of *phenylnitromethane*; these substances too are to be counted among the pseudo systems.

The same thing may be remarked about the *dimethylketol,* examined by PECHMANN and DAHL[3]), the *benzolazocyanogen acetic ester* studied by F. KRÜCKEBERG[5]), KIPPING'S *benzylidenehydrindon*[4]), and *tolanedibromide*[6]) of LIMPRICHT and SCHWANERT.

Also in the domain of structure isomery, tautomery or internal transformation has been observed. POLAK[7]) found a fine example of this in the *para-* and *metabenzoldisulphonic acid* and SMITS and VIXSEBOXSE[8]) in *methylrhodanide* and *methylmustard oil.* In connection with this TERWEN[9]) advanced the supposition that the structure isomers should be tautomers that very slowly pass into each other.

2. *Discussion of the binary pseudoternary systems consisting of an allotropic substance and a solvent.*

The survey of organic substances given here, of which it is certain that they are pseudo systems, can by no means lay claim to completeness, nor did we try to reach it. Our purpose was only to demonstrate by a mere enumeration of some facts, how enormously large is the territory in organic region, on which the theory of allotropy might be tested.

Here and there an attempt has been made to find a connection between the pseudo binary and the unary melting-point diagram, but this study has never been exhaustive.

BANCROFT and his pupils have proceeded furthest in this direction, but the theory of allotropy requires more at present.

Nor has a systematical investigation of tautomeric substances with a solvent, so that we get a pseudo ternary system to study, in which the situation of the isotherm for the internal equilibrium in

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[1]) Ber. **29**, 699, 2251 and 2253 (1896).

[2]) Kon. Akad. van Wetensch. Vol. XIV (1906).

[3]) Ber. **23**, 2421 (1890).

[4]) J. f. prakt. Chem. [2] **46**, 579 (1892).
 „ „ „ „ „ **47**, 591 (1893).

[5]) Journ. chem. Soc. **65**, 499 (1894).

[6]) Lieb. Ann. **145**, 348 (1868).

[7]) Thesis for the Doctorate, Amsterdam.

[8]) These Proc. Vol. **16**, p. 33.

[9]) Thesis for the Doctorate Amsterdam

the liquid phase leads to the knowledge which solid phase at a definite temperature is the stable one, which the metastable, been sufficiently carried out as yet.

As we shall show presently, DIMROTH has indeed, made very important investigations in this directions, but an investigation carried through systematically at different constant temperatures only can bring us further here.

To show this it is necessary to subject DIMROTH's important work, which is of great interest for us here, to a closer examination.

DIMROTH¹) has made use here of VAN 'T HOFF's formula²) about the change of the equilibrium through the solvent, but in a somewhat modified convenient form. viz. in this shape:

$$\frac{C_A}{C_B}=\frac{L_A}{L_B}.G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

in which C_A and C_B indicate the concentrations of the substances A and B in the state of (internal) equilibrium at a definite temperature.

L_A and L_B are the concentrations of saturation of A and B in the *pure* solvent at the same temperature, G being a constant independent of the solvent.

DIMROTH, now, points out that important conclusions can be drawn from this relation, which are of great importance for the preparation of isomers transforming themselves into each other.

He says: suppose that for a certain temperature $G=1$, it follows from this that when at this temperature we have saturated an arbitrary solvent with the two isomers A and B, and solid A and B lie on the bottom, the whole system remains unchanged in equilibrium. It might have been stated here that the temperature at which this takes place, would be the point of transition between A and B, the temperature, therefore, at which the two solid phases A and B are in equilibrium.

If $G<1$, then $\frac{C_A}{C_B}<\frac{L_A}{L_B}$. In this case the solution saturate with respect to two solid isomers A and B will contain more A than corresponds to the state of equilibrium. A consequence of this is that A is converted to B in the liquid, B crystallizing out, and solid A going into solution, till the solid A has entirely disappeared. The reverse will take place when $G>1$. In connection with these considerations he says: "Bringt man also zwei wechselseitig mit

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¹) Lieb. Ann. **377**, 133 (1910).

²) Vorlesungen über theor. u phys. Chemie, 219.

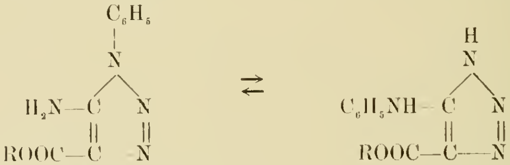
ausreichender Geschwindigkeit umwandelbare Isomere mit einer zur Lösung unzureichenden Menge eines Lösungsmittels zusammen, so muss, wenn der Satz von van 't Hoff zu Recht besteht, die Richtung des sich abspielenden Isomerisationsvorganges ausschliesslich von der Konstanten G abhängen, also gänzlich unabhängig sein von der Natur des Lösungsmittels".

Experience, says Dimroth, is however in conflict with this, for it often occurs that it is possible to convert isomers into each other by treatment with different solvents.

He refers in particular to the investigation of E. Bamberger [1]) on the isomers of *nitroformaldehydrazons*, the α-form of which is converted by water or alcohol into the β-form, the β-modification being reversely transformed into the α-modification by benzene, chloroform, or ligroine.

In this connection he states explicitly: "Es kann kein Zweifel sein, dass diese mit Erfolg geübte Laboratoriumspraxis mit dem van 't Hoff'schen Satze in Widerspruch steht."

This statement may seem somewhat strange, as in a test by means of the *aminoderivatives* of *triazol carbonic ester*, which show the following conversion,



1 Phenyl-5-aminotriazol-carbonic ester (neutral)

5 Anilinotriazol-carbonic ester (acid)

Dimroth himself found a very fine confirmation, so that doubt of the true interpretation of the said laboratory experience was sooner to be expected.

Dimroth determined the concentration of the two isomers C_A and C_B in different solvents, in which the isomers had assumed equilibrium at ± 60° under influence of the catalytic action of a trace of acid.

Further the solubility of each of the isomers, so L_A and L_B, was determined at the same temperature in the same solvent, and then the quantity G calculated by means of equation (1).

The investigation of the isomers of the *ethyl* resp. *methyl ester* yielded the following interesting result:

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[1]) Ber. 34. 2001 (1901).

Ethyl ester.

Solvent	$\frac{C_s}{C_n}$	$\frac{L_s}{L_n}$	G
Ether	20.7	8.4	2.4
Ethylalcohol	4.56	2.1	2.3
Toluol	1.53	0.74	2.1
Benzene	1.2	0.6	2.4
Nitrobenzene	0.85	0.33	2.6
Chloroform	0.32	0.19	1.7
	Methyl ester.		
Ether	21.7	53.0	0.4
Methylalcohol	2.3	7.0	0.33
Toluol	1.8	4.3	0.33
Benzene	1.02	3.2	0.32
Nitrobenzene	0.8	2.2	0.36
Chloroform	0.32	1.1	0.32

On the whole G yields a good constant value. As the value of G happens to be larger than 1 for the *ethyl ester*, and smaller than 1 for the *methyl ester*, it was to be foreseen that when the two isomers of the ethyl ester at 60 are left in contact with the saturate solution, the neutral form vanishes entirely, whereas the reverse must take place with the methyl ester. Experiment was in perfect harmony with this, so that the investigation of these isomers yielded a fine qualitative confirmation.

3. *A relation of general validity, by means of which both for isomers and for polymers it can be decided in an exceedingly simple way which modification is the stable one.*

The substances discussed here present the phenomenon of molecular allotropy, because they are built up of two kinds of molecules. Besides they present the phenomenon of phase allotropy, because the substance appears in two solid phases.

Hence the substance without solvent belongs to the pseudo binary systems, and only when the different kinds of molecules in the homogeneous phase(s) are in internal equilibrium, the system behaves as a *unary* substance, i.e. as a substance of one component.

When we consider the behaviour of the two modifications with a solvent, we have a pseudo ternary system, which becomes binary when the different kinds of molecules assume internal equilibrium in the homogeneous phases.

To set forth the cases discussed by DIMROTH in the most easily comprehensible way, I will follow the method which I discussed already before in the publication: "Das Gesetz der Umwandlungsstufen OSTWALDS im Lichte der Theorie der Allotropie" [1]).

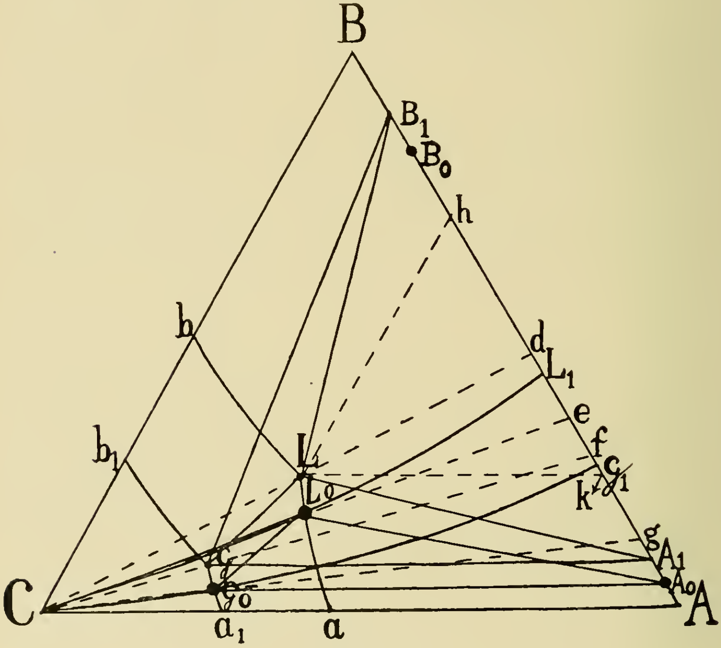

Fig. 1.

At the angles of the equilateral triangle Fig. 1 the letters *A*, *B*, and *C* are placed, of which *A* and *B* represent the pseudo-components, which are miscible in the solid state to a limited degree, *C* denoting the solvent.

In this triangle have been given among others the solubility isotherm of the mixed crystal series AA_1 represented by the curve

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[1]) Z. f. phys. Chem. **84**, 385 (1913).

aL, and that of the mixed crystal series BB_1, represented by the curve bL, for a definite temperature, so that the point of intersection L indicates the saturate solution coexisting with the mixed crystal phases A_1 and B_1.

We imagine the solutions here also in equilibrium with their vapour, in consequence of which the pressure is therefore not constant.

The vapour isotherm belonging to the solubility isotherm aL is the line a_1G, that which belongs to the solubility isotherm bL is denoted by b_1G, so that G represents the vapour phase coexisting with the saturate liquid L and the two solid phases A_1 and B_1 at the four phase equilibrium.

If now CL_0L_1 represents the isotherm of the internal equilibrium in the liquid phase, i. e. the line that indicates how the internal equilibrium between A and B in the liquid phase shifts through change of the concentration of the solvent C, we see immediately that as this line cuts the solubility isotherm of the mixed crystal series AA_1 (point L_0), in case of internal equilibrium between A and B of all the saturated solutions only the saturate solution L_0 is stable, which then of course will coexist with a mixed crystal phase which is likewise in internal equilibrium, and is denoted here by A_0.

Besides these also the isotherm of the internal equilibrium in the vapour CG_0G_1 is indicated. This line cuts the vapour isotherm a_1G in G_0, so that it immediately follows from this that in case of internal equilibrium of all the saturated vapours only the vapour G_0 is stable, so that the phases A_0, L_0, and G_0 coexist in the stable three phase equilibrium solid-liquid-vapour.

It is known that the concentration of an arbitrary phase can immediately be given. Thus the concentration of the liquid phase L_0 is found by a line being drawn in this point parallel to the side CB, and another parallel to the side CA, as this has been done in fig. 1. One line meets the side AB in h, and the other in k. The number of gr. mol. A to 1 gr. mol. total or x is now given by Bh, the number of gr. mol. B or y by Ak, and the number of gr. mol. solvent C or $1-x-y$ by hk.

I may further assume as known that if our end in view is only the ratio of the concentrations A and B, e.g. in the same point L, this is also directly found when a straight line is drawn through the points C and L. This line meets the side AB in the point d. The ratio of the concentrations of A and B is the same in every point of the line Cd, hence it is in d also the same as in L. In d this ratio is:

$$\frac{Bd}{Ad}=\frac{Bh}{Ak}=\frac{x}{y}.$$

Now it is perfectly clear that when the isotherm for the internal liquid equilibrium passes exactly through the point L, or the point of intersection of the two liquid isotherms, this implies that at the considered temperature the solution saturate with respect to the mixed crystal phases A_1 and B_1 is exactly in internal equilibrium. Accordingly it follows immediately from this, that also the coexisting solid phases will be in internal equilibrium in this case, and besides that also the vapour coexisting with L will be in internal equilibrium. The vapour G lying in the point of intersection of the two vapour isotherms will, therefore, in this case have to lie on the equilibrium isotherm for the vapour.

In this case, which presents itself at the transition temperature of the two modifications, we get a coincidence of the points L_0 and L, G_0 and G, A_0 and A_1, B_0 and B_1. Then coincide also the points e and d, g and f, which indicate the concentrations, the liquid phases, and the vapour phases as far as the substances A and B are concerned.

To simplify the discussion we shall now denote the concentration by small letters when the system is in internal equilibrium, capitals being used when the system is not in internal equilibrium.

The ratio of the concentration between A and B will therefore be indicated by $\frac{X_L}{Y_L}$ in the liquid L, and by $\frac{x_L}{y_L}$ in the liquid L_0.

In accordance with this the ratio between A and B in the vapour G is then indicated by $\frac{X_g}{Y_g}$, and that in the vapour G_0 by $\frac{x_g}{y_g}$.

Thus the ratio of concentration of A and B is denoted by $\frac{X_{s_1}}{Y_{s_1}}$ in the solid phase A_1, and that in the phase A_0 by $=\frac{x_{s_1}}{y_{s_1}}$, that in B_1 being given by $\frac{X_{s_2}}{Y_{s_2}}$, and that in B_0 by $\frac{x_{s_2}}{y_{s_2}}$.

For the temperature of the point of transition the following simple equations hold:

$$\frac{x_L}{y_L}=\frac{X_L}{Y_L} \quad . \quad . \quad . \quad (2) \qquad\qquad \frac{x_{s_1}}{y_{s_1}}=\frac{X_{s_1}}{Y_{s_1}} \quad . \quad . \quad . \quad (4)$$

$$\frac{x_g}{y_g}=\frac{X_g}{Y_g} \quad . \quad . \quad . \quad (3) \qquad\qquad \frac{x_{s_2}}{y_{s_2}}=\frac{X_{s_2}}{Y_{s_2}} \quad . \quad . \quad . \quad (5)$$

At another temperature, however, we get the following relations:

$$\frac{x_L}{y_L}=f_1\frac{X_L}{Y_L}\quad . \quad . \quad . \quad (6) \qquad \frac{x_{s_1}}{y_{s_1}}=f_3\frac{X_{s_1}}{Y_{s_1}}\quad . \quad . \quad . \quad (8)$$

$$\frac{x_g}{y_g}=f_2\frac{X_g}{Y_g}\quad . \quad . \quad . \quad (7) \qquad \frac{x_{s_2}}{y_{s_2}}=f_4\frac{X_{s_2}}{Y_{s_2}}\quad . \quad . \quad . \quad (9)$$

About the factors f we will only state here that they are in connection with each other and become at the same time $= 1$ at the temperature of transition.

These relations (6) and (9) are of *general validity*, and of these relations equation (6) is the most suitable to decide which modification is the stable one at a definite temperature.

Let us suppose that $f_1 > 1$, i.e. that the case presents itself indicated in fig. 1. The internal equilibrium L_0 requires here a greater concentration of A_1 than prevails in the solution L. If therefore at first we have the saturate solution L in coexistence with the two mixed crystal phases A_1 and B_1, the transformation

$$B \rightarrow A$$

will take place in the solution, which renders the solution unsaturate with respect to B-mixed crystals, and supersaturate with respect to A-mixed crystals, with this consequence that B-mixed crystals dissolve, and A-mixed crystals deposit. This process continues till the B-mixed crystals have entirely disappeared, and a solution L_0 is left, in which A and B are in internal equilibrium, which solution coexists with a mixed crystal phase A_0, which is then also in internal equilibrium.

For the case $f < 1$ we then get the reverse.

It is now perfectly clear that by consideration of the relations (7) or (8) and (9) we come to the same conclusion.

These now are all self-evident relations, which, indeed, only allow of a qualitative test, but which have this advantage, that as has been said, they have *general* validity.

It will repeatedly happen that we do not know which of the two forms of a substance is the stable modification at a definite temperature, and then equation (6), as has been shown, indicates an exceedingly simple way to decide this.

At the said temperature we determine the concentrations of A and B in the solution, *which is saturate with respect to the two solid phases A_1 and B_1* (which will be mixed crystals). Thus we find $\frac{X_L}{Y_L}$.

What is particular about this method is this that $\frac{x_L}{y_L}$ does not refer *to an arbitrary solution in which A and B are in internal equilibrium, but very specially to the solution L_0. We therefore take a part of the saturate solution with some crystals of the two solid phases, and let the internal equilibrium set in at the same temperature*, at which one kind of crystals disappears (except at the point of transition). We now determine the concentration of A and B in

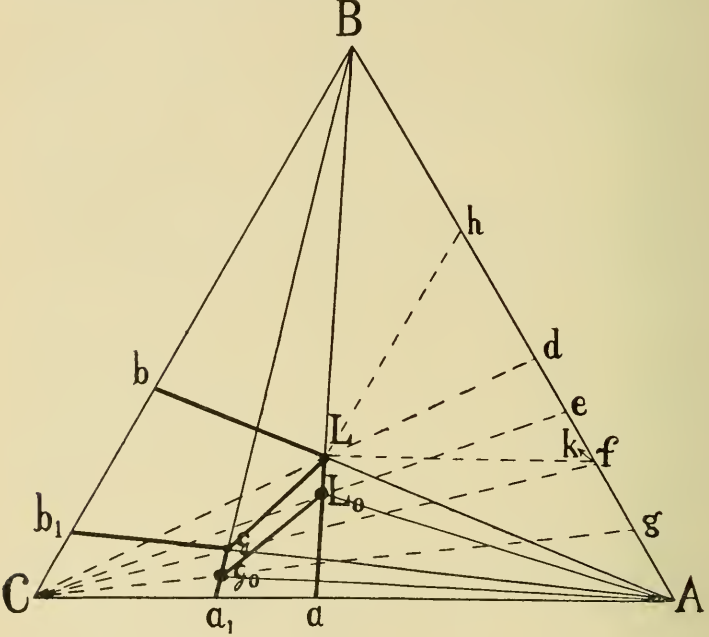

Fig. 2.

this solution, and thus find $\frac{x}{y}$, in which it is perfectly indifferent whether these concentrations are great or small. If we now calculate the quotient:

$$\frac{\frac{x_L}{y_L}}{\frac{X_L}{Y_L}} = f_1$$

we know with *perfect certainty that without any exception* A will be stable when $f > 1$, and that B will be stable when $f < 1$.

In this method it is quite immaterial whether A and B are isomers or polymers. Whatever molecular weights we may assume for the calculation of the concentration ratios between A and B, whether these are correct or wrong, all this is of no importance whatever, because the factor f_1 is not affected at all by this.

3. Dimroth's *relation for isomers.*

The relation of Dimroth.

$$\frac{C_A}{C_B}=\frac{L_A}{L_B}\cdot G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is not universally valid, and this is already seen by this that here $\frac{L_A}{L_B}$ is written instead of $\frac{X_L}{X_L}$, in which L_A indicates the solubility of A in the pure solvent. $\frac{L_A}{L_B}$ is therefore *not* the ratio of concentration of A and B in the liquid L saturated with respect to A and B in Fig 1, but:

$$L_A=\frac{Ca}{Aa} \text{ and } L_B=\frac{Cb}{Bb}.$$

This circumstance is to be explained by this that Dimroth's formula only holds for the ideal case that even to the liquid and the vapour phases saturated with respect to the solid phases the laws for the ideal solutions and gases may be applied, so that also a mutual influencing between A and B is excluded.

Accordingly it need not astonish us that this relation of Dimroth has a very limited validity, but on the other hand it can also give us further information about these ideal cases.

I shall demonstrate this by the aid of fig. 2, which likewise holds for an ideal ternary system. We see that this fig. differs from fig. 1; first in this that the solubility isotherms, at least for so far as they represent stable states, are straight lines, which join the points a resp. a_1 with the angular point B, and the points b resp. b_1 with the angular point A, which expresses that the substances A and B do not influence each other's solubility. Secondly it is noteworthy that the isotherms for the internal liquid resp. vapour equilibrium are also straight lines, because it is supposed here that A and B are isomers. And in the third place it is assumed that A and B do not form mixed crystals.

For the internal equilibrium in every liquid phase, hence also in L_0, holds:

$$K_{L_0} = \frac{x_L}{y_L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and for that in the coexisting vapour phase G_0

$$K_{g_0} = \frac{x_g}{y_g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If now, as was supposed above, the laws for the ideal solutions and gases may be applied, HENRY's law will also hold both with regard to A and to B for all the coexisting liquid and vapour phases to be considered here, independent whether or no internal equilibrium prevails in these phases.

If we now consider that in the application of HENRY's law the concentrations must be indicated per volume unity, we get what follows:

If the liquid possesses x_L gr. mol. A per 1 gr. mol. total, and if this quantity of 1 gr. mol. occupies a volume of v_L ccm., the concentration per liter of solution is $= \frac{1000\, x^L}{v^L}$.

If further the concentration of A in the coexisting vapour is x_g gr. mol. per gr. mol. total, and if the volume of this quantity of 1 gr. mol. gas at the considered temperature and the prevailing vapour tension amounts to v_g ccm., the concentration of A in the vapour is per liter of gas mixture $\frac{1000\, x_g}{v_g}$.

If we now apply HENRY's law, we may write:

$$\frac{\dfrac{1000\, x_L}{v_L}}{\dfrac{1000\, x_g}{v_g}} = \frac{\dfrac{1000\, X_L}{V_g}}{\dfrac{1000\, X_g}{V_g}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and

$$\frac{\dfrac{1000\, y_L}{v_L}}{\dfrac{1000\, x_g}{v_g}} = \frac{\dfrac{1000\, Y_L}{V_L}}{\dfrac{1000\, X_g}{V_g}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If now the quotients of the first member of equations (12) and (13) hold for the ratio of concentrations of the substances A and B between the coexisting phases L_0 and G_0, which are in internal equilibrium, and are also saturate with respect to solid A, we see that these quotients are equal to the corresponding ratios in the coexisting phases L and G, which are not in internal equilibrium and are saturate with respect to solid A and solid B.

From equation (12) (13) now follows the relation:

$$\frac{\frac{x_L}{y_L}}{\frac{x_g}{y_g}}=\frac{\frac{X_L}{Y_L}}{\frac{X_g}{Y_g}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

from which it appears that in the ideal case the factors f_1 and f_2 of equations (6) and (7) become equal, so that *the relative distance in concentration, as far as A and B are concerned, has the same value for the coexisting liquid and vapour-phase L and G in the four phase equilibrium of the pseudo ternary system as the relative distance between the internal equilibria Lo and Go in the binary system.*

Equation (14), therefore, says with reference to fig. 2 that:

$$\frac{\frac{Be}{Ae}}{\frac{Bg}{Ag}}=\frac{\frac{Bd}{Ad}}{\frac{Bf}{Af}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

If we now write equation (14) in the form:

$$\frac{x_L}{y_L}=\frac{X_L}{Y_L}\cdot\frac{x_g}{y_g}:\frac{X_g}{Y_g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

we may remark that according to DIMROTH's terminology:

$$\frac{x_g}{y_g}:\frac{X_g}{Y_g}=G.$$

If we introduce also this substitution, we get:

$$\frac{x_L}{y_L}=\frac{X_L}{Y_L}\cdot G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

whereas DIMROTH wrote:

$$\frac{C_A}{C_B}=\frac{L_A}{L_B}\cdot G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Now X_L and Y_L indicate the concentrations of A and B in the solution L (see fig. 2), which is saturate with respect to A and B, L_A and L_B representing the saturation concentrations of A resp. B in the pure solvent.

As a rule these are of course *not* the same quantities, but when, as in the ideal case, the substances A and B do not influence each other's solubility, this *is* the case, as also appears from fig. 2, for from this follows immediately:

$$L_A=\frac{Ca}{Aa}=\frac{Bd}{Ad}=\frac{X_L}{Y_L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

so that DIMROTH's formula is perfectly correct for the ideal case.

We must finally still point out here that in contradistinction with equation (6) *the quotient* $\frac{x_L}{y_L}$ *in equation* (17) *and* $\frac{C_A}{C_B}$ *in equation* (18) *is the ratio of concentration of A and B in an arbitrary solution, in which A and B are in internal equilibrium.*

4. *The relation for the case of polymery.*

Up to now we have supposed that A and B are *isomers*, but the same considerations are valid for the case of polymery.

Put the case that B is a polymer of A, and that the internal equilibrium is represented by:

$$B \rightleftarrows 2A$$

then the just given derivation may be applied also here. We must only bear in mind that to get a relation that is analogous to equation (16) i.e. in which the expression for the equilibrium constant in the liquid- and gasphase occurs, we must apply Henry's law to those concentrations of A and B which occur in the equation for the equilibrium constant. Hence we consider the concentration x^2 of A, and y of B.

In this way we then get the relation:

$$\frac{x^2{}_L}{y_L} = \frac{X^2{}_L}{Y_L} \cdot \frac{x^2{}_g}{y_g} : \frac{X^2{}_g}{Y_g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This equation expresses, indeed, the same thing as equation (16), which holds for isomers, but differs from it in shape. Of course this equation, too, can only be applied to the ideal case, and only then, written in the form:

$$\frac{x^2{}_L}{y_L} = \frac{X^2{}_L}{Y_L} \cdot h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

it can be used to examine which modification is the stable one at a certain temperature. This is however, *only possible when we know the size of the different kinds of molecules.* Now the great advantage of equation 6 is evident, as this can be applied, without the size of the molecules of A and B being known.

In this communication I have tried to treat the problem in the simplest way possible; in the next the relations considered here will be derived by a thermodynamic way, and there the significance of the phenomena known in practice which seem in conflict with this theory, will also be pointed out.

Amsterdam, 23 June 1915. *Anorg. Chem. Laboratory*
of the University.

Chemistry. — "*The Apparent Contradiction between Theory and Practice in the Crystallisation of Allotropic Substances from Different Solvents*". By Prof. A. Smits. (Communicated by Prof. J. D. van der Waals).

1. *Derivation of the equation for the connection between the saturation concentrations and those of the internal equilibrium.*

In this communication I will give in the first place the thermodynamic derivation of the equations derived in the first communication on this subject in simpler but less rigorous way.

We shall suppose for this purpose that in a homogeneous phase, a gas phase or a solution, at a definite temperature and pressure between two kinds of molecules of the same substance the following equilibrium prevails:

$$\nu_1 A \rightleftarrows \nu_2 B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We further suppose that in two separate spaces at the same temperature the solid substances A and B are in equilibrium with their saturate vapour resp. solution, hence:

$$A_s \rightleftarrows A_G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$B_s \rightleftarrows B_G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now we shall assume that ν_1 mol. of solid A by the aid of the homogeneous phase, which is a gas resp. a liquid phase, is converted into ν_2 mol. of solid B.

In the first process, which we shall consider now, the homogeneous phase is thought to be a gas phase, in which internal equilibrium prevails, and in the second process the homogeneous phase is thought to be a solution, in which the kinds of molecules A and B are likewise in internal equilibrium. In these two cases the increase of the molecular potential $\Sigma\nu\mu$ must, of course, be the same.

Before proceeding to the first process, I will first observe, that for the increase of the molecular potential or:

$$\Sigma\,(\nu\mu)_s = \nu_2\mu_{s_B} - \nu_1\mu_{s_A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

may be written:

$$\Sigma(\nu\mu)_s = \nu_2\mu_{s_B} - \nu_1\mu_{s_A} = \nu_2\mu_{s_B} - \nu_2\mu_{G_B} + \nu_2\mu_{G_B} - \nu_1\mu_{G_A} + \nu_1\mu_{G_A} - \nu_1\mu_{s_A} \quad (5)$$

in which μ_{G_A} and μ_{G_B} represent the molecular potentials of A and B in the saturate vapour.

For the heterogeneous equilibrium between solid A and its vapour and solid B and its vapour hold the following relations:

$$\mu_{s_B} = \mu_{G_B} \quad \text{or} \quad v_2 u_{s_B} = v_2 \mu_{G_B} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$\mu_{s_A} = \mu_{G_A} \quad \text{or} \quad v_1 \mu_{s_A} = v_1 \mu_{G_A} . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

By combination of (5) with (6) and (7) we then get:

$$\Sigma (v\mu)_s = v_2 \mu_{G_B} - v_1 \mu_{G_A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If we now express the internal equilibrium potentials of gaseous A and B by;

$$\mu'_{G_A} \quad \text{and} \quad \mu'_{G_B}$$

then

$$v_1 \mu'_{G_A} = v_2 \mu'_{G_B}$$

for internal equilibrium, so that instead of (8) we may also write:

$$\Sigma (v\mu)_s = v_2 \mu_{G_B} - v_2 \mu'_{G_B} + v_1 \mu'_{G_A} - v_1 \mu_{G_A} \quad . \quad . \quad . \quad (9)$$

in which $v_2 \mu_{G_B} - v_2 \mu'_{G_B}$ represents the work done or gained when we give the equilibrium potential to v_2 mol. of gaseous B, which possess the mol. potential of the saturate vapour, and thus

$$v_1 \mu'_{G_A} - v_1 \mu_{G_A}$$

represents the work performed or gained when v_1 mol. of gaseous A are brought from the equilibrium potential on the potential of the saturate vapour.

These two values for the work are easy to compute.

We start from the equation:

$$d\mu = - \eta dT + v dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

hence

$$(d\mu)_T = v dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or

$$(\mu)_T = \int v dp = RTlnp + C$$

from which follows that:

$$\mu'_{G_A} = RTlnp'_A + C$$

and

$$\mu_{G_A} = RTlnp_A + C$$

or

$$\mu'_{G_A} - \mu_{G_A} = RTln \frac{p'_A}{p_A} = RTln \frac{C'_{A_G}}{C_{A_G}} . \quad . \quad . \quad . \quad (12)$$

hence

$$v_1 \mu'_{G_A} - v_1 \mu_{G_A} = v_1 \, RTln \frac{C'_{A_G}}{C_{A_G}} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

In the same way we get for:

$$\nu_2 \mu_{G_B} - \nu_2 \mu'_{G_B} = \nu_2\, RTln \frac{C_{B_G}}{C'_{B_G}} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

so that equation (9) now assumes the following form:

$$\Sigma\, (\nu\mu)_S = \nu_2\, RTln \frac{C_{B_G}}{C'_{B_G}} + \nu_1\, RTln \frac{C'_{A_G}}{C_{A_G}} \quad . \quad . \quad . \quad (15)$$

Now we can apply the same considerations for the case that the homogeneous phase, in which there is internal equilibrium, is a solution (second process); then we get instead of equation (15):

$$\Sigma\, (\nu\mu)_S = \nu_2\, RTln \frac{C_{B_L}}{C'_{B_L}} + \nu_1\, RTln \frac{C'_{A_L}}{C_{A_L}} \quad . \quad . \quad . \quad (16)$$

As $\Sigma\, (\nu\mu)_S$ has the same value in the two cases, the second member of equation (15) will be equal to the second member of equation (16).

Then follows from equation (15) and (16), that:

$$\frac{C'^{\nu_1}_{A_L}}{C'^{\nu_2}_{B_L}} = \frac{C^{\nu_1}_{A_L}}{C^{\nu_2}_{B_L}} \cdot \frac{C'^{\nu_1}_{A_g}}{C'^{\nu_2}_{B_g}} : \frac{C^{\nu_1}_{A_g}}{C^{\nu_2}_{B_g}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The concentrations provided with accents indicate the internal equilibrium concentrations, and those without accents the saturation concentrations.

Let us suppose that we have to do with isomers, then:

$$\nu_1 = \nu_2 = 1,$$

hence:

$$\frac{C'_{A_L}}{C'_{B_L}} = \frac{C_{A_L}}{C_{B_L}} \cdot \frac{C'_{A_g}}{C'_{B_g}} : \frac{C_{A_g}}{C_{B_g}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This equation is the same as equation (16) in the first communication. ¹)

If we have the case of polymery, and if e.g.

$$\nu_1 = 2 \quad \text{and} \quad \nu_2 = 1$$

the general equation (17) passes into:

$$\frac{C'^2_{A_L}}{C'_{B_L}} = \frac{C^2_{A_L}}{C_{B_L}} \cdot \frac{C'^2_{A_g}}{C'_{B_g}} : \frac{C^2_{A_g}}{C_{B_g}} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

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¹) See preceding communication p. 361.

This equation is again the same as equation (20) in the first communication.

2. *Apparent contradiction between theory and practice.*

DIMROTH[1]), who wrote equation (18) as follows:

$$\frac{C'_{A_L}}{C''_{B_L}} = \frac{C_{A_L}}{C_{B_L}} G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

has pointed out that, the direction of the isomeration being exclusively dependent on the factor G, this must be *independent* of the nature of the solvent.

Experience, says DIMROTH, is in contradiction with this, for it is known that isomers can be transformed into each other by treatment with different solvents.

In this connection I must point out in the first place that there can be question of a test of formula (20) only when we start from a solution saturate with respect to A and B *in contact* with the two solid phases. Only in one case there will then come no change in this state, viz. when the temperature of the system is exactly the transition temperature of the two solid phases. In all other cases a transformation will take place *independent* of the solvent, in which the metastable solid modification disappears, and the stable one remains. For some systems this transformation will proceed slowly, but then we must try to accelerate the process catalytically.

When, working in *this way*, we find deviations, it will no doubt have to be ascribed to this that equation (20) is applied to *non-ideal* cases, or to the case of *polymers*. That practice is really in agreement with theory, can be demonstrated in such a case in a simple way by application of the *universally holding* equation (6) of the preceding communication:

$$\frac{x_L}{y_L} = f_1 \frac{X_L}{Y_L}$$

in the way indicated there.

That isomers can be converted into each other by treatment with different solvents is an entirely different phenomenon. By this we understand namely that when e.g. the α-form is dissolved in a certain solvent, and we then bring the solution to crystallisation in some way or other, the β-form appears.

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[1]) Lieb. Ann. 377, 127 (1910).

We should, however, bear in mind that the formulae discussed here refer to *equilibria*, whereas the last mentioned phenomenon is a question of *number of nuclei* and *spontaneous crystallisation*.

I discussed this question already fully on an earlier occasion [1]), so that I will only say a few words about it here.

Suppose that at a definite temperature and pressure, the situation of the solubility isotherms aL and bL and that of the line for the internal equilibrium in the liquid phase is as is indicated in fig. 1;

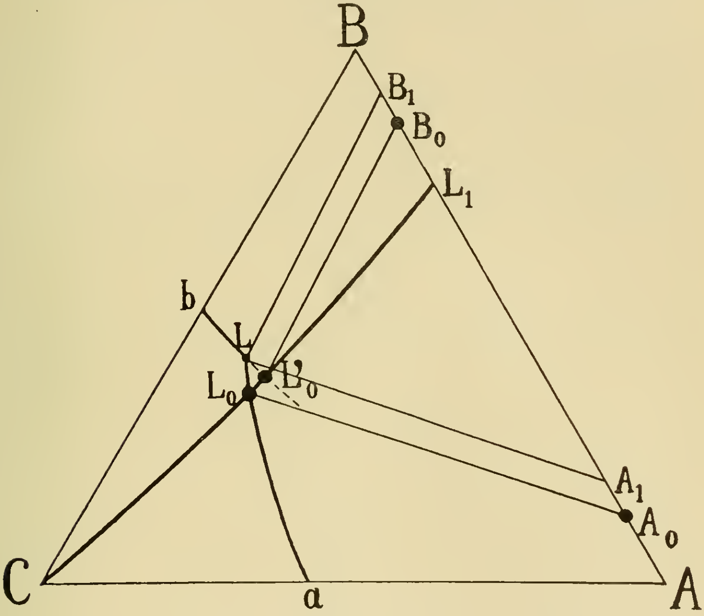

Fig. 1.

then we see immediately that from an supersaturate solution, in which A and B are in internal equilibrium, the stable modification A_0 or the metastable modification B_0 can deposit. The liquid L_0 is namely the stable saturate solution coexisting with A_0, L'_0 indicating the metastable saturate solution, which is in equilibrium with B_0. If the solutions L_0 and L'_0 lie under the point L, i. e. if L'_0 and L_0 contain more of the pseudo-component A than L, and if these points,

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[1]) Zeitschr. f. phys. Chem. 84 (1913).

as in fig. 1, lie pretty much on the B-side, it may occur that in consequence of the greater concentration of B than of A, the number of nuclei for the metastable modification B_0 reaches that value first, at which spontaneous crystallisation sets in. In this case, therefore, the metastable modification deposits from the supersaturate solution, and if under the given circumstances the velocity of conversion is small, the metastable modification that has crystallized out, continues to exist.

If, therefore, the situation is as Fig. 1 indicates, it is very well *possible* that when the stable modification A_0 is dissolved in C at higher temperature, i.e. at such a temperature that the internal equilibrium is entirely or almost entirely established, the metastable form is deposited when the solution is cooled.

For one solvent the situation will be as is indicated in Fig. 1, whereas this situation will be less one-sided when another solvent is used, and in this probably lies the explanation of the fact that by means of one solvent from the stable form the metastable form can be

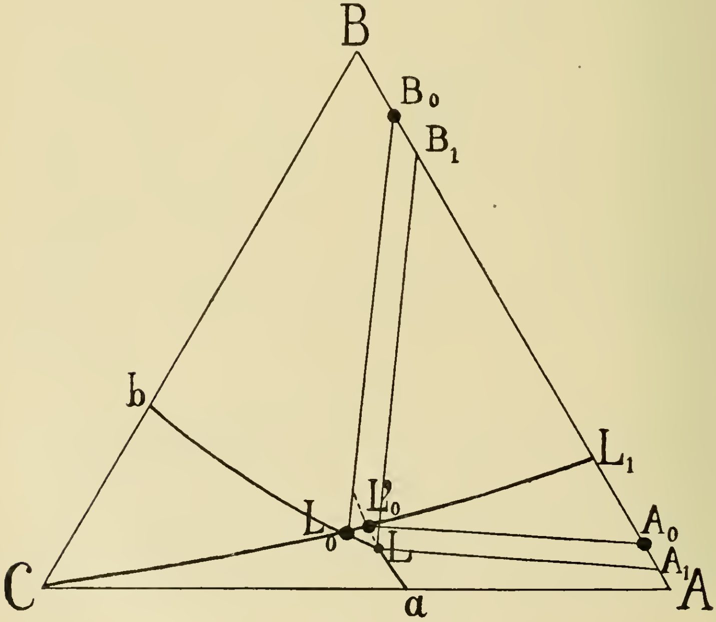

Fig. 2.

obtained, whereas another solvent always yields the stable modification.

If, therefore, the line for the internal equilibrium as Fig. 2 shows, lies above L, i.e. if at the considered temperature B_0 is stable, and L_0 and L'_0 lie greatly on the A-side, then for the same reason the *possibility* is to be expected that when B_0 is dissolved in C, the metastable modification A_0 deposits from the supersaturate solution at lower temperature.

Where this phenomenon presents itself it will be an interesting problem to determine the situation of the points L, L_0, and L'_0 at a definite temperature, to find out in this way in how far the given explanation is the true one.

Amsterdam, 24 June 1915. *Anorg. Chem. Lab. of the University.*

Chemistry. — "*Supersaturation and release of supersaturation.*" By DEVENDRA NATH BHATTACHARYYA and NILRATAN DHAR. (Communicated by Prof. ERNST COHEN).

The older literature on supersaturation, chiefly works of GAY LUSSAC [1]), SCHWEIGGER [2]), ZIZ [3]), THOMSON [4]), OGDEN [5]), and others, abounds with evidences showing that the phenomenon is rather common.

But after that, the general idea of the chemists was that only few substances could form supersaturated solutions.

But now a days chemists have recognised again that the phenomenon is common. Thus MENDELÉEFF [Principles of Chemistry, English translation (1905), p. 93] states that salts which separate out with water of crystallisation and form several crystallohydrates yield supersaturated solutions with the greatest ease, and the phenomenon is much more common than was previously imagined. OSTWALD has studied this case very thoroughly and is of opinion that this is very common. TUTTON also mentions in his book, "Crystals" (p. 238) that supersaturation is a phenomenon of frequent occurrence.

But the reminiscence of the old idea is still unconsciously present in the popular mind. For demonstration experiments, sodium acetate, or sodium sulphate, or sodium thiosulphate is invariably taken. Also

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[1]) Ann. Chim. **87**, 225; Schw. **9**, 70; Ann. Chim. Phys. **11**, 301.

[2]) Schw. **9**, 79.

[3]) Schw. **15**, 160.

[4]) Ann. Phil. **19**, 169.

[5]) N. Ed. Phil. J. **13**, 309

the idea is predominant that only hydrated salts can be easily supersaturated. Sodium chlorate is cited as a solitary example of an anhydrous salt capable of forming supersaturated solution. Again, no systematic work of a quantitative character is available in this direction. These led to the present investigation of showing the general tendency of almost all substances of forming supersaturated solutions.

At first qualitative experiments were done with varied substances. These were all performed in well cleaned, steamed test tubes fitted with similarly operated corks. The solution is boiled for a few minutes till all the particles of the substance on the side of the test tube have been dissolved away by the steam, the cork is immediately put in, and the hot solution, then, is glided over the side of the tube twice or thrice. The tube is then held under the tap and cooled down to the room temperature. The corks were always moist when they were inserted thus insuring against germ crystals being carried in that way. In open tubes the solution might evaporate and deposit minute crystals on the sides, which would then at once release the supersaturation.

But such things can hardly take place in this case, because the solution is in a partial vacuum saturated with water vapour. With ordinary amount of precaution many supersaturated solutions were prepared in this way which would not deposit crystals even when shaken vigorously.

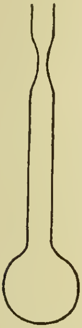
Thus it has been found that tartaric acid, citric acid, magnesium sulphate, lead acetate, cobalt chloride, microcosmic salt, sodium formate, ammonium acetate, copper sulphate, borax form highly supersaturated solutions. In the case of tartaric and citric acids the supersaturated solution is very much viscous, and even on the addition of a small germ crystal of the acid, some time elapses before crystallisation takes place, because the velocity of crystallisation depends on the fluidity of the solution.

In the case of lead nitrate, barium nitrate, ammonium chloride, strontium chloride, barium chloride, manganese chloride, potassium ferrocyanide, potassium sulphate, zinc sulphate, nickel sulphate, cobalt sulphate, barium chlorate, sodium chlorate, sodium bromate, sodium nitrate, ammonium nitrate, ammonium oxalate, oxalic acid, the amount of supersaturation is not as extensive as in the case of the previously mentioned group.

The sparingly soluble organic acids, namely, salicylic, benzoic, hippuric, succinic, cinnamic, gallic, phthalic acids can be supersaturated. Substances like potassium chlorate, cadmium iodide, boric acid also admit of supersaturation. But in all these cases, the amount of substance held in excess though appreciable, is small.

Copper chloride and nickel chloride which are highly soluble, can form fairly supersaturated solutions, but the range of dilution in which they can exist as such in good stability, is rather limited.

Thus it is shown qualitatively that the phenomenon of supersaturation is perfectly general, and all sorts of substances, hydrated or anhydrous, sparingly soluble or highly soluble, can form supersaturated solutions.



Now, experiments of a quantitative character were undertaken with a series of substances. The experiments were conducted in the following way: A bulb was blown at one end of a tube of about 10 mm. diameter, and a portion towards the other end drawn out a little so as to form a constriction there. The tube was then very carefully washed and steamed to dissolve away any nuclei, carefully dried, and weighed. A weighed amount of the pure dry substance was introduced into it, a little water was added to it, and a supersaturated solution produced by properly adjusting the amount of the solvent by boiling. The solution was freely boiled so that every particle on the side of the tube passed into solution. The tube was then partially cooled under the tap, and carefully sealed at the constriction by means of a blow-pipe. The solution was then rolled over the stem of the bulb to mix with the condensed droplets of water there, and thus a homogeneous solution was obtained. The tube was then thoroughly cooled and placed in a quiet place with a thermometer to indicate the temperature. The drawn out portion of the tube was dried, and this weighed with the sealed bulb, gave the weight of water added.

To reach the maximum amount of supersaturation, which can be maintained under ordinary circumstances for an hour or so, the method of trial was adopted. The solution was often boiled a little and cooled down in tap water to see whether crystals appear immediately. By a little practice no difficulty was felt to judge in this way whether the solution would crystallise shortly or not. The tube was sealed when this stage was reached.

The time for which the solution remained supersaturated, as well as the temperature at which crystallisation set in were carefully observed.

The following table shows the experimental data. The solubility

Substance	Temp. in degrees centigrade.	Grams of substance calculated as anhydrous which is contained in 1 gram of water.	Grams of substance calculated as anhydrous which ought to have been contained in 1 gram of water for saturation.	N^o. of gram molecules of the anhydrous substance held in excess in 1 gram of water.
Benzoic acid (C_6H_5COOH)	28°.8	0.008	0.004	0.00003
$Ba(NO_3)_2$	26	0.152	0.106	0.00017
K_2SO_4	22	0.166	0.115	0.0003
NH_4Cl	22	0.450	0.380	0.0005
$NaBrO_3$	30	1.288	0.423	0.0054
$Pb(NO_3)_2$	27	0.983	0.605	0.0011
$(NH_4)_2SO_4$	23	0.806	0.761	0.00034
CdI_2	25	1.001	0.879	0.0005
$NaNO_3$	28.2	0.995	0.940	0.0006
$NaClO_3$	26.6	1.921	1.070	0.0079
Tartaric acid ($C_2H_2(OH)_2 . (COOH)_2$)	22	3.37	1.46	0.0300
NH_4NO_3	26.5	2.939	2.224	0.0089
$BaClO_3 . H_2O$	26	0.570	0.387	0.0008
Oxalic acid ($(COOH)_2 . 2\,H_2O$)	25	0.237	0.113	0.0013
$BaCl_2 . 2\,H_2O$	23.8	0.448	0.268	0.0086
Lead Acetate ($Pb(C_2H_3O_2)_2 . 3\,H_2O$)	22	2.63	0.44	0.0067
$MnCl_2 . 4\,H_2O$	22	1.11	0.75	0.0028
$CuSO_4 . 5\,H_2O$	23	0.700	0.219	0.0030
$CoCl_2 . 6\,H_2O$	24.2	0.646	0.343	0.0023
$SrCl_2 . 6\,H_2O$	24	0.638	0.552	0.0054
$MgSO_4 . 7\,H_2O$	22	0.535	0.371	0.0013
$CoSO_4 . 7\,H_2O$	24	0.563	0.387	0.0011
$NiSO_4 . 7\,H_2O$	24	0.506	0.388	0.0006
$ZnSO_4 . 7\,H_2O$	23	0.691	0.565	0.0008
$Na_2B_4O_7 . 10\,H_2O$	24	0.649	0.031	0.00306
$K_2Al_2(SO)_4 . 24\,H_2O$	26.5	0.675	0.075	0.00116

of the substance was obtained from SEIDELL's Solubilities of Inorganic and Organic substances. The solubilities were calculated as grams of anhydrous substances per 1 gram of water. The substances appear in the list in the order of their water of crystallisation, and of their solubility. The substances crystallised in all cases in 1 to 5 hours after the sealing of the tubes.

Besides these, some 30 tubes were sealed with solutions of less supersaturation. They were watched for 3 months, in which time very few crystallised.

From the above tables it will be seen that no perfectly general deduction is obtainable; but the following facts are observable:

a. Hydrates easily form supersaturated solution.

b. Supersaturation is common in easily soluble substances.

c. Also the phenomenon is common in those substances, which easily form big well-defined crystals.

Physico-chemical Laboratory, Presidency College, Calcutta.

Chemistry. "*Temperature-coefficient of conductivity in alcoholic solutions, and extension of* KOHLRAUSCH's *hypothesis to alcoholic solutions.*" By DEVENDRA NATH BHATTACHARYYA and NILRATAN DHAR. (Communicated by Prof. ERNST COHEN).

In a former paper[1]), the results of conductivity measurements of ten sodium salts in alcoholic solutions were published. The measurements were carried out at three temperatures, and in this paper the values of the temperature coefficient of conductivity are calculated and some deductions made from the results.

If we suppose that the conductivity increases proportionally with the temperature, i. e. the conductivity is a linear function of the temperature, we find the following values for the temperature coefficient of conductivity of the ten sodium salts in alcoholic solutions investigated: (see table p. 374).

It is evident from the above table that in all cases the value of the temperature coefficient is about 0.024. Now, from the researches of BOUTY[2]) it is seen that the temperature coefficient of fluidity of alcohol is about 0.024 per degree centigrade. Thus for almost all the salts studied, the temperature coefficient of conductivity in alcoholic solutions is equal to the temperature coefficient of fluidity of the solutions; because the solutions being very dilute, their viscosities are practically identical to that of the pure solvent, namely alcohol.

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[1]) Zeitschr. für anorg. Chemie 82, 357 (1913).

[2]) Jour de Physique (2). 3, 351 (1884).

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Salt	Temperature-coefficient between 0° and 5° C.	Temperature-coefficient between 0° and 30° C.	Dilution
I. $NaClO_3$	0.018	0.027	1774.332
II. $NaCl$	0.016	0.026	1623.888
III. $NaNO_3$	0.019	0.026	1180.694
IV. $NaNO_2$	0.024	0.027	1916.937
V. NaCNS	0.022	0.028	2208.451
VI. Na_2PtCl_6	0.015	0.020	4236.345
VII. Sodium propionate	0.023	0.024	993.517
VIII. Sodium butyrate	0.027	0.025	1320.672
IX. Sodium benzoate	0.015	0.024	685.179
X. Sodium Salicylate	0.013	0.023	1306.449

From a consideration of equal effect of temperature on the conductivity and fluidity of aqueous electrolytic solutions of pure water, Kohlrausch [1]) presents the hypothesis that, round every ion, and moving along with it, there is an atmosphere of the solvent whose dimension is determined by the individual characteristics of the ion; and the electrolytic resistance of an ion is a frictional resistance which increases with the extension of the atmosphere, the direct action between the ion and the outer portion of the solvent diminishing as the atmosphere becomes of greater thickness. This hypothesis is in agreement with the fact that the most sluggish ions have the temperature coefficient of resistance very like the temperature coefficient of viscosity of the solvent. The hypothesis is in further agreement with the circumstance that the temperature formula for the mobility of the ions shows in all cases a convergence towards the zero value between — 35° C. and — 41° C., the zero value of the fluidity of water being reached at — 34° C.

From our work it is evident that the same hypothesis may be applied equally in alcoholic solutions. The electrolyte binds with it a few molecules of the solvent, the alcohol, which forms an atmosphere round it, and it moves through the solution with this alcoholic atmosphere surrounding it. The frictional resistance it meets, is not the frictional resistance between the ions and the solvent alcohol, but it is the frictional resistance of the alcoholic atmosphere round the ions against the solvent molecules.

Chemical Laboratory, Presidency College, Calcutta.

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[1]) Proc. Roy. Soc. 1903, 71, 338.

Chemistry. — "*Velocity of ions at 0° C.*" By Devendra Nath Bhattacharyya and Nilratan Dhar. (Communicated by Prof. Ernst Cohen).

From time to time attempts have been made to determine accurately the mobilities of ions at 0°. But there is no systematic work in this line; only isolated cases have been investigated. Even the velocity of hydrion at 0° is uncertain. An exact idea of our very much incomplete knowledge would be obtained from the following summary of the work previously done.

Wood [1]) was the first investigator in this line. Het determined the molecular conductivities of sodium chloride, potassium chloride, dichloracetic acid, and trichloracetic acid at 0°, and at various dilutions. But his measurements are inaccurate as will be shown subsequently. Archibald [2]), Barnes [3]) and Kohlrausch [4]) also studied some electrolytes. Whetham [5]) accurately determined the conductivities of some electrolytes at 0°; but he did not attempt in deducing the velocities of individual ions at 0° from his measurements. Kahlenberg [6]), and Jones and his pupils [7]) also studied some cases, but their measurements are not accurate. The measurements of Noyes and Coolidge [8]) agreed with those of Whetham. Evidently no systematic work is done in this line.

The ionic mobilities of various ions are fairly accurately known at 18° or at 25° (Noyes and Falk — J. Amer. Chem. Soc. **33** (1911), 1436). But the value for hydrion (H°) is not exactly certain even at 18° or 25°. Ostwald [9]) first used the value 342 at 25°, and then raised it to 347 in Lehrbuch der Chemie 1893, **2**, 675. Kohlrausch's [10]) provisional value was 318 at 18° or 352 at 25°. Until recently, these values were accepted. Noyes [11]), and then Noyes and Sammet [12]) obtained the unexpectedly high value of 365 at 25°. Roth-

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[1]) Phil. Mag. 1896 (5) XLI, 117.

[2]) Trans. Nov. Sco. Inst. Sci X, 33, 1898.

[3]) ibid X, 139, 1899.

[4]) Ann. Phys. Chem. 1898, **66**, 785—825

[5]) Phil. Trans. 1900.
Proc. Roy. Soc. **71**, 334 (1903).

[6]) Journal. Phys. Chem. **5**, 339 (1901).

[7]) Amer. Chem. Journ. **25**, 349 (1901); **26**, 428 (1901); **34**, 557 (1905).

[8]) Carnegie Institution Publications **63**, 47 (1907).

[9]) Zeit. Phys. Chem. 1888, **2**, 842.

[10]) Leitvermögen der Elektrolyte pp. 107—110, 200.

[11]) Zeit. Phys. Chem. 1901, **36**, 63—83.

[12]) Zeit. Phys. Chem. 1903, **43**, 49.

mund and Drucker[1]) suggested the value 338 at 25°; and then Drucker [2]) used the value 312 at 18° and 345 at 25°. Again, Drucker [3]), Goodwin and Haskell [4]), and Whetham [5]), by combining their molecular conductivity measurements with the transference ratios obtained by Jahn and his pupils, and Tower deduced the mean value for hydrion equal to 313 at 18° or 346 at 25°. Kohlrausch [6]) again, and Jahn and his pupils [7]), declared the most probable value of hydrion to be 315 at 18° or 348 at 25°. Gorke [8]) obtained the value 353 at 25° from measurements of picric acid. Noyes and Kato [9]) came to the value 315 at 18° or 348 at 25° from migration ratios of nitric and hydrochloric acids. Drucker and Kisnjair [10]) again gave the value 313 at 18° or 346 at 25°. It would be quite evident from these that the value for hydrion is far from being correctly known.

Now, by applying Kohlrausch's formula for the temperature coefficient of mobility we can get the values of ions at 0° from the values given at 18 or 25°. But this empirical formula holds good with rigidity in the neighbourhood of 18°; so results deduced at 0 are rather uncertain. Moreover Kohlrausch himself has changed these values of temperature coefficients many times. For comparison, are added below the tables (see p. 416) of temperature coefficients (α) as published by Kohlrausch [11]) in 1901, and 1908.

Thus extrapolation to 0° is rather uncertain. With a view to determine exactly the ionic velocities at 0°, this investigation was undertaken. Noyes and Falk [12]) have given very accurate tables collected from the work of numerous investigators for the transference numbers of various substances at almost infinite dilution and at 0°. From the molecular conductivity determination at 0°, the sum of the ionic velocities at 0° is obtained (since $\mu\infty = u + v$), and $\frac{u}{v}$ is taken from Noyes and Falk's tables; thus u and v are obtained.

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[1]) Zeit. Phys. Chem. 1903, **46**, 827.

[2]) Zeit. Phys. Chem. 1904, **49**, 563.

[3]) Zeit. Elektrochem. 1907, **13**, 81.

[4]) Proc. Amer. Acad. 1904, **40**, 399.

[5]) Zeit. Phys. Chem. 1906, **55**, 200.

[6]) Zeit. Elektrochem. 1907, **13**, 333.

[7]) Zeit. Phys. Chem. 1907, **58**, 641.

[8]) Zeit. Phys. Chem. 1908, **61**, 495.

[9]) Zeit. Phys. Chem. 1908, **62**, 420.

[10]) Zeit. Phys. Chem. 1908, **62**, 731.

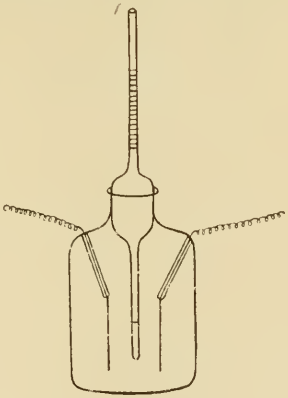
[11]) Sitzungsber. d. Berl. Akad. 1901, 1026; 1902, 572; Proc. Roy. Soc. **71**, 338 (1903). Zeit. Elektrochem. **14** (1908), 129.

[12]) loc. cit.

Ions	1901 α_{18}	1908 α_{18}
Li°	+ 0.0261	+ 0.0265
Na°	+ 0.0245	+ 0.0244
K°	+ 0.0220	+ 0.0217
Rl°	+ 0.0217	+ 0.0214
Ag°	+ 0.0231	+ 0.0229
H°	+ 0.0154	+ 0.0154
Cl′	+ 0.0215	+ 0.0216
F′	+ 0.0232	+ 0.0238
I′	+ 0.0206	+ 0.0213

The water used in these experiments was carefully purified by JONES and MACKAY's [1]) method, and collected in wellsteamed resistance glass vessels. Freshly purified water was used in all experiments. The conductivity of the water used varied from 4 × 10^{-6} to 5 × 10^{-6} at 0°.

The measurements were carried out by the alternating current-telephone method in a closed well platinised cell, with a thermometer tightly fitting its mouth. In our hot and moist climate, moisture condenses in the interior of vessels surrounded with ice; so there is the danger of dilution of the solutions in open mouth cells; but this difficulty is removed by having closed vessel for putting in solution. The bath was of pure melting ice.



The temperature as indicated by the thermometer was kept constant for nearly half an hour, and then readings were taken. The cell was now taken out of the bath and made to attain the ordinary laboratory temperature, and diluted with calibrated standard pipettes.

MERCK's chemically pure substances were purified by repeated crystallisation and dried according to the nature of the substance in question.

Hydrochloric acid was prepared by dissolving in conductivity

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[1]) Zeit. Phys. Chem. 22, 237, (1897).

water hydrochloric acid gas evolved out of the ordinary pure concentrated hydrochloric acid.

Concentrations of solutions were obtained in most cases by volumetric method, and the results were mostly checked by the concentrations obtained from the weights of the salts dissolved.

The following tables give the values of the molecular conductivities obtained:

I. *Hydrochloric acid.*

Dilution	Molecular conductivity μ_v
31.963	237.0
63.926	259.8
127.852	261.5
255.704	262.9
511.408	263.8
1022.816	264.2
2045.632	264.3
4091.264	264.4

Thus μ_∞ obtained = 264.4.
The value of μ_∞ calculated with KOHLRAUSCH's ionic velocities and temperature coefficients = 265.8.

II. *Ammonium Chloride.*

Dilution	μ_v
9.984	66.5
19.968	73.8
39.936	75.3
79.872	76.0
159.744	78.4
319.488	79.2
638.976	79.7
1277.952	79.9
2555.904	80.0

Thus μ_∞ obtained = 80.0
μ_∞ calculated from KOHLRAUSCH's data = 81.7.

III. *Lithium Chloride.*

Dilution	μ_v
7.437	47.0
14.874	53.2
29.748	55.6
59.496	57.5
118.992	59.2
237.984	59.7
475.968	59.9
951.936	60.1
1903.872	60.1

μ_∞ obtained = 60.1
μ_∞ calculated from KOHLRAUSCH's data = 60.5.

IV. *Strontium Chloride.*

Equivalent dilution	Equivalent μ_v
19.576	53.2
39.152	61.3
78.304	64.0
156.608	66.0
313.216	66.7
626.432	68.8
1252.864	70.7
2505.728	71.9
5011.456	72.3

μ_∞ is taken to be 72.5
μ_∞ calculated from KOHLRAUSCH's data = 73.1.

V. *Magnesium Chloride.*

Equivalent dilution	Equivalent μ_v
30.396	58.8
60.792	59.5
121.584	60.5
243.168	62.3
486.336	64.0
972.672	65.3
1945.344	66.1
3890.688	66.4

μ_∞ is taken to be 66.6
μ_∞ calculated from KOHLRAUSCH's data = 68.3

VI. *Ammonium Nitrate.*

Dilution	μ_v
30.231	77.7
60.462	78.6
120.924	79.2
241.848	79.7
483.696	80.0
967.392	80.2
1934.784	80.2
3869.568	80.3

μ_∞ obtained = 80.3
μ_∞ calculated from KOHLRAUSCH's data = 80.3

VII. *Sodium Nitrate.*

Dilution	μ_v
22.277	62.6
44.554	63.7
89.108	65.1
178.216	65.8
356.432	66.0
712.864	66.5
1425.728	66.8
2851.456	66.9

μ_∞ obtained = 66.9
μ_∞ calculated from KOHLRAUSCH's data = 66.1

VIII. *Potassium Nitrate.*

Dilution	μ_v
39.068	78.4
78.136	80.3
156.272	81.3
312.544	82.5
625.088	83.0
1250.176	83.2
2500.352	83.3
5000.704	83.4

μ_∞ obtained = 83.4
μ_∞ calculated from KOHLRAUSCH's data = 81.1

IX. *Ammonium Sulphate.*

Equivalent dilution	Equivalent μ_v
53.633	73.5
107.267	76.7
214.534	79.2
429.068	80.6
858.136	81.3
1716.272	81.6
3432.544	81.7

μ_∞ taken to be 81.8
μ_∞ calculated from KOHLRAUSCH'S data = 82.4.

X. *Potassium Sulphate.*

Equivalent dilution	Equivalent μ_v
33.156	72.9
66.312	75.7
132.624	79.0
265.248	81.9
530.496	83.5
1060.992	84.0
2121.984	84.2

μ_∞ taken to be 84.4
μ_∞ calculated from KOHLRAUSCH'S data = 83.2.

XI. *Sodium Sulphate.*

Equivalent dilution	Equivalent conductivity
17.325	55.9
34.651	58.2
69.302	61.6
138.604	63.8
277.208	65.9
554.416	67.1
1108.832	67.9
2217.664	68.1
4435.323	68.2

μ_∞ obtained = 68.2
μ_∞ calculated from KOHLRAUSCH'S data = 68.3.

XII. *Calcium Sulphate.*

Equivalent dilution	Equivalent μ_v
467.913	63.3
935.826	67.7
1871.652	71.0
3743.304	71.7

μ_∞ is taken to be 72.

XIII. *Magnesium Bromide.*

Equivalent dilution	Equivalent μ_v
44.182	59.3
88.365	61.8
176.730	63.7
353.460	65.1
706.920	66.1
1413.840	66.9
2827.680	67.3

μ_∞ is taken to be 67.5
μ_∞ calculated from KOHLRAUSCH's data = 69.3

XIV. *Calcium Bromide.*

Equivalent dilution	Equivalent μ_v
21.333	62.7
42.667	65.0
85.334	66.8
170.668	68.4
341.336	69.5
682.672	70.4
1365.344	71.0
2730.688	71.2

μ_∞ obtained = 71.2

Now, NOYES and FALK [1]) give the cation transference numbers for HCl and NH_4Cl at 0° at almost infinite dilution as 0.847 and 0.490 respectively. By using these values, the ionic velocities are calculated from μ_∞ determinations for HCl and NH_4Cl. Thus,

Substance		Cation transport number	Ionic velocities
HCl	264.4	0.847	$H^\cdot$ 223.9 Cl' 40.5
NH_4Cl	80.0	0.490	$NH_4^\cdot$ 39.2 Cl' 40.8

Now, the ionic velocity of Cl' is taken as 40.8 as the more accurate figure, and from it the following ionic velocities are deduced by applying KOHLRAUSCH's law $\mu_\infty = u + v$

Substance	Equivalent μ_∞	Ionic velocities
LiCl	60.5	$Li^\cdot = 19.3$
$SrCl_2$	72.5	$\frac{1}{2} Sr^{\cdot\cdot} = 31.7$
$MgCl_2$	66.6	$\frac{1}{2} Mg^{\cdot\cdot} = 25.8$

Again, by using these values, other ionic velocities are calculated as is shown in the following table:

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[1]) Loc. cit.

Substance	Equivalent μ_∞	Known ionic velocities	Required ionic velocities by difference from μ_∞	Remarks
$(NH_4)_2SO_4$	81.8	$NH_4^{\cdot} = 39.2$	$\frac{1}{2} SO_4'' = 42.6$	
Na_2SO_4	68.2	$\frac{1}{2} SO_4'' = 42.6$	$Na^{\cdot} = 25.6$	
K_2SO_4	84.4	$\frac{1}{2} SO_4'' = 42.6$	$K^{\cdot} = 41.8$	
$CaSO_4$	72.0	$\frac{1}{2} SO_4'' = 42.6$	$\frac{1}{2} Ca^{\cdot\cdot} = 29.4$	
NH_4NO_3	80.3	$NH_4^{\cdot} = 39.2$	$NO_3' = 41.1$	
$NaNO_3$	66.9	$Na^{\cdot} = 25.6$	$NO_3' = 41.3$	$NO_3' = 41.1$ from NH_4NO_3
KNO_3	83.4	$NO_3' = 41.3$	$K^{\cdot} = 42.1$	$K^{\cdot} = 41.8$ from K_2SO_4
$MgBr_2$	67.5	$\frac{1}{2} Mg^{\cdot\cdot} = 25.8$	$Br' = 41.7$	
$CaBr_2$	71.2	$Br' = 41.7$	$\frac{1}{2} Ca^{\cdot\cdot} = 29.5$	$\frac{1}{2} Ca^{\cdot\cdot} = 29.4$ from $CaSO_4$
$BaBr_2$				

It would be noticed from the column headed "Remarks" that in no case have ionic velocities differed by more than 0.3, as obtained from different sources.

Below, is added a comparative table of the ionic velocities as obtained by this direct method, and as obtained from KOHLRAUSCH's table[1]) by calculating with his temperature coefficients:

Ions	Velocities at 0° C as obtained directly	Velocities as calculated with temp. coefficients.
$H^{\cdot}$	223.9	224.3
$NH_4^{\cdot}$	39.2	40.2
$Li^{\cdot}$	19.3	19.0
$Na^{\cdot}$	25.6	26.0
$K^{\cdot}$	42.1	40.9
$\frac{1}{2} Ca^{\cdot\cdot}$	29.5	X
$\frac{1}{2} Sr^{\cdot\cdot}$	31.7	31.6
$\frac{1}{2} Mg^{\cdot\cdot}$	25.8	26.8
Cl'	40.8	41.5
NO'_3	41.3	40.1
Br'	41.7	42.5
$\frac{1}{2} SO''_4$	42.6	42.2

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[1]) Loc. cit.

Evidently then, the temperature coefficients of KOHLRAUSCH can not be relied on to obtain accurate values at 0° C.

WOOD[1]) has given the following values for μ_∞ at 0°: for KCl = 77.8, for NaCl = 65.0, for dichloracetic acid = 227.0, for trichloracetic acid = 224.7. Thus from the values obtained by me it is seen that his values for KCl and NaCl are a little too low, whilst his values for the acids are very much too low, since the most probable value of H° is 223.9.

JOHNSTON'S[2]) rough estimation of the value of H° at 0° = 240 is also far from being correct.

NOYES and STEWART[3]) have deduced values for H° in an indirect way which can hardly be relied on. Whilst from data for HCl they obtained the velocity for H° at 0° = 224, they, at the same time obtained, by considering H_2SO_4 in the same way the value 235 at 0°.

NOYES and COOLIDGE[4]) give 81.4 as the value of μ_∞ for KCl at 0°; but it is a little too low.

JONES and WEST[5]) have given μ_∞ at 0° for NH_4Cl = 74.84; evidently it is too low.

JONES and CALDWELL[6]) give the value for ammonium nitrate = 78.0, which is a value a little too low.

KAHLENBERG[7]) obtains for strontium nitrate the value 66.1. Evidently it is too low, since the correct value would be about 31.7 + 41.3 = 73 (loc. cit).

HILL and SIRCAR[8]) take a very high value for H° at 0°. They write: For μ_∞ in the case of hydrogen fluoride, we have taken the number 364 at 18° and 325 at 0°. The first number is derived from the ionic conductivities at 18° which are 318 for the hydrogen ion and 46.6 for the fluorine ion. The second number is derived from the following data:

"OSTWALD gives 325 as the ionic conductivity of the hydrogen ion at 25°; at 18° the value is 318 (KOHLRAUSCH and V. STEINWEHR, Sitz.-ber. Berlin. Akad. 1902), being a fall of one unit per degree. Hence at 0° the value would be approximately 300. Correcting the ionic conductivity of fluorine for temperature, the temperature coefficient being 0.0238, we get the value at 0° = 26.6. The sum

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[1]) Loc. cit.

[2]) J. Amer. Chem. Soc. **31**, 1015 (1909).

[3]) J. Amer. Chem. Soc. **32**, (1910), 1140—1141.

[4]) Carnegie Institution Publications 63, 47 (1907).

[5]) Amer. Chem. Jour. **34**, 557 (1905).

[6]) Amer. Chem. Jour. **25**, 349 (1901).

[7]) Jour. Phys. Chem. **5**, 339 (1901).

[8]) Proc. Roy. Soc. Vol. **83** A, p. 130.

of these ionic conductivities is 326. This number may be derived in another way. H. E. Jones gives 380 as the limiting value for H F at 25°. The value as calculated above for 18° is 364. The difference per degree is 2.3 units, hence the value at 0° is 324. The approximate correctness of the number 325 is shown by the fact that if we assume the amount of dissociation to be little affected by temperature, at any rate in the more concentrated solutions, we get $\alpha = \frac{\mu_v^{0^\circ}}{\mu_\infty^{0}} = \frac{\mu_v^{18}}{\mu_\infty^{18^\circ}}$. Substituting 0.0576 for α and 18.30 for μ_v which is the value for the acid of 29.83 %, we get $\mu_\infty = 318$ (at 0°).

"The temperature coefficient for H at 18° is about 0.0153. If this is used to calculate the limiting value for the hydrogen ion at 0°, the number for $\mu_\infty^{0^\circ}$ becomes very much lower than any of these 3 numbers given above, and as a coefficient is only correct in the neighbourhood of 18° we discard this method of calculating."

It is evident that Hill and Sircar have calculated μ_∞ at 0° for H F assuming a very high value for H°. Their value for H° at 0° is about 100 units higher than the value obtained in this investigation in the direct way. Consequently all their calculations for the degree of dissociation of H F with this value for H° are not reliable.

Chemical Laboratory,
Presidency College, Calcutta.

Chemistry. — "*Properties of elements and the periodic system*". By Nilratan Dhar. (Communicated by Prof. Ernst Cohen).

In a former paper (Dhar Zeit. Elektro-Chem. (1913) it has been shown that the heats of ionisation of elements and the temperature coefficient of mobility of ions are periodic functions of their atomic weights. In this paper it will be shown that some other properties are also periodic functions of their atomic weights.

Surface tension, capillary rise etc.

The surface tension of liquids being an important property has been investigated by various workers. There are several methods of determining the value of the surface tension of liquids, the most important ones are (1) the rise in a capillary tube, (2) measurements of bubbles and drops by QUINCKE, MAGIE and WILBERFORCE, 3) determination by means of ripples (Lord RAYLEIGH Phil. Mag. XXX p. 386), (4) LENARD's (Wied. Ann. XXX p. 209) method of determination by oscillations of a spherical drop of liquid, (5) determination by the size of drops (RAYLEIGH Phil. Mog. **48**, p. 321) (6) WILHELMY's method of measuring the downward pull exerted by a liquid on a thin plate of glass or metal partly immersed in the liquid, (7) JAEGER's method of measuring the least pressure which will force bubbles of air from the narrow orifice of a capillary tube dipping into the liquid, (8) by measuring the pull required to drag a plate of known area away from the surface of a liquid etc.

Besides (γ) the surface tension, another constant is sometimes employed; it is called specific cohesion, and is usually denoted by a^2. The relation between a^2 and (γ) is expressed as follows: $a^2 = \frac{2\gamma}{d}$ = specific cohesion, where d = density of the liquid, whence since $(\gamma) = \frac{1}{2} r h d$ (where r = radius of the capillary tube, h = = rise in the tube), it is seen that the specific cohesion is measured by the height to which a liquid rises in a capillary tube of unit radius.

WALDEN [Zeit. Phys. Chem. **65**, 129, 257 (1908)] has recently found that specific cohesion may be applied in another way to estimate the degree of association of both liquids and solids. A comparison of the experimental data showed the relationship

$$\frac{T_\sigma}{a^2_\sigma} = \text{constant} = 17.9$$

where T_σ is the latent heat of vaporisation at a boiling point and a^2_σ, the specific cohesion at the same temperature. Combining this expression with TROUTON's rule, we see that the molecular cohesion of a liquid at its boiling point is proportional to the boiling temperature expressed on the absolute scale. This relation holds only for non-associated liquids.

Moreover WALDEN points out that if substances are in corresponding states at their melting points, there would be a similar relation between the latent heat of fusion and the specific cohesion at the melting point.

The specific cohesion of fused metals and salts has been investigated by QUINCKE in a very thorough manner. The measurements were obtained from the weight of falling drops of a liquid, or from the curvature of flat drops of the solidified material.

It was found (Pogg. Ann. **135**, 643, 1868) that all salts and metals and some organic substances near their melting points have specific cohesions which are simple multiples of the constant number 4.3. For various reasons it seems clear that these relations are only apparent. In the first place, the divergence from the constant is in many cases considerable.

Moreover there are errors of experiment [cf. Meyer. Wied. Ann. **54**, 415 (1895); Lohnstein. ibid. **54**, 722 (1895) etc]. Under the stress of criticism (ibid, **53**, 1070 (1894), **61**, 267 (1897)), Quincke somewhat modified his views.

It has now been found out that the specific cohesion of elements is a periodic function of their atomic weights.

The following data are collected from the works of various investi-

Name of elements.	Specific Cohesion.
Sb	7.635
Pb	8.339
Br	3.895
Cd	16.84
F	25.81
K	85.74
Cu	14.44
Na	52.97
Pd	25.26
P	4.475
Pt	17.88
Hg	8.234
S	4.28
Se	3.42
Ag	15.94
Bi	8.019
Zn	24.05
Sn	16.75
Cl	4.176
O	3.018
N	2.541

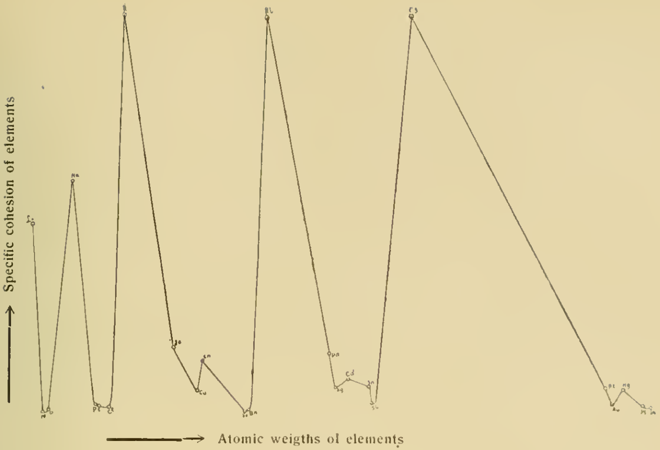

Fig. 1.

gators using the previously described methods. By plotting the following data, well-defined periodic curves are obtained.

From the curve it is seen that the alkali metals lie on the top most points, whilst Zn,Cd and Hg lie on a straight line on the descending portion of the curve. P,As,Sb, and Bi occupy similar positions in the minima.

Temperature coefficient of electric conductivity of elements.

The reciprocal of the resistance of a conductor is called its conductivity. Thus if S is the conductivity of a wire, Ohm's law is expressed by $C = SE$. In the same way the specific conductivity is the reciprocal of the specific resistance and is connected with the conductivity by the relation $S = ms/l$, where l is the length and s the cross section; the conductivity is directly proportional to the cross section and inversely proportional to the length.

In the case of pure metals the specific conductivity always decreases with increase of temperature. Dewar and Fleming have shown that at absolute zero the resistance of all pure metals approximates to zero. As a result it has been found that if R_t is the resistance of a platinum wire at the temperature t° C. on the air thermometer and R_0 is the resistance at a temperature of 0° C., then the connection between these quantities can be expressed by an equation of the form

$$R_t/R_0 = 1 + \alpha t + \beta t^2.$$

In the expression α and β are constants which vary very slightly from one specimen of wire to another. The value of these constants is determined by measuring the resistance of the wire at three known temperatures. Just as KOHLRAUSCH has shown that the effect of temperature on the conductivity of a solution is very nearly linear, so over comparatively small ranges of temperature the increase of resistance of pure metals is very nearly proportional to the increase in temperature. Hence if R_0 is the resistance at a standard temperature, say 0° C. and R_t the resistance at a temperature t, then we may express the relation between R_0 and R_t by an expression of the form $R_t = R_0(1 + \alpha t)$, where $\alpha = 0.00366$. There are distinct variations in the value of α from one element to another.

It has now been observed that the temperature coefficient of electric conductivity of elements is distinctly a periodic property of the elements.

By plotting the values of the temperature coefficients given in LANDOLT and BÖRNSTEIN's tables well marked periodic curves are obtained.

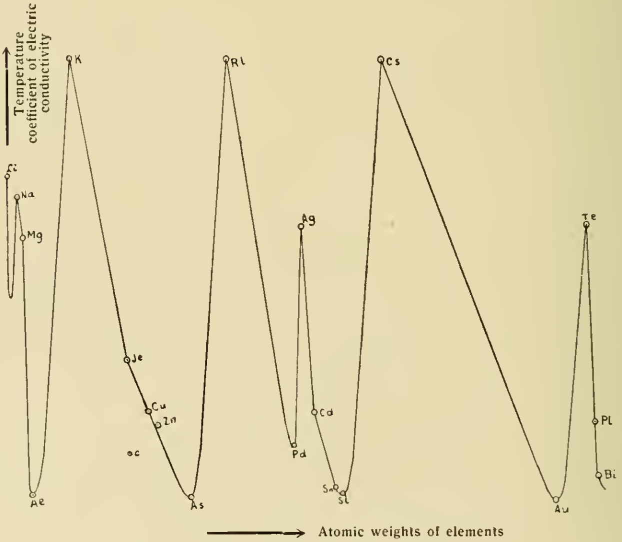

Fig. 2.

Elements of the same group lie very nearly on a straight line and occupy similar positions on the curve.

This curve resembles the one that is obtained by plotting the temperature coefficient of ionic mobility of elements (cf. DHAR loc. cit.).

Temperature coefficient of conductivity of heat.

The change of thermal conduction with temperature was noticed by **Forbes** [Phil. Trans. Roy. Soc. Edin. Vol. **33** (1862), p. 133]. Generally there is a decrease of conductivity with increase of temperatnre and as a similar decrease takes place in the electric conductivity of metals, it was supposed by **Forbes** that in general the thermal conductivities of metals like their electric, diminished with rise of temperature.

Wiedemann and **Franz** [Pogg. Ann. **89**, (1853), 497] appeared to show that there is some connection between conducting power for heat and for electricity.

For the metals were found not only to follow the same order for the two conductivities, but in many cases the numbers bore nearly the same ratio to each other.

More recent work has confirmed this supposition. The following are some of the values for metals of the ratio of the thermal conductivity and the electrical conductivity or k/c at 18° C. as determined by **Jaeger** and **Diesselhorst** [Phys. Tech. Reichsanstalt Wiss. Abh. 3, (1900)], together with the themperature coefficient of the ratio.

	$10^{-10}\frac{K}{c}$	Temp. coeff.
Cu	6.65	0.0039
Ag	6.86	0.0037
Au	7.09	0.0037
Zn	6.72	0.0038
Cd	7.06	0.0037
Pb	7.15	0.0040
Sn	7.35	0.0034

The electron theory of conduction for heat and for electricity gives an explanation of the connection between the two quantities.

According to that theory the ratio should be proportional to the absolute temperatnre i. e. should have a temp. coeff. 0.00367 and at 0° C., its value should be $6.3 \cdot 10^{10}$. The temperature coefficient of heat conductivity has been determined by **Lorenz** [Wied. Ann. **13**, 422, 582 (1881)], **Stewart** [Proc. Roy. Soc. **53**, 151 (1893), **Lees** (Phil. Trans. A. **183**, 481 (1892)] etc.

But the data of only a few elements are available, so it is impossible to obtain a curve with the insufficient data, which at present we can have. It has already been found that the conductivity of heat and electricity is a periodic function of the atomic weights of elements and now it is seen that the temperature coefficient of electric conductivity of metals is also a periodic function of the atomic weights and as the two properties, as has been already observed, are very much related, it seems very probable that the temperature coefficient of the conductivity of heat of elements would also be a periodic function of their atomic weights.

Torsional rigidity, Young's *modulus and their temperature coefficients.*

The following table is obtained from Landolt und Börnstein's Tabellen. E represents the Young's modulus, Δ_1 its temperature coefficient. T indicates the values of torsional rigidity and Δ_2 its temperature coefficient.

Metals	E	Δ_1	T	Δ_2
Al	6570	21.3	2580	24.7
Pb	1493	—	550	78.7
Cd	7070	—	2450	46.7
Cs	—	—	—	180
Fe	18347	2.25	7337	3.04
Au	7580	—	2850	3.01
K	—	—	—	150
Cu	9897	3.63	3967	4.49
Li	—	—	—	120
Mg	4260	—	1710	30 2
Na	—	—	—	130
Ni	20300	2.46	7820	3.28
Pd	11284	1.98	4613	2.7
Pt	16029	0.73	6594	1.78
Rb	—	—	—	170
Ag	7790	7.65	2960	8.21
Bi	3190	—	1240	—
Zn	10300	—	3880	—
Sn	5410	—	1730	82

From the above table it is seen that in these properties also there are distinct indications of periodicity. The transitional elements Fe and Ni have practically equal values for these properties.

As the atomic weight of elements in the same periodic group increases the value for Young's modulus and torsional rigidity decreases. In the sub group *B* of the first group of periodic classification (Cu, Ag, Au), gold having the highest atomic weight has the smallest values for Young's modulus and torsional rigidity. Similar are the behaviours of zinc, cadmium, tin and lead.

Sufficient data are available in the case of the temperature coefficient of torsional rigidity and hence distinct periodic curves are obtained; the alkali metals, Li, K, Na, Rb and Cs lie on the topmost points whilst copper, silver and gold lie on a straight line on the minima.

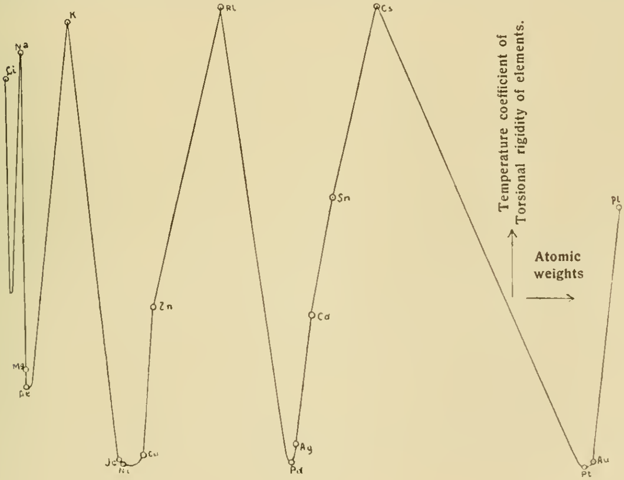

Fig. 3.

Specific heat. During recent years the determination of specific heats of substances at low temperatures was attracting the attention of numerous investigators.

Richards and Jackson (Zeit. Phys. Chem. 1910. **70, 414**) have carefully determined the specific heats of various elements between — 188° and + 20°. From their experimental data, they come to the conclusion that the atomic heats of various elements between the above range of temperature conform approximately to Dulong and Petit's law, the value of the constant being 5.3. *There are* *certain deviations and these show distinct periodicity, the general tendency being towards increasing atomic heat with increasing atomic weight.*

Schimpf (Zeit. Phys. Chem. 1910. **71,** 257) has determined the specific heats of many elements at various temperatures (e.g. —150°, —100°, —50° etc.).

From his work he concludes that the atomic heats diverge in a marked way as the temperature falls, whilst conversely a rise of temperature produces, as is well known, a marked convergence towards a fixed value for all elements.

Evidently, it is seen from the above investigations, that there are distinct indications showing the period nature of atomic heats at low temperatures.

Very recently a decided advance in this direction was made by Dewar [Proc. Roy. Soc. A. Vol. 89 p. 158 (1913)]. He determined the specific heats of 53 elements between the boiling points of liquid nitrogen and hydrogen at about 50° absolute.

When the atomic heats are plotted in terms of their atomic weights they reveal definitely a periodic variation resembling generally the well-known Lothar Meyer atomic volume curve.

The author concludes that if experiments were similarly made between the boiling points of hydrogen and helium then in all probability the atomic heats would be all very small and nearly constant.

However interesting these results may be there is a great difficulty in these investigations. The temperature range is very high with these workers. In the case of Richards of Jackson's experiments it was about 200° and in the case of Dewar's it was 57°.5.

From these works only the mean specific heat between so large a range of temperature is available and not the specific heats at a fixed temperature. Since there is a marked variation of specific heats with temperature, the results obtained in experiments carried on with large range of temperature lose much of their significance.

Nernst and his pupils have determined the specific heats at low temperatures (Jour. de Phys. tome IX. 1910, p. 721); E. H. Griffiths and E. Griffiths have also attacked the same problem (Phil. Trans. 1913 A **213,** 119.). These experiments are advantageous, since the temperature range is very small. In Nernst's experiments it is only 2°.7 C. It is well known that the atomic heats of elements can be calculated from Einstein's formula

$$C = 3\,R\,\frac{e^{-\frac{a}{T}\left(\frac{a}{T}\right)^2}}{\left(e^{-\frac{a}{T}}-1\right)^2} + b\,T^{\frac{3}{2}}$$

where R is a gas constant, equal to 1.98 gram calories, for Pb $a = 58$, $b = 7.8 \times 10^{-5}$.

In the following tables (see p. 431) the values of atomic heats of lead and silver at various temperatures are recorded.

Lead (atomic heat).

Absolute temp.	Nernst's observed value	Calc. from Einstein	Calc. from Griffiths
62°	5.63	5.58	5.62
66°	5.68	5.63	5.64
79°	5.69	5.75	5.68

Dewar's value at about 50° abs. = 4.96

Silver (atomic heat).

64°	3.72	3.61	—
84°	4.43	4.44	—
86°	4.40	4.50	—

Dewar's value at 50° abs. = 2.62.

Though Nernst's, Einstein's and Griffiths' values agree with each other, Dewar's values are divergent owing to a large range of temperature.

Griffiths and Griffiths have calculated the following values of the atomic heats at —273° C., Al = 3.54, Fe = 0.73; Cu = 4.73, Zn = 4.294, Ag = 5.378, Cd = 4.95, Sn = 4.997, Pb = 4.527.

These figures also do not agree with the statement of Dewar that atomic heats of elements between the boiling points of liquid hydrogen and helium would be all very small and nearly constant. Evidently Dewar's data show the mean atomic heat between his experimental range of temperature.

Since the product of atomic weight and specific heat at the ordinary temperature is very nearly constant, if we plot the atomic heats at the ordinary temperature against the atomic weights, we shall get a straight line parallel to the axis representing the atomic weights. On the other hand by plotting the specific heats of elements at the ordinary temperature against their atomic weights, very nearly a rectangular hyperbola is obtained, since the product of specific heat and atomic weight is constant.

This non-periodic curve is quite unique amongst the physical properties of the elements, since almost all important physical properties are periodic functions of their atomic weights.

By plotting Dewars's values of specific heat at about 50° absolute, we get a distinct periodic curve; evidently at about 50° absolute,

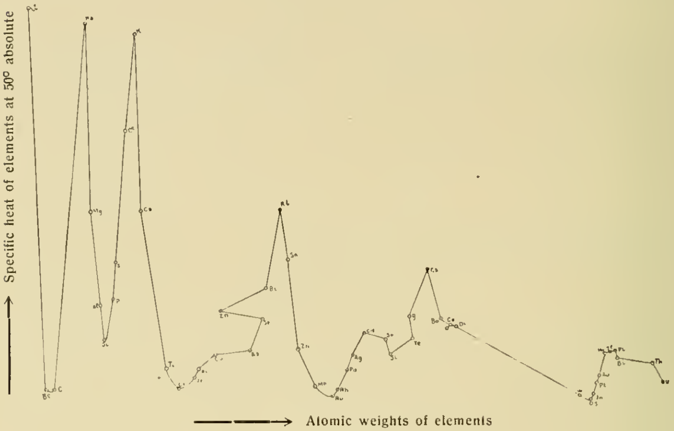

Fig. 4.

specific heat, like other physical properties of elements, is a periodic function of the atomic weight of the elements. The alkali metals, lithium, sodium, potassium, rubidium, caesium etc. lie on a straight line at the top of the curve. The halogen elements lie on a straight line on the ascending portion of the curve near the alkali metals, on the descending portion nearing the alkali metals lie Mg, Ca, Sr etc. S, Se and Te may be connected by a straight line. So also Zn, Cd and Hg. The platinum metals, (Osmium, iridium, platinum, ruthenium, rhodium, and palladium) lie on the minima of the curves.

Coefficient of linear expansion. The researches of Fizeau show that the volatile elements occurring in the ascending curve possess, almost without exception, a larger coefficient of expansion by heat between 0° and 100° than the not easily fusible elements occupying the minimum of Lothar Meyer's curve.

Similar vague suggestions are collected in Lothar Meyer's "Theories of Chemistry" Eng. Trans. p. 131 from the works of Carnelly (Journ. Chem. Soc. 1879, 565); Wiebe (Ber. 1878, 2289; 1880, 1258); Raoul Pictet (Compt. rend. 1879 LXXXVIII, 855) on the relations between melting point, expansion etc. But no definite statement of the periodicity of coefficient of linear expansion of elements with their atomic weights is available.

Grüneisen [Ann. Phys. 1910 (IV), **33**, 33—64] has found that the observed expansion of metals by heat is, in general, in close agreement with that required by Thiesen's (Ber. Deut. Phys. Ges. 1908, **6**, 947) exponential formula $l_2 - l_1 = y\,(T_2^{1+e} - T_1^{1+e})$ and this agreement is particularly good at low temperatures. The experimental given e is a periodic function of the atomic weight of the metal and that its maximum values are reached when the atomic volumes are at their respective minima. It has now been found out that the coefficient of linear expansion of elements is also a periodic property.

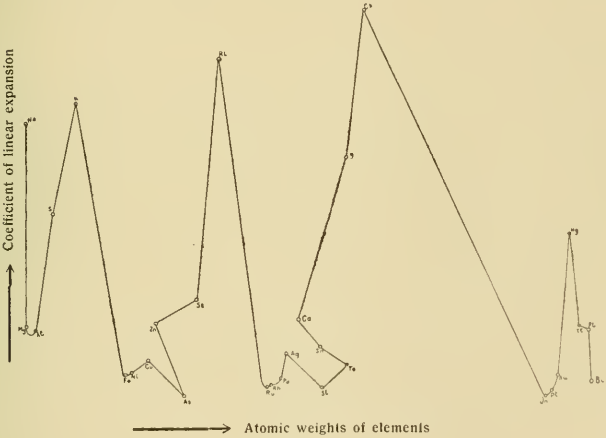

Fig. 5.

By plotting the values given in Landolt und Börnstein's Tabellen well defined periodic curves are obtained. The alkali metals lie on the topmost points, whilst S, Se and Te lie on a straight line on the ascending portions of the curve.

Cu, Ag and Gold, as well as As, Sb and Bi occur in similar positions in the minima.

Molecular Magnetic Rotation.

If we imagine a layer of unit length of any substance placed in a magnetic field of unit intensity and traversed by a beam of homogeneous plane polarised light in the direction of the lines of force of the field, then the rotation which the plane of polarisation undergoes at a known temperature is the absolute magnetic rotation of the substance.

Generally we do not require the absolute value and the relative value with reference to a standard substance is sufficient.

Perkin, the veteran worker in this line, chose water as the standard substance.

Hence denoting the specific rotation by r we have the expression, $r = \frac{a}{a}$, where a is the rotation of the given substance $\therefore$ M (molecular magnetic rotation) $= \frac{a\,\delta\,m}{a\,d\,\mu}$, where m and d are respectively the molecular weight and density of the substance and μ and δ the corresponding values for the standard (since in Perkin's work, tubes of equal length were always used).

The magnetic rotation of the plane of polarised light is measured in the same way as the permanent rotation of a substance, but the apparatus is more complex, since an arrangement for placing the substance in a magnetic field is provided. The tube containing the liquid is placed either between the poles or as in Perkin's latest form of apparatus in the hollow cone of a powerful electromagnet. The chief precaution to be observed in addition to those of an ordinary polarimetric determination, is in preserving a constant strength of the magnetic field.

The rotations of the standard and of the substance are measured in the same tube under identical conditions of temperature and magnetic intensity [Perkin, Trans. chem. Soc. 421 (1884); **69** 1025 (1896); **89**, 605 (1906)].

From an exhaustive study of organic compounds, Perkin has shown that the addition of CH_2 causes an approximately constant increase in molecular rotation and this increase is very nearly the same in different classes of compounds. Perkin has calculated the average value for CH_2 from a wider range of material and he found that $CH_2 = 1.023$.

If there are n CH_2 groups in a compound whose molecular rotation is M, then the expression $M - n\ (1.023) = S$ represents the rotatory effect of the remainder of the molecule. In a large number of organic compounds it is seen that S is approximately constant for all the higher members of a given series. Thus S is called the series constant. The series constant 0.508 of the normal paraffins $C_n\ H_{2n+2}$ is obtained by subtracting the value of n CH_2 from the rotation of any member of the series. This residue must represent the value for 2 H, since $\mathrm{Cn}\,H_{2n+2} - n\,\mathrm{CH}_2 = 2\,H$. Hence we may write $2\,H = 0.508$ or the value of hydrogen as 0.254. Then again, it is known that $CH_2 = 1.023$, whence by deducting the value of 2 H we may obtain the value for carbon = 0.515. Again, when hydrogen is removed from a compound and replaced by chlorine, there is an increase in rotatory power of 1.480; hence the value for chlorine may be assumed to be 1.480 + 0.254 = 1.734. Similarly, bromine and iodine may be calculated to be equivalent to 3.562 and 7.757 respectively.

It has been found out that molecular magnetic rotation of elements is also a periodic function of their atomic weights.

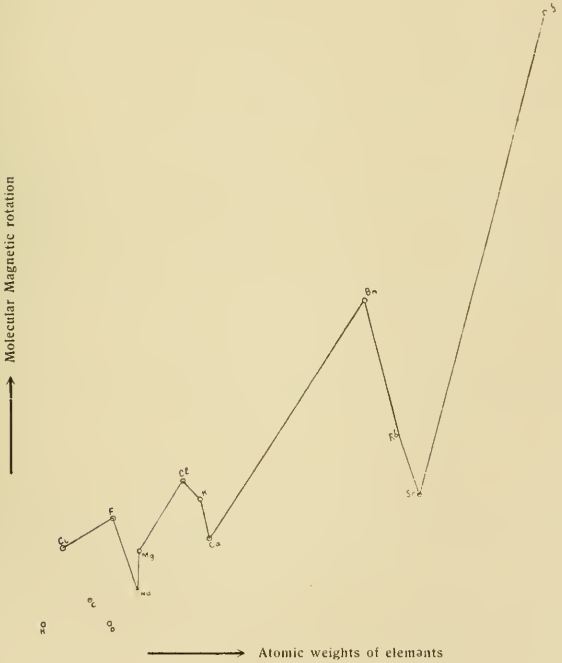

Fig. 6.

The curve is obtained from the following data (see table p. 436) collected from the works of different investigators.

Magnetic rotatory power.

Name of element	Observed by	
	Perkin	Humburg
H	0.254	—
C (in Ketones)	0.850	—
O (in OH)	0.191	—
Br	3.562	3.563
Cl	1.734	1.675
I	7.757	—
N	0.717	—
Na	0.558	—
K	1.535	—
Li	1.124	—
Ca	2.143	—
Mg	2.029	—

Distinct periodic curves are obtained. The halogen elements occupy the topmost points.

Physico-Chemical Laboratory, Presidency College, Calcutta.

Physics. — "Fresnel's *coefficient for light of different colours.*" (Second part). By Prof. P. Zeeman.

(Communicated in the meeting of May 29, 1915.)

A first series of experiments was made with yellow, green, and violet (4358) mercury light. As Fresnel's coefficient changes only slowly with the wavelength, such a high homogeneity of the incident light is unnecessary. With regard to the intensity of the light it is even recommendable to work with a limited part of a continuous spectrum. In a second series of experiments I therefore analysed the light of an electric arc (12 Amp.) with a spectroscope of constant deviation, which I had arranged as a monochromator by taking away the eye-piece and replacing it by a slit. The monochromator had been calibrated with mercury and helium lines. The prism stood on a table, which could be turned by means of a screw. Each reading on the scale attached to this screw gave the *mean* wavelength of the light used with an accuracy of a few Ångstrom-units. By repeating the calibration during the experiments it was proved, that this mean wavelength could always be reproduced with the above mentioned accuracy. This now is more than sufficient, as for instance in the green part of the spectrum a change of $\lambda = 5400$ into $\lambda = 5500$ and at the greatest possible velocity of the water the shift of the interference fringes becomes 0.660 instead of 0.675 of the distance between two fringes. Even a change of 10 Å.U. in the wavelength of the light used corresponds to 0,0015 only of the distance between the interference fringes, while the probable error of the final result is of the order of magnitude of 0.005.

In order to determine the place of the interference fringes I used two or rather three different methods and in a few experiments only eye observations were made. In one series of experiments a wire-net, which could be turned and shifted was adjusted in the focal plane s (see Fig. 1)[1]. In the focal plane of the telescope f we took photos of the interference fringes, while care was taken that one wire was parallel to the fringes and that the other passed through the middle of the field.

An advantage of this method is, that the interchanging of the photographic plates in the focal plane of f does not disturb the relative position of the interference fringes and the wires. With this method however it is rather difficult to adjust the wire-net accurately as it is so far away from the observer. Moreover the net must be very fine because of the strong magnifying power of the telescope. On the proposal of Prof. Wood I used in a second method Rowland's artifice[2]) for the comparison of spectra. Rowland puts in front of the photographic plate a brass plate with longitudinal aperture of the same width as the thickness of the plate, which could turn round a horizontal axis in front of the photographic plate. The rotation could easily be limited to an angle of 90°. By means of two fine quartz wires adjusted perpendicular to the plane of the brass plate the position of the plate could be measured accurately and corrected if necessary.

Two photos taken by this method are reproduced in the Plate (Fig. 4 and 5). The outer system of interference fringes has been obtained while the water was streaming in one direction; the inner system corresponds to a current in the opposite direction.

Fig. 5 shows also the shadow of the fine quartz wires.

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[1]) See the first part.

[2]) Ames, Phil Mag. (5) **27**, 369. 1889.

Though this method gives a clear survey of the shift of the interference fringes and e. g. shows immediately, that the shift for red light (Fig. 4) differs from that for violet (Fig. 5), it is not very fit to obtain quantitative results. By a detailed investigation I found, that the uncertainty of the measurements was greater than I had expected from eye observations. A disadvantage of this method is first, that for the measurement of the negative we must once point on an interference fringe and then on the two pieces of a broken fringe. For spectral lines this does not matter much, but the difficulty becomes greater for the more hazy interference fringes. It is however an essential disadvantage of this method that pointings cannot be made on corresponding points of the interference fringes.

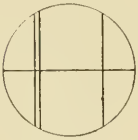

Fig. 4.

Quite satisfying results I got with the third method, concerning which I shall give some details. In the focal plane of the telescope a system of wires as is shown in fig. 4 was adjusted. There are three vertical wires (and one horizontal wire), so that we can always choose the best one as a fixed mark and read along the horizontal wire. It is very improbable that the three wires are all badly situated with respect to the interference fringes. Just behind the cross wires the photographic plate is adjusted on *a plate-holder which is mounted independently of the telescope with the cross wires.* The photographic plate can be brought in the right position and slidden to take successive photos without touching the telescope. Examples of the obtained photos are reproduced on the Plate (Fig. 1*a*—3*b*), 4 or 5 times enlarged. The photos 1*a* and 1*b*, 2*a* and 2*b* etc. belong together. Comparing two such photos the shift of the interference fringes is evident. The displacement is also given on the Plate in parts of the distance between two fringes. As mentioned above the measurement was made along the horizontal wire.

The width of the interference fringes can be chosen according to the circumstances. p gives the pressure of the water in kilograms per cm², measured during the streaming of the water with a manometer coupled to the main tube, just before it divides into two less wide ones. The times of exposition for the making of the negatives amounted between 3 and 5 minutes. It therefore sufficed to read the pressure of the water each 30 seconds. The mean of these readings was taken as the pressure during the measurement. The variations in the pressure most times amounted only to some hundredth parts of a kilogram. If by accident (what happened very seldom) the variation in pressure was greater, the corresponding measurement was not used.

If $2l$ is the length of the whole water-column that is in motion, the double shift to be expected is

$$\frac{8l\left(1-\frac{1}{\mu^2}-\frac{\lambda}{\mu}\frac{d\mu}{d\lambda}\right)\mu^2}{c\,.\,\lambda}\,w_{\max}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

expressed in parts of the distance between two fringes, $w_{\max}$ is the axial velocity, while μ, λ, and c are respectively the index of refraction of the water, the wavelength of the light used, and c the velocity of light in vacuo.

For l has been taken 302,0 cm ; that is the distance between corresponding points of contact of the dotted lines with the axis in the head-pieces at the ends of the tube (see fig. 3). If the current in the tubes was governed by the laws of Poiseuille for viscous fluids, the maximum velocity would be equal to twice the mean velocity and the distribution of the velocities over the transverse section would be represented by a parabola. In our experiments however the velocity of the water was more uniform ; we are in the region of the turbulent motion. From the axis of the tube towards the side the velocity decreases much more slowly than in the case of a parabolic distribution and finally only decreases very rapidly. In the neighbourhood of the axis of the tube there is thus a considerable region, where the velocity may be regarded as being constant, at least more constant than in the case of a distribution of the velocities according to Poiseuille. From numerous and very careful researches of American engineers [1]) the ratio of the mean velocity to that along the axis of the tube has been deduced. The result was always found in the neighbourhood of 0,84, so that the mean velocity w_0 becomes $w_0 = 0{,}84\, w_{\max}$.

The mean velocity for a definite pressure was determined by measuring the quantity of the fluid that streamed out in a certain time or rather the time (about half an hour) necessary to let stream out 10 m^3. By the latter method the determination was independent of the excentricity of the scale division, which gives the volume of the water that has passed through the watermeter. For the pressures used between 1.95 and 2.40 kg/cm² it was proved, that

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[1]) Williams, Hubbel and Frenkell, Trans. Am. Soc. of Civ. Eng. Vol. **47**. 1902. Lawrence and Braunworth ibid. Vol. **57**. 1906.

Cf. also R. Biel. Heft 44 der Mitteilungen über Forschungsarbeiten herausgegeben v. Ver. deutsch. Ing. 1907.

the connection between the mean velocity (the volume) and the pressure could be represented by a parabolic curve. So it was possible to reduce observations at a pressure p to a standard pressure (for which 2,14 k.g. cm^2 was chosen) by multiplying the shift of the interference fringe, measured at the pressure p, by $\sqrt{\frac{2.14}{p}}$ or graphically by means of the curve.

Before relating the obtained results I shall give in extension an arbitrary example of one of the 32 determinations of the change of phase. The four cocks in Fig. 2*B* (first communication) will be called *A*, *B*, *C*, *D* respectively.

Photo n°. 154 wavelength 4580 Å.U.

Photo a.	*Photo b.*
B, *D* open; *A*, *C* shut.	*A*, *C* open; *B*, *D* shut.
Pressure on manometer.	Pressure on manometer.
2.12	2.15
2.14	2.14
2.14	2.15
2.17	2.18
2.18	2.17
2.18	2.16
2.16	2.18
Mean: 2.16	2.16

Mean pressure during the experiment 2.16 k.g./cm^2.

We have mentioned already that the given pressures refer to the times 0, 30″, 60″ etc.

Measurement of photo N°. 154 *a*. Readings with the Zeiss-comparator in m.m.

on the interference fringes.		on the fixed wire.
54.217	53.591	52.689
224	591	686
220	599	688
218	593	692
225	599	689
219	594	688
225	598	52.689
223	600	
Mean: 54.221	53.596	thus middle: 53.908
		52.689

Distance between the fringes $d_1 = 0.625$

Distance from the fixed wire 1.219

Measurement of photo N°. 154 *b.* Readings:

	on the interference fringes.		on the fixed wire.
	53.675	53.037	52.264
	675	041	263
	680	046	266
	681	045	262
	683	051	52.264
	680	046	
	686	046	
	683	044	
Mean:	53.680	53.044	Thus middle: 53.359
			52.264

Distance between the fringes $\Big\}$ $d_2 = 0.636$ Distance from the fixed wire $\Big\}$ 1.095

$$\text{Mean distance of the fringes} \left.\begin{matrix} 0.625 \\ 0.636 \end{matrix}\right\} 0.630$$

Shift of the fringes by the motion $1.219 - 1.095 = 0.124$ or reckoned in the right direction $0.630 - 0.124 = 0.506$.

Thus shift in parts of the fringe distance

$$\Delta = \frac{506}{630} = 0.803 \text{ for } p = 2.16 \text{ k.g./cm}^2.$$

thus $\Delta = 0.799$ for $p = 2.14$ k.g./cm².

The obtained results may be summarized in a table.

Shift of the interference fringes by reversing the direction of the current.

$p = 2.14$ k.g./cm². $w_0 = 465$ cm/sec. $w_{max} = 553.6$ cm/sec.

λ in A°.	Δ_{Fr}	Δ_L	$\Delta_{exp.}$	Number of experiments
4500	0.786	0.825	0.826 ± 0.007	6
4580	0.771	0.808	0.808 ± 0.005	6
5461	0.637	0.660	0.656 ± 0.005	9
6440	0.534	0.551	0.542	1
6870	0.500	0.513	0.511 ± 0.007	10

Under Δ_{Fr} and Δ_L are given the shifts calculated with the formula with Fresnel's coefficient without the term of dispersion for the value $w_{max} = 553.6$ cm/sec. belonging to $p = 2.14$. Under Δ_{exp} are found the observed shifts with the probable error in the final reading. The number of experiments is given in the last column.

For the reading at λ 6443 no probable error is given as only one reading was made for that colour. The agreement of the experiments with the formula of **Lorentz** is evident.

In Fig. 5 I have represented graphically the results obtained. For λ 4500 and λ 4580 the theoretically and experimentally determined points coincide. Perhaps it is interesting to give also the values of **Fresnel**'s coefficient ε:

λ in A°.	ε_{Fr}	ε_L	ε_{exp}
4500	0.443	0.464	0.465
4580	0.442	0.463	0.463
5461	0.439	0.454	0.451
6870	0.435	0.447	0.445

Here $\varepsilon_{Fr} = 1 - \frac{1}{\mu^2}$, $\varepsilon_L = 1 - \frac{1}{\mu^2} - \frac{\lambda}{\mu}\frac{d\mu}{d\lambda}$ and $\varepsilon_{exp.}$ is found from the numbers in the fourth column of the table concerning the shift of the interference fringes (under $\Delta_{exp.}$) by multiplication by $\frac{\lambda c}{8 l \mu^2 \cdot w_{max.}}$.

A few words may be said concerning the determination of the mean velocity $w_0 = 465$ cm/sec., $p = 214$ k.g./cm², which was important for the interpretation of our observations. We have mentioned already that there was a watermeter in the main tube. This meter (of the **Woltmann**-type) ran very regularly, so that no vibrations were transferred to the system of tubes. It was destined however for large quantities. Its errors were known in rough approximation only. If the meter was supposed to indicate accurately, we found taking into consideration the above mentioned precaution (see p. 401) concerning the reading at a complete rotation of the nands of the counting-piece, $w_0 = 475$ cm/sec, $p = 2.14$ k.g./sec. With this value I found a difference of about 2.1 % between the results of my experiments and the formula of **Lorentz**. In order to investigate, whether this difference might be ascribed to an error in the watermeter, I decided to put a more accurate measuring apparatus at the end of the system of tubes to control the first watermeter. With extreme kindness Mr. Ing. **Pennink**, Director of the Amsterdam waterworks put at my disposal a calibrated so-called "Ster" meter, which begins to indicate at a quantity of 10 L. per hour and which indicates accurately for 30 L. and more per hour. If this "Ster" meter was connected to the end of the system of tubes, while the principal cock was quite open, the mechanical vibrations of the systems would

P. ZEEMAN: "ON FRESNEL'S COEFFICIENT FOR LIGHT OF DIFFERENT COLOURS" (2nd PART.)

Current
first
direction.

1a $\lambda = 6870$ $p = 2.13$

2a $\lambda = 4580$ $p = 2.16$

3a $\lambda = 4580$ $p = 2.26$

Current
opposite
direction.

1b $\lambda = 6870$ $p = 2.13$

From a and b : $\Delta = 0.522$

2b $\lambda = 4580$ $p = 2.16$

$\Delta = 0.803$

3b $\lambda = 4580$ $p = 2.26$

$\Delta = 0.812$

4 $\lambda = 6870$ $p = 2.21$

$\Delta = 0.53$

5 $\lambda = 4500$ $p = 2.30$

$\Delta = 0.86$

HELIOTYPIE, VAN LEER AMSTERDAM

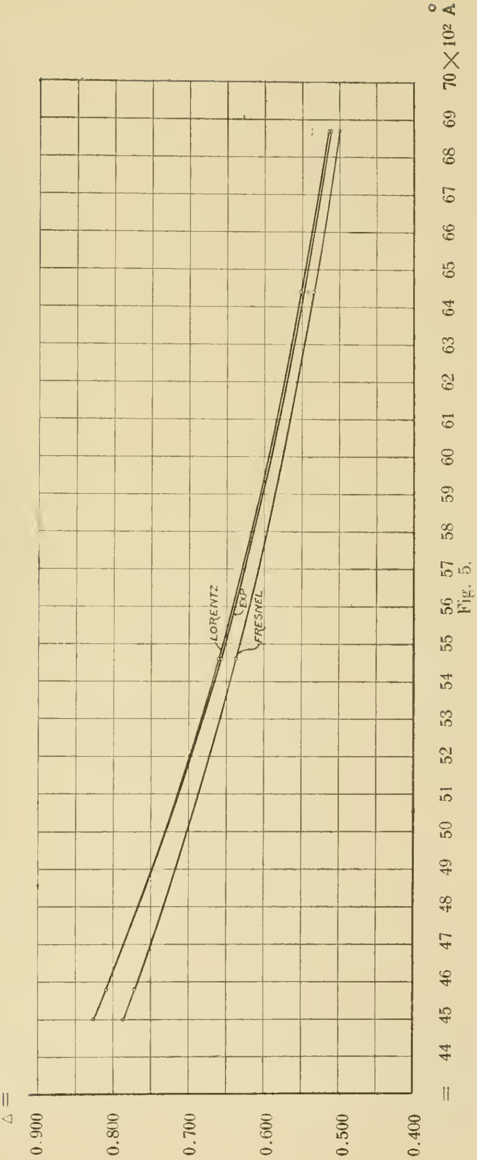
Δ =
0.900
0.800
0.700
0.600
0.500
0.400
= 44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70 × 10² Å
LORENTZ
EXP
FRESNEL

Fig. 5.

have been propagated from the "Stermeter" and have badly influenced the optical observations.

The only purpose however was to compare the indications of the two meters. By two independent, quite corresponding measurements on different days it was proved, that the large meter gave 10000 L., when the accurate "Ster" meter registrated 9810 L. only. This is a difference of 1.9°/₀. Now the error of the "Ster" meter itself is about 0.2°/₀ as had been determined by direct measurement of the volume transmitted to a large tank on the grounds of the waterworks. Altogether, taking the error of 0.2°/₀ with the right sign, the error in the indication of the large watermeter amounts to 2.1°/₀. We have seen already, that theory and experiment agree extremely well, if we introduce this correction, which reduces the values of w_0 from 475 c.m./sec. to 465 c.m./sec. for $p = 2.14$ k.g./c.m^2.

The value of w_0 at $p = 2.14$ K.g./c.m.^{2} may thus be regarded as well established and the same may be said of the value of t, at least within the limits of the accuracy of the final result. About the factor 0.84 however some doubt may exist. Therefore it seems to us interesting to show, that even if the *absolute* value of the LORENTZ dispersion-term might have been determined less accurately than has been the case, there might have been drawn a conclusion about the necessary existence of this term [1]). *This conclusion is independent of the values given to l and $w_{max.}$.*

For, writing down equation (4) for two different colours with the wavelengths λ_1 and λ_2 we see, that l, $w_{max.}$ and c fall out by the division. The ratio of the shifts $\triangle\lambda_1$ and $\triangle\lambda_2$ becomes then according to LORENTZ

$$\frac{\triangle\lambda_1}{\triangle\lambda_2} = \frac{\left(1 - \frac{1}{\mu_1^2} - \frac{\lambda_1}{\mu_1}\frac{d\mu_1}{d\lambda_1}\right)\frac{\mu_1^2}{\lambda_1}}{\left(1 - \frac{1}{\mu_2^2} - \frac{\lambda_2}{\mu_2}\frac{d\mu_2}{d\lambda_2}\right)\frac{\mu_2^2}{\lambda_2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and according to FRESNEL

---

[1]) I will still make one remark. If we wished to explain the difference of 5 °/₀ between our observations and the formula of FRESNEL by an error in the factor 0,84, we should have to change this factor into 0,88 in order to obtain coincidence of the experimental curve and that of FRESNEL. But such a great inaccuracy does by no means exist in that factor.

$$\frac{\Delta_{\lambda_1}}{\Delta_{\lambda_2}}=\frac{\left(1-\frac{1}{\mu^2_1}\right)\frac{\mu_1^2}{\lambda_1}}{\left(1-\frac{1}{\mu_2^2}\right)\frac{\mu_2^2}{\lambda_2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Taking $\lambda_1 = 4500$, $\lambda_2 = 6870$ we find from (6) $\frac{\Delta_{\lambda_1}}{\Delta_{\lambda_2}} = 1{,}572$, from (5) $\frac{\Delta_{\lambda_1}}{\Delta_{\lambda_2}} = 1{,}608$, whereas the experiment (Table p. 403) gives $\frac{\Delta_{\lambda_1}}{\Delta_{\lambda_2}} = 1{,}616$.

For $\lambda_1 = 4580$, $\lambda_2 = 6820$ the ratios become respectively 1,542, 1,575, 1,581.

So there is only a difference of 0,5 resp. 0,4 °/₀ between the formula of LORENTZ and the experiments, but a difference of 2,2 resp. 2,0 °/₀ between these and the formula of FRESNEL.[1]

Even if we had not succeeded in giving to l, w_{max} and the coefficient 0.84 very probable values, even then the result of our experiments had been very favourable to equation (5).

Further we must mention, that the light beam was limited by rings of tin-foil to a width of 11 m.m., whereas the glass plates allowed a beam of 18 m.m. diameter to pass along the axis, the horizontal tubes through which the water flows being of an inner diameter of 40 m.m. By this precaution the optically effective change of the velocity over the section of the tube is diminished and this is also the case with the broadening of the interference fringes caused by the curving of the wavefronts by inequality of the velocities in them.

Sometimes (not always) there is a small change in the distance between the interference fringes after reversing the direction of the water current. It is easily proved, that, neglecting quantities of the second order, we get a right result by dividing the mean value of the distance between the interference fringes before and after change of the current in the shift of the fringes.

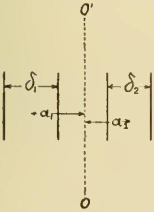

Fig. 6.

Let δ_1 and δ_2 be the distances between the fringes in the two cases and a_1 and a_2 the shifts of them from the original position OO'. From the measurements we find $\frac{a_1+a_2}{\delta_1+\delta_2}$ or rather the double of this. We want to know $\frac{a_1}{\delta_1}=\frac{a_2}{\delta_2}$. The difference between the first and the second expression gives the error we make. Let us put

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[1] Our conclusion is confirmed by a recent, more accurate series of observations. [Note to the translation].

$$d_1 = d - x$$
$$d_2 = d + x$$

where x represents a small quantity.

We calculate how much $\frac{a_1 + a_2}{2d} - \frac{a_1}{d - x}$ differs from zero.

It is easily found that $\frac{a_1 + a_2}{2d} - \frac{a_1}{d - x} = \frac{-a_1 x^2}{2d^3} = -\frac{a_1}{d} \cdot \frac{x^2}{2d^2}$, an error of the second order of magnitude.

In the example on p. 402 $\frac{x}{d}$ is equal to $\frac{1}{100}$, so that the change in the distance between the fringes might be still 4 or 5 times greater without making the error larger than 1 per thousand.

In the above cited paper [1]) JAUMANN derives on p. 462 with his theory for the FRESNEL-coefficient the formula $\frac{1}{2} \frac{n_0^2 - n^2}{n_0^2}$, where n_0 is the index of refraction for very long waves and n that for the colour considered.

For water $n_0^2 = 80.0$ and $n^2{}_{Na} = 1.78$, so that JAUMANN finds for the FRESNEL-coefficient of sodium light 0.488. This value does not agree with the result of our experiments and these are so accurate, that we may say with security, that the theory of JAUMANN is in conflict with reality. There is still another point of disagreement between experiment and this theory. The latter gives for decreasing wavelength a *decrease* of the FRESNEL-coefficient, while the experiments (see p. 404) prove the contrary.

Resuming we may say, that we have repeated FRESNEL's experiment with different colours and have proved the exactness of the FRESNEL coefficient $1 - \frac{1}{\mu^2} - \frac{\lambda}{\mu} \cdot \frac{d\mu}{d\lambda} = \varepsilon_L$ within the limits of the experimental errors. It is perhaps interesting to notice that the relative values of ε_L for different colours have also been confirmed by these experiments, because these relative values are independent of the effective length of the moving watercolumn and of the exact value of a numerical coefficient that was put equal to 0.84. So the measurements from which the absolute value of the FRESNEL-coefficient has been derived, might be considered as an experimental determination of the ratio $w_{\max} : w_0$. The FIZEAU-effect would from this point of view form the fixed theoretical base, as it is an effect of the first order, quite based on the ascertained fundamental equations of electrodynamics,

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[1]) See the first part of this paper.

Physics. — "*Isothermals of diatomic substances and their binary mixtures. XV. Vapour pressures of oxygen and critical point of oxygen and nitrogen*". By Prof. H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST. *Errata* to Communication N°. 145*b* from the Physical Laboratory at Leiden, Jan. 1914).

In the Proceedings of the Meeting of January 30, 1915 p. 952 table I is to be read:

TABLE I.

Vapour pressure of oxygen.

$\theta = T - T_{0^\circ C.}$	T in KELVIN degrees	p in atm.
— 154°.87 C.	118°.22 K.	9.096
149.25	123.84	12.506
138.95	134.14	21.328
138.92	134.17	21.342
135.96	137.13	24.528
130.64	142.45	30.914
125.28	147.81	38.571
121.34	151.75	45.138
121.33	151.76	45.142
121.31	151.78	45.217
120.02	153.07	47.258
118.88	154.21	49.640

p. 953 in table II:

TABLE II.

Critical point of oxygen.		
$\theta_k = -118^\circ.82$ C.	$T_k = 154^\circ.27$ K.	$p_k = 49.713$ atm.

(September 8, 1915).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday September 25, 1915.
Vol. XVIII.

President: Prof. H. A. Lorentz.
Secretary: Prof. P. Zeeman.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 25 September 1915, Dl. XXIV).

CONTENTS.

Physics. — *"On the passage of light through the slit of a spectroscope."* By Prof. P. ZEEMAN.

(Communicated in the meeting of June 26 1915).

Though the full resolving power of a spectroscope can be reached with an infinitely narrow slit only, we can get a near approach to it with a very narrow slit already.

This is evident, when with SCHUSTER [1]) we introduce the so-called "normal" width of the slit d defined by the relation $d = \frac{f\lambda}{4D}$, where f is the focal distance of the collimator objective with the diameter D and λ the wavelength of the incident light. For an exceedingly narrow slit the "purity" [2]) of the spectrum becomes equal to the resolving power. For normal width the purity is only 1,4 % below its maximum value. With a slit of twice the normal width we get about the double quantity of light, while the purity deviates 5,7 % only from the maximum value. More than four times the normal width of the slit must never be taken, for then the purity of the spectrum decreases rapidly, while even for an infinitely wide slit the intensity of the light never exceeds four times the value obtainable with normal width.

Resuming, we may conclude that for sufficiently intense sources of light a width of slit in the neighbourhood of $\frac{f\lambda}{4D}$ is the best. A narrower slit causes loss of light without gain in resolving power and a wider one already soon decreases the resolving power considerably. As example I choose a collimator with a lens, for which $D = 15$ cm., $f = 325$ cm., while λ may be 5×10^{-5} cm. Then we have $d = \frac{f\lambda}{4D} = 0{,}0027$ mm.

Some time ago [3]) I pointed out, that by very narrow slits the observation of the *polarized* components of magnetically resolved lines may be rendered very difficult. When gradually the slit was made narrower, the (electric) vibrations that are perpendicular to the length of the slit, are hardly transmitted at last.

It seems interesting to communicate some measurements concern-

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[1]) A. SCHUSTER The optics of the spectroscope Astrophys. Journ **21**, 197. 1905.

[2]) SCHUSTER. l.c. See also e g ZEEMAN. Researches in magneto-optics. p 7. London, Macmillan. 1913.

[3]) "On the polarisation impressed upon light by traversing the slit of a spectroscope and some errors resulting therefrom." These Proceedings p. 599. October 1912.

ing the width of slit necessary for the appearance of the mentioned polarisation phenomena. Then we can get an idea in how far we must expect disturbances caused by the narrowness of the slit.

With the arrangement shown in Fig. 1 the relative decrease in intensity of the horizontal vibrations may easily be measured.

Monochromatic green light falls upon a slit S, behind which a calcite rhomb K is placed at such a distance that two adjacent images of the slit are formed, one containing the vertical vibrations, the other the horizontal ones. By means of a nicol N the intensity of the two images may be made equal.

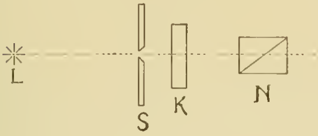

Fig. 1.

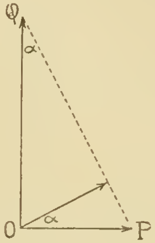

Fig. 2.

Let (fig. 2) OP and OQ be the directions of the vibrations in the two images. If the direction of vibration of the nicol is perpendicular to PQ, the condition for equal intensities of the two images will be tg. $\alpha = OP : OQ$. The ratio of the intensities of the horizontal and vertical vibrations is then given by tg.$^2\alpha$.

A first experiment was made with a slit (of platinoid) from a spectroscope with constant deviation of Hilger.

The results are contained in the following table:

green light

width of slit in m.m.	tang. α
0.010	1
0.004	0.5
0.002	0.3
0.001	0.2

The value of the width of the slit for $tang.\, \alpha = 1$ is that for which the first extinction of the horizontal vibrations becomes perceptible.

A second series of observations has been made with a slit (also of platinoid) belonging to the collimator of an echelon spectroscope and for two different colours.

red light		*green light*	
width in m.m.	tang. α	width in m.m.	tang. α
0.0017	1	0.0015	1
0.0015	0.7	0.0013	0.6
0.0013	0.5	0.0010	0.5
0.0010	0.3	0.0007	0.3
0.0005	0	0.0004	0

Interesting is the difference in absolute width at which for the two slits the same phenomena occur. For, though the measurements may not claim great accuracy, yet the different behaviour in the two cases seems to be beyond doubt. Very probably the form of the edges of the slit is here of much importance. The variation with wavelength has the direction we should expect.

We also made some experiments with white light. When the slit is gradually narrowed the image formed by the horizontal vibrations becomes fainter and at the same time of bluish hue.

So we come to the result that with widths of slit often used with spectroscopes in laboratories, polarisation phenomena are already of some importance. The greater the ratio $\frac{fk}{D}$ is taken, the less these appearances will be noticed. So with the 75 feet spectrograph of the Mount Wilson Solar observatory we surely shall not see anything of the mentioned polarisation phenomena.

Recently a problem connected with the passage of light through a narrow slit has been treated theoretically by RAYLEIGH in a paper: "On the Passage of waves through fine slits in thin opaque screens" [1]). But as is observed by RAYLEIGH: "It may be well to emphasize that the calculations of this paper relate to an aperture in an infi-

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[1]) RAYLEIGH. Proc. R. S. London. Vol **89**. 194. 1914.

nitely thin perfectly conducting screen. We could scarcely be sure beforehand that the conditions are sufficiently satisfied even by a scratch upon a silver deposit. The case of an ordinary spectroscope slit is quite different. It seems that here the polarisation observed with the finest practicable slits corresponds to that from the less fine scratches on silver deposits".

With the last words RAYLEIGH refers to an observation by FIZEAU, who on scratching in a silver layer on glass perceived that the transmitted light was polarized perpendicularly to the direction of the scratch, if the width of the latter was $\frac{1}{1000}$ mm. If this width however was estimated at $\frac{1}{10000}$ mm. the polarisation was in the direction of the scratch, viz. the electric vibrations were chiefly perpendicular to it. With spectroscope slits the latter case does not occur.

It will be remembered that DU BOIS and RUBENS[1]) found with a wire grating a point of inversion for ultra-red light, just as FIZEAU observed with scratches.

Geology. — "*On the occurrence of nodules of manganese in mesozoic deep-sea deposits from Borneo, Timor, and Rotti, their significance and mode of formation*". By Prof. G. A. F. MOLENGRAAFF.

(Communicated in the meeting of January 30, 1915).

The question whether deep-sea deposits, and more especially oceanic abysmal deposits, of earlier geological ages, take part in more or less appreciable degree in the formation of the existing continental masses, may be considered of prime importance for the solution of several geological problems. If answered in the affirmative, the conclusion at once follows that movements of the earth's crust must have taken place of an amplitude, sufficiently great, to bring deposits formed at a depth of 5000 metres or more, above the surface of the sea.

Some twenty years ago the opinion prevailed, that true abysmal deposits of former geological ages, had nowhere been proved, with certainty, to exist in the continental areas. It must be admitted that at that time, descriptions of occurrences of such abysmal deposits were scanty and far from convincing. This may have been partly caused by the fact, that fossil deep-sea deposits are not conspicuous

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[1]) H. DU BOIS and H. RUBENS. Ber. Berl. Akademie 1129. 1892.

as such, and that the organisms they contain, being only clearly visible with the aid of a strong pocket lens, or a microscope, are easily overlooked.

At all events, MURRAY and RENARD, in their classical treatise on recent deep-sea deposits, were very sceptical with regard to the question whether these play a role of any importance in the structure of the continents, as can clearly be proved by the following quotations: "With some doubtful exceptions it has been impossible to recognise in the rocks of the continents formations identical with these (i. e. the recent) pelagic deposits", [1]) and "It seems doubtful if the deposits of the abysmal areas have in the past taken any part in the formation of the existing continental masses". [2])

Later, it must be admitted, strong proofs have been given [3]) of the deep-sea character of certain red shales with radiolaria, and certain cherts and hornstones with radiolaria, the former being the fossil equivalents of the recent red clay, the latter, the typical radiolarites, being the fossil equivalents of the recent radiolarian ooze. And it also has been pointed out that their occurrences in the continents, must be found strictly limited to folded mountain ranges of recent and earlier ages i. e. to the movable or geosynclinal areas of the earth's crust[4]) and cannot be expected to occur in the original stable or continental masses i. e. the "aires continentales" in the sense of HAUG. Although it has thus been distinctly proved that the occurrences of deep-sea deposits of earlier ages in the continental masses cannot be regarded as "some doubtful exceptions" yet, as is clearly reflected in the most modern handbooks of geology, the doubt regarding their importance has not yet been dispelled.

One of the most prominent American geologists recently in a study on the testimony of the deep-sea deposits [5]) strongly supports the view held by MURRAY and RENARD in 1891.

It is evident that in proportion to the strength of the arguments

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[1]) Report on the scientific results of the voyage of H. M. S. Challenger. J. MURRAY and A. F. RENARD. Deep-sea deposits, p 189, London 1891.

[2]) Ibidem, Introduction p. XXIX.

[3]) See i. a. G. A. F. MOLENGRAAFF. Geological explorations in Central Borneo p. 91 and again pp. 439—442. Leiden 1900 and G. STEINMANN. Geol. Beobachtungen in den Alpen. 2. Die SCHARDT'sche Ueberfaltungstheorie und die geologische Bedeutung der Tiefseeabsätze und der ophiolitischen Massengesteine. Berichte d naturfor. Ges. zu Freiburg XVI, p. 33, 1905.

[4]) G. A. F. MOLENGRAAFF. On oceanic deep-sea deposits of Central-Borneo. Proc. of the Royal Academy of Sciences, Amsterdam XII, p. 141. Amsterdam. 1909.

[5]) T C. CHAMBERLIN. Diastrophism and the formative processes. V. The testimony of the deep-sea deposits. Journal of Geology XXII p. 137, 1914.

afforded for the identity between *all* the characteristics of the rocks which are maintained to be the fossil equivalents of the recent deep-sea deposits and of those latter deposits themselves the probability must increase of this equivalency being generally accepted. Up to the present it must be admitted, notwithstanding the almost absolute similarity, which has been proved to exist between recent radiolarian ooze, and triassic and jurassic radiolarites from some Alpine localities, from Borneo, and some other islands in the East Indian archipelago, one *important and remarkable characteristic* of recent abysmal deposits, i.e. *the concentration of oxides of manganese* in nodules has hitherto never been observed in fossil deep-sea deposits forming part of continental areas [1]).

To what extent, and in which way manganese nodules are characteristic of abysmal deposits?

The accumulation of oxide of manganese or shortly of manganese in recent deep-sea deposits is very striking; almost without exception manganese [2]) is found in all deep-sea deposits. Concretions of manganese of various dimensions are especially abundant in true abysmal deposits, i. e. the red clay and the radiolarian ooze.

Murray [3]) in his latest book on deep-sea deposits remarks: "The oxydes of iron and manganese ... in certain abysmal regions of the ocean ... form concretions of larger or smaller size, which are among the most striking characteristics of the oceanic red clay."

The question arises, whether, and to what extent, nodules of manganese must be considered characteristic *exclusively* of abysmal deposits; do they occur in such deposits *only* or also elsewhere?

In the report of the Challenger-expedition, and in the memoir of Murray and Hjort [4]) quoted above it is reported that such nodules of manganese have been dredged from shallow depths, and that they have been found to occur there even in abundance, in some places,

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[1]) Philippi says about this while treating the probability of the occurrence of deep-sea deposits in former geological formations: "Auch sind meinens Wissens die für recente Tiefseeablagerungen so charakteristischen Manganknollen . . . . bisher noch aus keiner Formation bekannt geworden." E. Philippi. Ueber das Problem der Schichtung und über Schichtbildung am Boden der heutigen Meere. Zeitschr. d. deutschen geol. Ges. LX, p. 356, 1908.

[2]) T. Murray and A. F. Renard say: "Rarely can a large sample of any mud, clay or ooze be examined with care without traces of the oxides of this metal being discovered, either as coatings or minute grains."

[3]) J. Murray and J. Hjort. The depths of the ocean, p. 155, Londen 1912.

[4]) l.c. p. 157.

where volcanic material forms a large proportion of the constituents of the deposit on the bottom of the sea.

In the Kara-sea, highly ferruginous nodules of manganese have been brought to the surface from terrigenous muds, at a moderate depth by the Netherlands Arctic expedition in the years 1882/83.

During the Siboga-expedition, Weber, in the deep-sea basins of the Netherlands East-Indian archipelago, has found manganese nodules on one spot only between the islands of Letti and Timor, at a depth of 1224 metres, in mud containing a strong proportion of terrigenous material, being in no way a true pelagic deposit; manganese forming an incrustation on a fragment of dead coral, has moreover been observed in a sample dredged from a depth of 1633 metres, between the islands of Misol and Ceram. [1])

As to the fossil occurrences, I have found in Upper-Triassic deposits, on the eiland of Timor, roots of Crinoids which certainly did not grow on the bottom of an ocean of abysmal depth, heavily incrusstated with a coating of concretionary manganese.

Nodules and concretions of manganese therefore are not characteristic of abysmal deposits in this way, that from the occurrence of such concretions in a certain deposit, one would be justified in concluding that the deposit could be nothing else than an abysmal deposit and could only have been formed on the bottom of a very deep ocean. On the contrary, concretions of manganese have been formed on the bottom of all oceans in varying depths when the conditions for their formation were favourable.

Murray and Renard maintain — and I have no reason to diverge from this opinion — that these favourable conditions are afforded by the presence of basic volcanic material in an easily decomposable form. As soon as this condition is fulfilled the possibility is realized for the formation of concretions of manganese, but the chemical process of their growth is a very slow one, as has been amply proved by the researches of the Challenger-expedition. In shallow seas, especially at small distances from the mainland, sediments derived from land or from a planctonic and neritic fauna accumulate rapidly, so rapidly indeed, that there is only a remote chance of finding by dredging, concretions of manganese, which in the mud in odd places grow very slowly. In abysmal seas far from land very different conditions prevail, the rate of accumulation of sediment is an extremely slow one there, the afflux of terrigenous material is reduced almost to nil, whereas from the plankton only the siliceous

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[1]) Siboga-Expeditie I. M. Weber. Introduction et description de l'expédition, p. 81 and p. 137. Leiden 1902.

G. A. F. MOLENGRAAFF. "On the occurrence of nodules of manganese in mesozoic deep-sea deposits of Borneo, Timor and Rotti, their significance and their mode of formation."

Fig. 1. Manganese nodule in jurassic marl with chert-nodules and radiolaria from Sua Lain, Island of Rotti. Original size.

Fig. 2. Manganese nodule in triassic deep-sea deposits, in the vicinity of the mountain Somoholle, district Beboki, Island of Timor. Original size.

tests i. e. these of radiolaria and diatoms reach the bottom, the calcareous test being dissolved by the cold water of the deep seas with its high ratio of oxygenium and carbonic acid held in solution, before they reach the bottom. The growth of the concretions of manganese, however, is not hampered in these depths; on the contrary it even appears as if in abysmal depths in water of a temperature very near the freezing point and containing much oxygenium in solution, the conditions for the formation of concretions of oxydes of manganese, are more favourable than in shallow seas, provided that traces of volcanic material occur as a source of manganese from whence the manganese could have been derived. Thus, concretions of manganese, slow as they are in their process of formation, and inconspicuous as they are in sediments in places where the rate of accumulation is rapid, can become an important constituent where the rate of accumulation of a deposit is extremely slow, as is the case in the abysmal areas.

Consequently concretions of manganese are *in this manner characteristic of abysmal deposits that they may form an important percentage in proportion to other constituents exclusively in such deposits.*

And from this it is easy to conclude that concretions of manganese are characteristic of abysmal deposits in the same manner as the tests of radiolaria. The latter sink to the bottom of the ocean from the plankton everywhere within the limits of their geographical distribution, just as well near the mainland as far from the shore. Near the land these tests, owing to their minuteness, however, disappear being incorporated in enormous quantities of other chiefly terrigenous material which there comes to deposition; far from land, on the contrary, at the bottom of the very deep ocean-basins at depths over 5000 metres, where calcareous tests sinking down are dissolved before reaching the bottom of the ocean, these siliceous tests, small as is their individual mass, may form a great, sometimes a preponderating portion of whatsoever is deposited.

It is therefore quite justifiable to maintain, that radiolaria and concretions of manganese, form part of the most characteristic constituents of abysmal oceanic deposits, and further that nodules of manganese containing radiolaria almost with certainty must have been formed in the deeper portions of the ocean basins.

Localities where concretions of manganese have been found in deep-sea deposits of mesozoic age.

Concretions of manganese have been discovered by the geological expedition to the islands of the Timor group in 1910—1912 in triassic and jurassic deep-sea deposits, on the Island of Timor, and also well developed in similar jurassic deposits on the Island of Rotti, and previously, (in 1894, and later) I had noticed them in abysmal deposits of the precretaceous probably jurassic Danau formation, occurring in West and East Borneo.

Rock specimens were collected by the undermentioned observers, and their examination has afforded proof from which several deductions have been included in this paper.

a. In 1894 in Central Borneo by the author.

b. In 1898--1900 in the basin of the Mahakkam River by Prof. A. W. Nieuwenhuis.

c. In 1902 in the Long Keloh, a small branch of the Long Kelai, which is one of the great tributaries of the Berau-stream in East-Borneo, by Mr. van Maarseveen,

d. in 1911, on the island of Timor by the Netherlands Timor-expedition led by the author,

e. in 1911 and 1912, on the island of Rotti, by Dr. H. A. Brouwer, one of the members of the same expedition.

All the specimens collected with the exception only of these of Central-Borneo are stored in the geological museum of the Technical Highschool at Delft.

On the mode of occurrence of the manganese in the rocks.

In the rocks just mentioned the manganese has been concentrated in various ways:

1. *As grains*, i.e. minute concretions, frequently only recognisable as such under the microscope, occurring throughout the rock. This form of concentration is very common in red shales, which are the equivalent of recent red clays. These shales vary in colour from brick red to chocolate brown, they invariably include a noticeable proportion of silica, (in places a little lime) and, in varying quantities, tests of radiolaria. The characteristic red colouration is due to the presence of oxide of iron, and this tint deepens into chocolate brown in proportion to the increase in the percentage of manganese, entering into the composition of the rock.

This mode of accumulation is of almost general occurrence in all deep-sea deposits containing much clay ¹), but is of less import-

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¹) In modern deep-sea deposits the bulk of the manganese is just as well concentrated in small grains, causing the brownish red and chocolate brown colour of the deep sea silt, especially of the *red-clay* of the Pacific and the Indian Ocean. Compare J. Murray and A. F. Renard l. c. p. 191, p. 341 and Pl. XXII fig. 1.

ance, and may even be wanting in siliceous deposits, i.e. the cherts and hornstones, which are predominantly composed of tests of radiolaria.

I have observed manganese accumulated as grains in the following deep-sea rocks:

a. in red limeless siliceous clayshales with radioloria, probably of jurassic age, which are the prevailing rocks in the entire area of the Danau-formation of Central-Borneo, and in lesser quantities also in the cherts, jaspers and hornstones, which occur interstratified between the layers of the clayshales.

b. in red and brown, mostly limeless, siliceous clayshales of triassic age in several localities spread over the island of Timor, and also less abundant in the nodules and layers of chert and hornstone accompanying these shales.

c. in siliceous limestones, marls[1]) and more or less siliceous and calcareous clayshales with radiolaria, as well as in the nodules and layers of hornstone contained in those rocks of jurassic age which occur very plentiful in a great portion of the island of Timor.

d. in jurassic deep-sea deposits on the island of Rotti[2]), being identical which those just mentioned from Timor.

Probably the precipitation and accumulation of manganese is always initiated by the formation of such grains and a gradual transition can be observed between this mode of concentration and others by which the ore is more strongly localized.

2. *as nodules.* Nodules of manganese are accumulations or rather concretions of larger size than grains, being either perfectly round, or more irregular and nodular, but always well rounded[3]). They

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[1]) The strong proportion of lime contained in these rocks gives rise to the question, whether the jurassic deep-sea deposits of Timor and Rotti, although they are formed far from land and thus truly oceanic, might have been deposited in water less deep than the sea, in which the entirely limeless precretaceous deep-sea deposits of the Danau-formation of Central-Borneo have been formed The author intends to discuss elsewhere the far reaching problem, connected with this question.

[2]) Possibly also triassic and cretaceous deposits are comprised within this series of folded strata. Compare H. A. Brouwer. Voorloopig overzicht der geologie van het eiland Rotti. Tijdschr Kon. Ned. Aardr. Genootsch 2, XXXI, p. 614, 1914.

[3]) As far as the shape is concerned, the nodules found in radiolarites of jurassic age on the island of Rotti, are in every respect similar to those which have been dredged at great depths from the bottom of the ocean Compare J. Murray and J. Hjort. The depths of the ocean p. 156: "The commonest form of the manganese nodules is that of more or less rounded nodules . . . looking like marbles at one place, like potatoes or like cricket balls at other places".

are found both in the red deep-sea shale and in the hornstone and chert with radiolaria (radiolarite).

As to their occurrence the following information may be given:

a. The author possesses from the island of Borneo a single, mediumsized nodule, only collected by VAN MAARSEVEEN in chert from the Danau-formation in the bed of the Long Keloh river in East-Borneo.

b. On the island of Timor nodules of manganese have been observed in several places in deep-sea deposits; a very beautiful specimen (Pl. I, fig. 2) was collected in clayshale with radiolaria, probably of triassic age near the hill Somoholle in the Beboki-district, about 720 metres above sea-level.

c. On the island of Rotti nodules of manganese were found in several localities in siliceous limestones, marls, siliceous and calcareous clayshales with nodules and flat concretions of chert all of jurassic age, which are full of tests of radiolaria. Exceedingly well preserved are the nodules of manganese in rocks from fatu Sua Lain[1]) on the north coast of Rotti and the author refers to this locality where in the following pages he describes the composition and the mode of formation of these nodules. They are always macroscopically well demarcated from the enclosing rock and in consequence of their greater resistance to weathering they gradually more and more protude from the red shales, and white marls in which they are found included, and thus often get detached from the rocks by the process of weathering. Such detached nodules of manganese can be collected in quantities on the beach near Sua Lain. Thus there is evidently a great chance that these loose nodules may be incorporated later on in younger deposits. VERBEEK, on the island of Rotti near Bebalain, has found nodules of manganese in marls of plistocene age. I have examined these nodules, and have found that they contain radiolaria identical to those which occur in the nodules found "in situ" in radiolarites of jurassic age at different localities on the island of Rotti. These nodules of Bebalain evidently have not originated in the marls of plistocene age, but have been incorporated as such in the rock.

3. *as slabs or flat concretions.* The concretions of mangenese often, are flat, and in this case more or less restricted to definite layers of great horizontal extent; in this way true bedded manganese deposits may originate.

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[1]) Fatu = isolated rock or isolated group of rocks. R. D. M. VERBEEK gives a picture of the Fatu Sua Lain in his report on the geology of the Moluccas. Jaarboek van het Mijnwezen. 37. Wetensch. ged. p. 317 Batavia 1908.

Manganese accumulated in this manner has been found by the author in more than one locality.

A good example of this mode of occurrence is given in a complex of upper-triassic deep-sea deposits in the left slope of the valley of the Noil Bisnain, near the track from Kapan to Fatu Naisusu (commonly called the rock of Kapan) in Middle Timor. The ore-bearing portion of this complex of strata is 25 metres thick, and about 10 beds of manganese are found in it closely connected with variegated, siliceous clayshales and cherts with radiolaria, the entire complex being intercalated in strata containing limestones with tests of Radiolaria and shells of Halobia. The beds of manganese vary in thickness between 2 and 30 centimeters. Microscopical examination reveals traces of tests of radiolaria in the ore as well as in the rock.

4. in thin films on fragments of rock formed by the infiltration of manganese in cracks of the rock from which these fragments were derived.

In this way manganese is found infiltrated in the cracks of all the shales and in the majority of the cherts of the abysmal series on the islands of Borneo, Timor, and Rotti.

The chemical composition of the nodules of manganese.

I am indebted to Prof. H. Ter Meulen in Delft for a chemical analysis of a nodule of manganese taken from a marl bed with concretions of hornstone, from Sua Lain mentioned previously.

The result of the analysis in as follows:

Nodule of manganese from Sua Lain	
SiO_2	2.9 [1]
$Fe_2O_3 + Al_2O_3$	2.3
MnO_2	57.7
MnO	10.5
CoO	0.3
BaO	11.7
CaO	5.6
Na_2O	1.1
CO_2	small quantity

The substance loses 1.05 % of its weight at a temperature of 125° C. and 15.3% on roasting.

A similar analysis has been made by Mr. G. Witteveen of the

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[1] In the original Dutch edition of this paper erroneously the figure 2.09 has been given for the percentage of SiO_2.

small nodules of manganese mentioned above, which have been collected by VERBEEK[1]) in plistocene marl near Bebalain on the island of Rotti. The result of their analyses was as follows:

Nodule of manganese from Bebalain	
SiO_2	3.44
Al_2O_3	—
Fe_2O_3	1.45
MnO_2	62.06
MnO	6.03
BaO	9.18
H_2O	8.86
CaO and alkalis	not determined

Obviously there is a great similarity in chemical composition between the concretions of manganese from Sua Lain and those of Bebalain. Baryum figures highly in both the analyses. Comparing these two analyses with 45 analyses[2]) made from concretions of manganese dredged by the Challenger from recent deep-sea deposits, the proportion of iron proves to be low in the mesozoic nodules of Rotti. In recent nodules of manganese from the deep-sea the proportion of iron, determined as oxyde of iron, varies from 6.46 to 46.4. The proportion of manganese determined as MnO, in these two extreme cases proved to be 63.23 and 14.82 respectively.

On the relations between the concentration of manganese in the form of grains and of nodules.

It is not an easy matter to study the manner in which the accumulation of manganese in recent deep-sea oozes takes place, because in the process of dredging the samples from a great depth, the sediment is agitated more or less and therefore the sample does not show any more the original position and mutual arrangement of the grains and the nodules of manganese in the mud or ooze at the bottom of the ocean. As soon as, however, the deep-sea ooze is cemented into rock as is the case with these deposits of former geological ages the mutual arrangement of the grains and nodules of manganese is no more modified, and can be studied under the microscope in slides made of these rocks. These slides will show

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[1]) R. D. M. VERBEEK l.c. p 393.

[2]) J. MURRAY and A. F. RENARD l.c. p. 464—487.

so to say the process of the accumulation of the manganese in full progress but fixed or petrified at a certain moment.

Rocks from certain localities on the island of Rotti, which proved to be suitable for microscopical examination, have been studied by the author, and therefore a few words on the mode of occurrence of these rocks may serve as an introduction, before the results of this study will be dealt with.

On the island of Rotti deep-sea deposits, both of triassic and of jurassic age occur, but concretions of manganese in their original position, have as yet only been found in sediments the jurassic age of which has been determined in more than one locality. These sedimentary rocks are characteristically exposed in the rocky cliffs of Sua Lain near Termanoe situated on the north coast[1]) of the island.

They are well stratified here, and the strata folded and tilted, but not so disturbed, that the original sequence of the beds could not be determined with certainty.

The bulk of this complex of strata is composed of true abysmal deposits in which exclusively tests of radiolaria occur, but in the same complex also limestones are found which contain both radiolaria and belemnites of jurassic[2]) age. The geological age of these deep-sea deposits has thus been proved beyond doubt.

The deep-sea deposits are here represented by siliceous and slightly calcareous red clay shales, which pass into reddish marls and limestones in proportion as the content of lime in the rock increases, the latter containing numerous concentrations of silica in nodules grouped together in more or less distinct layers. The shales, marls, limestones and cherts are completely studded with tests of radiolaria. Manganese is concentrated irregularly in fairly equal proportions, however, in the calcareous clay shale, in the siliceous limestone

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[1]) H. A. Brouwer. l. c p. 614.

[2]) Wichmann, who in his journey to the island of Rotti in the year 1889 visited Sua Lain, reports as follows on the geological structure of this groups of rocks: "Der Fels besteht aus einem wahrscheinlich tertiären Kalkstein, die sehr reich an Foraminiferen, namentlich Globigerinen ist und ausserdem von zahlreichen Kalkspathtrümmern durchzogen wird." (A. Wichmann, Tijdschr. Kon. Ned. Aardr. Genootsch. 2, IX, p. 231, 1892). This statement is erroneous. Verbeek has proved that the rock is not filled by tests of Globigerina but of Radioloria and Hinde takes them to be of triassic age. (compare: R. D. M. Verbeek l.c. p. 317 and G. J. Hinde, ibid. p. 696) moreover, in the numerous samples, taken by Brouwer from the strata of these rocks, no Globigerina, but exclusively Radiolaria are found, whereas it follows from the Belemnites, occurring in the same complex of strata, that these rocks cannot possibly be of tertiary age."

and in the chert. Manganese is present in small grains and in nodules, which are either spheroidal (Pl. I, fig. 1) or possess various irregular, often flat cake-like shapes, but are always rounded.

Microscopical examination shows that the ore is found as black dust all through the rock, and that it is, moreover, concentrated on numerous spots in larger grains, which tend to cluster together. In some spots these grains are so congregated together that with the naked eye the presence of a concretion of pure manganese is surmised, but the microscope reveals that in such a case the grains, though very closely packed together and thus resembling a cloud, still remain isolated from each other.

In other spots the accumulation is still more compact and a true concretion or nodule is thus formed, composed exclusively of manganese and tests of radiolaria.

Surrounding such a nodule or concretion, there is generally a concentration of the grains of ore, forming an opaque halo or border, which however rapidly diminishes in density with increasing distance from the nodule.

The larger and smaller nodules are more or less arranged and connected together in layers, thus tending to form beds or flat deposits of manganese. In recent deep-sea deposits flat concretions forming a kind of cake or slab of ore are similarly found. [1])

A great number of slides of nodules have been examined under the microscope in order to determine whether, in the interior of the nodulus, particles of minerals or remains of organisms were present, that had acted as a centre or nucleus, around which the ore had grown, thus giving rise to a concentrical structure of the nodule around one or more nuclei. As a rule no nuclei and no arrangement in concentric layers have been found within the nodules. Sometimes the manganese is first deposited within the tests of radiolaria, and the author has found cherts in which the accumulation of manganese has remained strictly limited to the interior of the tests of radiolaria. In some cases the nodules may grow from such filled tests as centres, and thus polynucleal concretions may be formed. This is, however, rather of rare occurrence, and as a rule no nucleus whatever, and no concentric arrangement could be detected in the fossil nodules [2]).

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[1]) J. Murray and A. E. Renard. l c. Pl. III fig. 3.

[2]) In this respect there is a difference between the fossil nodules of manganese and those of the existing deep-seas, for the latter very often, although not always, show a concentric arrangement around a nucleus as e.g. around a crystal of phillipsite, a shark's tooth or an otolith of a cetacean. It is clear that otoliths could

Polished slabs of nodules, examined in reflected light, in many cases proved to be better fitted for microscopic study than slides, the coherence in the nodulus being often not sufficient for the preparation of thin slides.

In cases where slides of sufficient thinness could be made, the effect was striking, the perforated tests of the radiolaria, which are composed of silica, and are distinctly pellucid, contrasting strongly with the completely opaque manganese both without and within.

On the mode of accumulation of manganese in the deep-sea ooze.

From the mutual relations between grains and nodules of manganese in mesozoic deep-sea deposits and the peculiarities of the occurrence of radiolaria therein, deductions may be made regarding the mode of accumulation of ore in deep-sea ooze.

Manganese is precipitated on numerous spots as minute grains in the deep-sea ooze, which is a siliceous and somewhat argillaceous colloid in which tests of radiolaria are found suspended. In some places the precipitation is evidently more rapid than in others, and thus grains of different size are formed, all of them floating in a similar manner to the tests of radiolaria in the siliceous colloid. It appears that by mutual attraction [1]) the grains pack together and thus form stronger and stronger centra of attraction for other grains, forming eventually clouds, which on closer packing together, are gradually transformed into concretions or nodules, composed of pure ore.

During this process of gradual concentration of the ore into nodules, the tests of radiolaria are surrounded by the ore, without being shifted from their position, and finally are found in the nodules just at these places where they had been floating, suspended in the ooze. As long as the ooze remains viscous, a nodule once formed, continues to be a centre of attraction and collecting more and more minute grains of

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not be expected in jurassic deposits, but sharks' teeth and remains of other animals as e. g. belemnites could be expected to occur as nuclei in the jurassic nodules of manganese This difference, certainly, is remarkable, and as yet cannot be explained, but not too much importance ought to be attached to it, according to the author's opinion, firstly because many nodules from recent deep-sea deposits in a similar manner do not show a concentrical structure, and secondly because the fossil nodules, which hitherto have been examined microscopically, come from three localities only, not far distant from each other, all from the island of Rotti.

[1]) The existence of this attraction is deduced by the author from the observed facts, without giving an explanation of its cause; a fair proportion of iron always entering into the composition of the nodules of manganese it might be suggested that magnetic forces could be the cause of the mutual attraction of the small grains.

ore, becomes surrounded by a kind of halo in which grains of ore travelling slowly towards the focus of attraction, become more numerous than at a certain distance from the growing nodule beyond its sphere of influence, where the grains are found equally distributed in the ooze. The grains, it may be safely admitted, travel very slowly towards the larger nodules, and evidently the position of the tests of radiolaria in the ooze is not altered by their slow movement. The radiolaria are just as numerous and are spread in the same irregular manner both without or within the nodules.

Although the mode of formation of the concretions by the close packing together of grains of manganese fairly well explains the observed facts, it is, however, not quite clear how finally concretions are formed, composed of manganese and tests of radiolaria exclusively without traces of the ooze being enclosed.

It might be supposed that in the ooze diffusion currents around the growing nodules, carrying manganese in solution towards them are stronger around grains which are larger, and that consequently the latter grow faster, and by their growth may incorporate and absorb the smaller ones, and finally by this process a concretion or nodule may be formed. Also in this case the tests of radiolaria might be surrounded and absorbed by the growing concretions without being shifted from their original position, but it is not possible to explain why in this case halos of higher concentration with minute grains of manganese abundantly in suspension, should be found around the larger grains.

Probably these two processes collaborate in the mode of formation of the nodules, firstly growth by precipitation of manganese from convergent diffusion currents and secondly growth by accumulation and packing of preexisting minute grains ¹).

The result is the formation of a concretion with fairly well demarcated outlines, surrounded by a cloud of smaller grains rapidly diminishing in density. The concretion itself is composed almost

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¹) In the discussion following on the reading of this paper Mr. WICHMANN remarked that according to his opinion, the nodules in deep-sea deposits are not formed by anorganic processes, but by biochemical processes caused by bacteria He drew the attention of the members to experiments made by Mr. BEIJERINCK, who proved the existence of bacteria possessing the quality to precipitate manganese as superoxyde from solutions of carbonate of manganese. The author admitted the possibility of such biochemical processes as the cause of the accumulation of manganese in deep-sea ooze, but he pointed out that hitherto the existence of bacterial life in abysmal depths had not been proved. Compare M. W. BEIJERINCK. Oxidation of mangano carbinate by microbes. Proc. of the section of sciences of the Kon. Akad. der Wetensch. Amsterdam XVI 1. p 397, 1914.

exclusively of manganese but as a rule [1] contains numerous tests of radiolaria, which in the nodules show a lack of any regular arrangement just as is the case outside the nodules in the surrounding ooze.

The mutual relation between the accumulation of manganese and of silica.

The study of fossil deep-sea deposits reveals that, before these deposits had been converted into rock, the silica in the ooze has been concentrated in the same manner as the manganese, with this difference only, that the concretions of silica, as chert, or hornstone have much greater dimensions, and are far more numerous than those of manganese.

Silica just as well as manganese is accumulated in fossil deep-sea deposits in concretions or nodules of manifold shapes, originally having been formed in an ooze or colloid, which itself by cementation (petrification) has been converted later into siliceous clayshale, marl or limestone.[2] The process of aggregation of the silica is, however, posterior to that of the manganese. The silica, in concentrating, not only envelops, and encloses, the tests of radiolaria which float suspended in the ooze, but in the same way also the nodules of manganese. Both, the tests of the radiolaria and the nodules of manganese, remain in their places, and, being enveloped by the silica, are not shifted from their original position.

The radiolarites (radiolarian rocks) from the island of Rotti thus prove that in their origin and development the nodules of manganese are absolutely independent of those formed of silica; they are just as numerous within as without the nodules of hornstone, and frequently one nodule of manganese is found enclosed partially by hornstone, and partially by siliceous clayshale or marl. Radiolaria occur just as plentiful and scattered in the same way in the nodules of manganese, in the concretions of hornstone, and in the surrounding clayshale of marly clayshale.

It is further obvious that the two processes of the accumulation of manganese and of silica are not only entirely independent of each other, but are also not synchronous; in fact, the process, i.e.

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[1] On the island of Rotti the author has found several jurassic nodules of manganese containing hardly any test of radiolaria.

[2] According to the results of an analysis, for which I am indebted to Mr. J. DE VRIES, in a siliceous limestone with nodules both of manganese and hornstone, the proportion of silica of the rock outside of the nodules of hornstone amounted to 4.94$^0/_0$, notwithstanding obviously the bulk of the silica in this rock had been concentrated into the nodules of hornstone.

the accumulation of the manganese, must have reached its final stage, before the second commenced. This is quite in harmony with the testimony given by modern deep-sea deposits. Nodules of manganese are found in abundance in the deep-sea oozes, but concretions of silica e. g. as nodules of hornstone, have not yet been met with. Obviously, in the recent deep-sea oozes (especially in the red clay and the radiolarian ooze), the process of accumulation of manganese partly has been completed, partly is still in full progress, but the process of concentration of silica into hornstone, chert, jasper etc. has not yet commenced.

It might be questioned, whether possibly the concentration of the manganese and a fortiori of the silica, might have taken place after the deep-sea deposits, by diastrophism, had been brought into the position, where they take part now in the formation of mountain-ranges. This question has to be answered in the negative; the concretions of manganese and those of silica have been influenced by the mountain-building processes precisely in the same way as the rocks in which they are found enclosed, and it is easy to prove that before the mountain-making processes came into operation they had already been solidified, and had attained their full size.

It is only the last of the possible modes of accumulation mentioned on p. 421—423 i.e. the infiltration of manganese in the cracks of the rocks, which according to the opinion of the author has taken place entirely, or almost entirely after the deep-sea ooze had been solidified into firm rock, and had been crushed more or less by pressure.

Iron and manganese are generally found together in cracks of fossil deep-sea deposits, especially in cherts. In some places, as is the case in West-Borneo, iron predominates, in other places, as in East-Borneo, manganese prevails. In case of strong pressure the chert is often converted into a crush breccia cemented by manganiferous iron-ore. Frequently the chert is then found altered into white amorphous silica, in which case beautiful rocks originate, being composed of a mosaic of pure white angular fragments, cemented by chocolate-brown films of iron-ore. ¹)

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¹) G. A. F. Molengraaff, Geological explorations in Central-Borneo, p. 92, 1902.

Mathematics. — *"Bilinear congruences of twisted curves, which are determined by nets of cubic surfaces."* By Prof. JAN DE VRIES.

(Communicated in the meeting of May 29, 1915)

1. The base-curves ϱ^9 of the pencils belonging to a general net $[\Phi^3]$ of cubic surfaces, form a bilinear congruence. For through an arbitrary point passes *one* curve ϱ^9, and the involution of the second rank, which the net determines on an arbitrary straight line, has *one* neutral pair, so that there is *one* ϱ^9 for which that straight line is bisecant.

The 27 base-points of the net are fundamental points of the congruence. Any straight line f passing through one of those points F is *singular bisecant*; for through any point of f passes a ϱ^9, at the same time containing F. As the points of support of the curves resting on f form a parabolic involution, f may be called a parabolic bisecant.

Let t be a trisecant of a ϱ^9; through an arbitrary point of t passes *one* Φ^3, and this surface contains *all* the points of t. By the remaining surfaces of the net, t is intersected in the triplets of an involution; consequently t is a *singular trisecant*. The singular trisecants therefore form a congruence of rays; it is at the same time the congruence of the straight lines lying on the surfaces of the net.

A curve ϱ^9 has 18 apparent nodes, is therefore of genus 10. The cone of order eight $\mathfrak{d}^8$, projecting it out of one of the points F has therefore 11 double edges t [1]).

Any point F is a singular point for the congruence $[t]$, consequently vertex of a cone $\mathfrak{S}$ formed by trisecants t. With $\mathfrak{d}^8$ this cone has, besides the 26 straight lines FF' to the remaining fundamental points, the 11 double edges of $\mathfrak{d}^8$ in common. Consequently $\mathfrak{S}$ is a cone of order six; the congruence $[t]$ has therefore 27 *singular points of order six*.

The trisecants of a ϱ^9 form a ruled surface, on which ϱ^9 is an elevenfold curve. With an arbitrary surface Φ^3 this ruled surface has moreover the 27 straight lines of Φ^3 in common; the complete section is consequently a figure of order 126, and the ruled surface in question has the order 42.

Let us now consider the axial ruled surface $\mathfrak{A}$, formed by the rays of the congruence $[t]$ resting on a straight line a. With an arbitrary ϱ^9 it has first in common the 27 sextuple points F; the

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[1]) A curve ϱ^n with h apparent nodes is intersected in each of its points by $h-(n-2)$ trisecants.

remaining intersections lie three by three on the 42 trisecants of ϱ^9, resting on a. From this it follows that $\mathfrak{A}$ is a ruled surface of order 32. As an arbitrary point bears *eleven* straight lines t, a is elevenfold straight line of $\mathfrak{A}^{32}$, and a plane passing through a contains moreover 21 straight lines t. *The singular trisecants form therefore a congruence* (11, 21).

In order to investigate whether the congruence $[\varrho^9]$ possesses other singular bisecants besides, we consider the surface Π, which contains the points of support of the chords, which the curves ϱ^9 send through a given point P. A straight line r passing through P, is, in general, chord of *one* ϱ^9, therefore contains two points of Π lying outside P. One of those points of support comes in P, as soon as r becomes chord of the ϱ^9, passing through P. The cone $\mathfrak{K}^8$ projecting this ϱ^9 out of P, is therefore the cone of contact of the octuple point P and Π is of order 10. The 11 straight lines t passing through P are nodal edges of $\mathfrak{K}^8$ and at the same time nodal lines of Π^{10}. The complete section of these two surfaces consists of the 11 double lines mentioned, the curve ϱ^9_P and the 27 straight lines PF. From this it ensues that the straight lines f are the only singular bisecants.

With an arbitrary ϱ^9 Π^{10} has the points of support of the 18 chords in common, which the curve sends through P; the remaining 54 intersections lie in the points F; consequently Π^{10} has nodes in the 27 fundamental points.

2. If two surfaces Φ^3 touch each other, the point of contact D is node of their section δ^9 and at the same time node of a surface belonging to the net. The locus of D is a curve δ^{24}. In order to find the locus of the nodal curves δ^9, we consider two pencils of the net. Each surface of the first pencil has 72 points D in common with δ^{24}, is therefore touched by 72 surfaces of the second pencil; by this a correspondence (72,72) is determined between those pencils. The intersections of homologous surfaces with a straight line l are homologous points in a correspondence (216,216); and both pencils produce therefore a figure of order 432. But the surface that the pencils have in common has been assigned 72 times to itself; the real product is therefore of order 216 only. From this it appears that *the nodal curves δ^9 form a surface of order* 216, Δ^{216}.

An arbitrary ϱ^9 can intersect this surface in the points F only; consequently Δ^{216} has the fundamental points as 72-fold points.

3. The pencils mentioned above are brought in a correspondence

(3,3), when each two surfaces, intersecting on a straight line l, are considered as homologous. It is found then that the locus of the curves ϱ^9, resting on l, is a surface Λ of order *nine*, which has the fundamental points as *triple* points.[1])

Two straight lines are therefore intersected by *nine* curves ϱ^9.

The curves ϱ^9, intersecting a straight line f, form therefore a surface of order six, with nodes F.

A plane passing through l, intersects Λ^9 moreover along a curve λ^8, the latter has in common with l the points of support of the curve ϱ^9, which has l as chord (*nodal curve* of Λ^9). In each of the remaining points of intersection of l with λ^8 the plane is touched by curves ϱ^9. The points, in which a plane φ is touched by curves of the congruence lie therefore in a curve φ^6. The latter is the *curve of coincidence of the nonuple involution* which $[\varrho^9]$ determines in φ; this involution possesses no exceptional points; each point belongs to *one* group.

As each point of intersection of φ^6 with a surface Λ^9 belonging to an arbitrary straight line l indicates a curve ϱ^9, which touches φ and rests on l, the curves ϱ^9 touching φ form a surface Φ^{54}. This surface has moreover in common with φ a curve φ^{42}; as the latter can only touch the curve φ^6, there are 126 *curves* ϱ^9, *osculating a given plane*.

If the curve φ^6 is brought in connection with the surface Ψ^{54}, belonging to a plane ψ, then it appears that *two arbitrary planes are touched by* 324 *curves* ϱ^9.

4. If the surfaces of a net $[\Phi^3]$ have the straight line q in common, the *base-curves* ϱ^8 of the pencils form a bilinear congruence with *singular quadrisecant* q. As a ϱ^8 is cut by a surface Φ, outside q, in 20 points, the congruence has 20 fundamental points F.

Each point S of q is singular; the ∞^1 curves ϱ^8 passing through S form a monoid Σ^3 belonging to the net, with nodal point in S. In order to confirm this more specially we consider two pencils of the net, and make them projective by associating any two surfaces, which touch in S. The figure which they produce then consists of the common figure of the pencils and the monoid Σ^3.

If Σ^3 is represented by central projection out of S on a plane φ, the images of the curves ϱ^8 form a pencil of curves φ^7. The image of the quadrisecant is triple base-point, the images of the five trisecants t, which a ϱ^8 sends moreover through S, are double base-points. The remaining 20 base-points are the images of the points

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[1]) A ϱ^9 which does not intersect l will cut Λ^9 only in the 27 points F.

F. The five straight lines t lie, like q, entirely on Σ^3; they are apparently *singular trisecants*. Each straight line t is intersected by the curves ϱ^8 in S, and in a pair of an involution.

Two monoids have the straight line q and a ϱ^8 in common. Consequently in general a curve of the congruence is determined by two of its intersections with q. The sets of four points of support form therefore an involution of the second rank. So there are on q three pairs of points, which each bear ∞^1 curves ϱ^8; in other words, the net contains *three binodal surfaces*, of which the two nodes lie on q. We may further observe that q is stationary tangent of *six* ϱ^8 and bitangent of *four* ϱ^8.

Each trisecant t of a ϱ^8 is singular (§ 1); the straight lines t form a congruence of order 8, with 20 singular points F. The cone $\mathfrak{F}^7$, with vertex F, which projects a ϱ^8, has 8 double edges and contains 19 straight lines FF'; from this it ensues that the straight lines passing through F form a cone $\mathfrak{F}^5$, so that F appears to be a *singular point of order five.*

In any plane passing through q lie 6 chords of a ϱ^8, through any point of q pass 8 chords. The straight lines resting on q and twice on ϱ^8, form therefore a ruled surface of order 14. As they belong to the trisecants of the figure (q, ϱ^8), the trisecants of ϱ^8 must form a ruled surface of order 28.

Let us now again consider the axial ruled surface $\mathfrak{A}$, formed by the trisecants resting on the straight line a. With a definite ϱ^8 $\mathfrak{A}$ has the 20 quintuple points F and 28 triplets of points of support in common; from this it ensues that $\mathfrak{A}$ is of order 23. *The singular trisecants consequently form a congruence* (8, 15).

5. The surface Π is here of order 9; it contains q and has 20 nodes F (§ 1). Its section with the cone, $\mathfrak{K}^7$, which projects the ϱ^8 laid through P, consists of that curve, 8 singular trisecants (which are nodal lines for both surfaces) the 20 singular bisecants PF (each with a parabolic involution of points of support) and moreover three straight lines b, which apparently must also be *singular bisecants.* These straight lines we find moreover by paying attention to the intersections of $\mathfrak{K}^7$ with q; to them belong the four points, which q has in common with the ϱ^8 projected by that cone. If S is one of the remaining three intersections the straight line PS belongs to a Φ^3 of the net, is consequently cut by that net in the pairs of an involution and is therefore bisecant of ∞^1 curves ϱ^8.

For a point S of q Π consists of the monoid Σ^3 and a *cone of order six*. For, a bisecant of a ϱ^8 not laid through S is at the same time bisecant of a ϱ^8 belonging to Σ^3, consequently a singular bisecant b. The locus of the straight lines b drawn through S forms therefore with Σ^3 the surface Π. An arbitrary plane consequently contains six straight lines b, and *the singular bisecants form a congruence* (3,6). The three rays b out of a point P lie in the plane (Pq); the six rays in a plane π meet in the point (πq).

The curves ϱ^8 meeting a straight line l form again a surface Δ^9. On it q is *triple straight line,* for each monoid Σ^3 contains three curves resting on l and meeting in S. Two surfaces Δ have besides q the 9 curves ϱ^8 in common, resting in the two straight lines l. The points F appear this time again to be *triple.*

In a plane φ the congruence $[\varrho^8]$ determines an *octuple involution,* which possesses a *singular point of order three* (intersection S of φ). The *curve of coincidence* φ^6 (§ 3) has now a *node* S.

As Δ^9 and φ^6 have now, outside S, 48 points in common, the curves ϱ^8, which touch the plane φ, form a surface Φ^{48}. On it q is a 16-fold straight line; for the monoid that has an arbitrary point of q as vertex, cuts φ^6, outside q, in 16 points. The plane φ cuts Φ^{48} moreover along a curve φ^{36} with 12-fold point S. The curves φ^{36} and φ^6 have 24 intersections in S; as their remaining common points must coincide in pairs, there are 96 *curves ϱ^8 osculating φ*.

The curve φ^6 has with the surface Ψ^{48} (belonging to a plane ψ) $6 \times 48 - 2 \times 16 = 256$ points in common outside q; there are consequently 256 *curves ϱ^8, which touch two given planes.*

6. If the surfaces Φ^3 of a net have two non-intersecting straight lines q and q' in common, they determine a bilinear congruence of *twisted curves* ϱ^7, of genus *four,* for which q and q' *are singular quadrisecants*; it has 13 *fundamental points* F. The curves ϱ^7 have 11 apparent nodes.

If the monoid Σ^3 containing the curves ϱ^7, which intersect q in S, is represented in the usual way, the system of those curves passes into a pencil of curves φ^6, which has a triple base-point on q and double base-points in the intersections of three other straight lines t of the monoid; the remaining base-points are the images of the points F, and the intersections of the two straight lines b^*, which may moreover be drawn on Σ^3 through S (and which apparently rest on q'). The straight lines b^* are *singular bisecants* (parabolic bisecants), the straight lines t are *singular trisecants.* The locus of the singular bisecants b^* is a ruled surface of order four with nodal lines q and q'.

Through an arbitrary point P pass six singular trisecants; they are nodal lines of the surface Π^8 determined by P and nodal edges of the cone $\mathfrak{K}^6$, which projects the curve ϱ^7 laid through P. These two surfaces have besides that ϱ^7 and the six straight lines t, moreover the 13 parabolic bisecants PF and *four singular bisecants* b in common. The straight lines b are found back if $\mathfrak{K}^6$ is brought to intersection with q and q'; on each of the singular quadrisecants rest therefore two straight lines b.

Each point of q or q' bears a cone of order 5 (completing Σ^3 into a surface Π^8) formed by singular bisecants. *The singular bisecants* consequently *form two congruences* (2,5).

The locus of the trisecants of the figure (q, q', ϱ^7) consists of four ruled surfaces, together forming a figure of order 42. The straight lines intersecting q, q' and ϱ^7 apparently form a ruled surface $\mathfrak{R}^6$. The bisecants of ϱ^7 resting on q or on q' lie on a $\mathfrak{R}^8$ with quintuple straight line. Consequently the trisecants t of ϱ^7 will form a $\mathfrak{R}^{20}$ (with sextuple curve ϱ^7).

According to the method followed above (§§ 1, 4) we find now that *the singular trisecants* t form *a congruence* (6, 10), possessing in the 13 fundamental points F singular points of order six.

On two arbitrary straight lines nine curves of the congruence rest now too. The surface Λ^9 has two triple straight lines, q and q'. In a plane φ arises a *septuple involution* with a curve of coincidence γ^6 possessing *two nodes*, where the involution has *singular points of order three.* The curves ϱ^7 touching φ, form a Φ^{42} with 14-fold straight lines q and q'.

There are 70 curves ϱ^7 *osculating* a plane φ, and 196 curves *touching two given planes.*

7. If the surfaces Φ^3 of a net have a conic σ^2 in common they determine a bilinear congruence of *twisted curves* ϱ^7, of genus *five.* Every ϱ^7 rests in six points on the singular conic σ^2. The congruence possesses consequently 15 *fundamental points* F.

In representing the monoid Σ^3, containing the curves ϱ^7, which intersect σ^2 in a point S, the system of those curves passes into a pencil of curves γ^6. They have five nodes in the intersections of the singular trisecants t, meeting in S; the remaining base-points are the images of the 15 points F, and the intersection of the straight line b^* of Σ^3, which forms with the 5 straight lines t the set of six straight lines passing through S. Apparently b^* is here also a *singular bisecant* (parabolic bisecant).

The surface Π^8 belonging to a point P and the corresponding cone $\mathfrak{K}^6$ have in common a ϱ^7, five singular trisecants t (nodal lines for both surfaces), the 15 parabolic bisecants PF and *six singular bisecants* b.

For a point S of σ^2 Π^8 consists of the monoid Σ^3 and a cone of order five formed by straight lines b. Hence *the singular bisecants b form a congruence* (6, 10).

Let us now consider the straight lines which intersect the figure (ϱ^7, σ^2) thrice, consequently form together a figure of order 42. Any point of σ^2 bears 10 chords of ϱ^7; in the plane σ of that conic there are 6 of them, viz. the straight lines connecting the 6 intersections of σ^2 and ϱ^7 with the point R, which ϱ^7 has moreover in common with σ. The chords of ϱ^7 meeting σ^2 consequently form a $\mathfrak{R}^{26}$. The chords of σ^2 meeting ϱ^7, form the plane pencil (R, σ). Consequently the trisecants of ϱ^7 form a $\mathfrak{R}^{15}$.

In connection with this we easily find now that the *singular trisecants* form *a congruence* (5,10) possessing 15 singular points F of order four.

The surface Λ^9 has now a triple conic, σ^2, and 15 triple points F. In a plane q $[\varrho^7]$ determines again a septuple involution with two singular points of order three. In connection with this we find for this congruence $[\varrho^7]$ the same characteristic number as for the $[\varrho^7]$ treated in § 6.

8. Passing on to congruences of twisted curves ϱ^6, we suppose in the first place, that the surfaces of $[\Phi^3]$ have three non-intersecting straight lines q, q', q'' in common. They are then *singular quadrisecants* of the congruence $[\varrho^6]$; consequently the curves ϱ^6 (genus *one*) pass through *six fundamental* points F.

The curves ϱ^6 intersecting q in S form again a monoid Σ^3. They are represented by a pencil (γ^5), having a triple base-point on q and double base-points in the intersections of two straight lines t. To the base belong further the images of the points F and the intersections of two straight lines b^* (singular bisecants).

The sixth straight line of Σ^3, passing through S, is component part of a *degenerate curve* ϱ^6. It is the transversal d of q' and q'' passing through S; for through an arbitrary point of that transversal pass ∞^1 surfaces Φ^3 having d in common and therefore intersecting moreover along a curve δ^5 (of genus *one*), which has q, q', q'' as trisecants. The planes (dq') and (dq'') each intersect Σ^3 along one of the straight lines b^*.

The ruled surface $\mathfrak{D}^2$ with directrices q, q, q'' contains all the straight lines d forming the second system of straight lines. With a monoid Σ^3 $\mathfrak{D}^2$ has three straight lines d in common of which one passes through S. Consequently there lie on Σ^3 two curves δ^5, which pass through S. The locus Δ of the curves δ^5 has consequently three nodal lines q, q', q''; its section with a Σ^3 consists further of three curves δ^5, is therefore of order 21. Hence Δ is *a surface of order seven.*

The figures (d, δ^5) determine on q a correspondence (3,2); so there lie on q five points $D = (d, \delta^5)$. The locus of the points D is therefore a *twisted curve* $(D)^6$, intersecting each of the straight lines q, q', q'' five times.

Now $\mathfrak{D}^2$ and Δ^7 have the three straight lines q and the curve $(D)^6$ in common, consequently another figure of order two. This figure must consist of two straight lines d, hence there is a figure of $[\varrho^6]$ consisting of two straight lines d and a curve δ^4. This curve has q, q', q'' as bisecants and intersects $\mathfrak{D}^2$ moreover in two points D.

Through an arbitrary point P pass five singular trisecants; they are nodal lines of Π^7 and $\mathfrak{K}^5$. These surfaces have moreover in common the curve ϱ^6_P laid through P, the six parabolic bisecants PF and three straight lines b. The straight lines b are determined by the points which the straight lines q outside the curve ϱ^6_P have in common with the cone $\mathfrak{N}^5$; hence they are *singular bisecants.*

If P is supposed to be on q, Π^7 is replaced by the figure composed of Σ^3 and a cone $(b)^4$. *The singular bisecants form consequently three congruences* (1, 4).

The locus of the straight lines which intersect a figure (ϱ^6, q, q', q'') thrice, consists of the hyperboloid $(q\, q'\, q'')$, three ruled surfaces $\mathfrak{R}^4$ with nodal lines q, q' and the ruled surface of the trisecants of ϱ^6; this is therefore of order 16.

From this it is now deduced, in the way followed before, that *the singular trisecants* form *a congruence* (5, 6) possessing six singular points F of order three.

The surface Λ^9 has three triple straight lines q, q', q''. In a plane φ the congruence $[\varrho^6]$ determines a *sextuple involution with three singular points of order three,* which are at the same time nodes of the curve of coincidence φ^6. The curves ϱ^6, touching φ, form a Φ^{36} with 12-fold straight lines q, q', q''. There are 48 curves ϱ^6, *osculating* one plane, and 144 curves *touching two planes.*

9. Let us now consider the case that all the surfaces of the net $[\Phi^3]$ have in common a conic σ^2 and a straight line q not intersecting it. Any two surfaces then determine a *twisted curve* ϱ^6, which rests in six points on σ^2, in four points on q. A third surface intersects ϱ^6 moreover in eight points. The congruence $[\varrho^6]$ possesses therefore *eight fundamental points* F. The curves ϱ^6 have eight apparent nodes, they are consequently of genus *two*.

The monoid Σ^3 belonging to a point S of the *singular quadrisecant* q contains *a singular trisecant* passing through S. From the image of Σ^3 it appears that the remaining four straight lines of Σ^3 passing through S are *singular bisecants* b^*.

The curves ϱ^6 intersecting the singular conic σ^2 in a point S^* also form a monoid Σ^3. These curves are represented by a pencil (φ^5), which has double base-points in the intersections of the *four singular trisecants* t meeting in S^*. The simple base-points are the images of the 8 points F and the intersection of a *singular bisecant* b^*.

The sixth straight line passing through S^* must be component part of a *compound* ϱ^6. It must cut σ^2 and q, belongs therefore to the plane pencil in the plane σ of σ^2, which has the point Q of q as vertex.

Any ray d of that plane pencil is component part of a degenerate σ^6, for an arbitrary point of d determines a pencil (Φ^3) of which all figures pass through d, consequently have a curve ϱ^5 in common besides, which intersects σ^2 four times, q three times, consequently possesses four apparent nodes. To the surfaces Φ^3 passing through the figure $(\sigma^2, q, d, \delta^5)$ belongs the figure composed of the plane σ and the *hyperboloid* $\mathfrak{D}^2$ passing through q and the points F; this degenerate figure apparently replaces the monoid belonging to Q. The hyperboloid $\mathfrak{D}^2$ is *the locus of the curves* δ^5; its intersection δ^2 on σ contains the points $D = (d, \delta^5)$; all curves δ^5 pass through the four intersections of δ^2 with σ^2.

From the consideration of the surfaces Π^7 and $\mathfrak{K}^5$, which are determined by a point P it follows readily that P bears five singular bisecants b. Four of these straight lines rest on σ^2, the fifth on q. Any point of σ^2 or of q is the vertex of a cone of order four, formed by straight lines b. The *singular bisecants* consequently form two congruences; a *congruence* (1,4) with directrix q, a *congruence* (4,8) with singular curve σ^2.

The singular trisecants t form a congruence possessing eight singular points, F, of order three. The trisecants of a ϱ^6 form a ruled surface $\mathfrak{R}^{12}$. In connection with this we find that the straight lines t determine a *congruence* (4,6).

As $[\varrho^6]$ again intersects a plane φ along a *sextuple involution* with three singular points of order three, we find for the characteristic numbers connected with it the same values as in § 8.

10. A net $[\Phi^3]$, of which the figures have a cubic σ^3 (or a degeneration of it) in common, determines a congruence of twisted curves ϱ^6, of genus *three*, intersecting the singular curve σ^3 eight times [1]. The congruence possesses accordingly *ten fundamental points* F.

As ϱ^6 has seven apparent nodes, σ^3 is intersected in each of its points S by *three singular trisecants* t. Using the image of the monoid Σ^3 belonging to S, we find that the remaining three straight lines of Σ^3 meeting in S are *singular bisecants* b^*.

Through an arbitrary point P pass seven singular bisecants b. Each point of σ^3 is vertex of a cone of order four formed by straight lines b. From this it ensues that *the singular bisecants* form *a congruence* (7,12).

The *singular trisecants* form *a congruence* (3,6) with ten singular points, F, of order three.

The characteristic numbers, connected with the surface Δ^9, have the same values as with the congruence $[\varrho^6]$ already dealt with.

11. The surfaces of a net $[\Phi^3]$, which have a plane curve σ^3 in common, determine a congruence of *twisted curves* ϱ^6 of genus *four*, which possesses *twelve fundamental points* F.

As ϱ^6 has now six apparent nodes, each point S of the singular curve σ^3 bears *two singular trisecants*.

To the surfaces Φ^3 passing through a figure (σ^3, ϱ^6) belongs a figure consisting of the plane σ of σ^3 and a hyperboloid; ϱ^6 is therefore the complete section of a hyperboloid with a cubic surface. In connection with this the curves ϱ^6 intersecting σ^3 in a point S, form a *hyperboloid* Σ^2, passing through the points F. The surfaces Σ^2 form a pencil [2]) with *base-curve* β^4, which determines in σ a pencil of conics ϱ^2. Any point of the plane σ bears therefore a *figure consisting of a* ϱ^2 *and the curve* β^4.

The section of σ with the surface Δ belonging to the straight line l consists of the nodal curve σ^3 and the conics ϱ^2 intersected by l; hence Δ is of *order eight*.

Two surfaces Δ^8 have the singular curve σ^3, the curve β^4, and eight curves ϱ^6 in common.

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[1]) If σ^3 is replaced by a conic σ^2 and a straight line s intersecting it, we understand easily that any ϱ^6 has five points in common with σ^2, and three points with s.

[2]) The net $[\Phi^3]$ may be represented by the equation

$$a_x^3 + \lambda\,(a_x^3 + b_x^2\,x_4) + \mu\,(a_x^3 + c_x^2\,x_4) = 0.$$

Through a point of $x_4 = 0$ passes the pencil for which $1 + \lambda + \mu = 0$. It consists therefore of the plane $x_4 = 0$, and the pencil $\lambda\,(b_x^2 - c_x^2) - c_x^2 = 0$, with base-curve $b_x^2 = 0$, $c_x^2 = 0$.

The sextuple involution, which $[\varrho^6]$ determines in a plane φ, has *three singular points S of order two* lying in a straight line s and (in the intersections of β^4) *four singular points of order one*, which are completed into sets of six by the pairs of an involution lying on s.

Any trisecant t of a ϱ^6 is trisecant of ∞^2 curves of the congruence and in particular of a figure (ϱ^2, β^4). The *congruence of the singular trisecants* is therefore identical with the congruence of the chords of β^4, is consequently a (2, 6).

The cone projecting a ϱ^6 out of one of its points has in common with σ^3 the 6 intersections of the two curves; the remaining 9 points determine each a singular bisecant b.

The surface Π^7 belonging to a point S of σ^3 consists of Σ^2, the plane σ (of which any straight line is singular bisecant) and a cone $(b)^4$. Consequently the *singular bisecants b form a congruence* (9, 12).

A plane φ contains a curve φ^5 being the locus of the points of contact of curves ϱ^6. As φ^5 has 34 points in common with Δ^8, outside σ^3, the curves ϱ^6 touching φ form a Φ^{34}, which is moreover intersected by φ in a curve φ^{24}. As φ^5 is intersected by an arbitrary Σ^2 in 10 points, σ^3 is decuple curve of Φ^{34}; so φ^{24} has three octuple points S. From this it ensues further that φ^5 and φ^{24}, apart from the points S, have 96 points in common, so that φ is *osculated* by 48 curves ϱ^6.

As φ^5 has outside σ^3 140 points in common with Ψ^{34} there are 140 curves ϱ^6 *touching two planes*.

The bilinear congruences of twisted curves ϱ^5 and ϱ^4, which are determined by nets of cubic surfaces I have considered in communications published in volume XVII, p. 1250, in volume XVIII, p. 43 and in vol. XVI, p. 733 and 1186 of these *Proceedings*. The congruence of twisted cubics determined by a $[\Phi^3]$ was extensively treated by STUYVAERT (Bull. Acad. de Belgique, 1907, p. 470—514).

Mathematics. — "*Associated points with respect to a complex of quadrics.*" By CHS. H. VAN OS. (Communicated by Professor JAN DE VRIES).

(Communicated in the meeting of May 29, 1915).

Let a triply infinite linear system (*complex*) be given of quadrics Φ^2. The surfaces passing through a point P form a net and have moreover *seven* points Q in common. If we associate those points to P we get a correspondence, which will be considered here.

§ 1. We first prove the proposition: Any straight line l joining two associated points P and Q contains an involution of pairs of associated points. Any pencil of the complex has *one* Φ^2 in common with the net determined by P and Q, and intersects l therefore along an involution containing the pair of points P, Q. If two pencils have *one* Φ^2 in common (if they "intersect" as we shall say for the sake of brevity) the associated involutions have moreover *one* pair of points in common and so coincide. If the two pencils do not intersect a third may be introduced intersecting each of them and it may be seen that the involutions coincide in that case too. All pencils therefore intersect l along the same involution, any pair of points of it consequently determines an infinite number of pencils, sets apart a net out of the complex, by which the proposition has been proved.

§ 2. Let us determine the locus of the points P coinciding with one of their associated points. For this purpose we determine the number of those points lying on the section ϱ^4 of two Φ^2 of the complex. The sets of eight associated points on ϱ^4 are cut out on ϱ^4 by the Φ^2 of a pencil (Φ^2) from the complex. Now a pencil (Φ^2) contains *sixteen* (Φ^2), touching a twisted quartic of the first kind; this is easily seen by making the curve to degenerate into a quadrilateral, each of the sides of which touches then at two Φ^2, while through each angle passes *one* Φ^2, which must be counted twice.[1]) The number of points lying on ϱ^4 amounts therefore to 16, their locus is therefore a *surface of order four*, Δ^4.

§ 3. What is the locus of the points Q, if P describes a straight line l?.

Any Φ^2 of the complex intersects l in two points P, and so contains also the 14 points Q associated to them; the locus of these points is therefore a *curve of order seven*, ϱ^7. It has in common with l the four intersections of l and Δ^4.

A plane V passing through l intersects ϱ^7 outside l moreover in 3 points Q, each associated to a point P of l. The 3 joining lines PQ, which we shall indicate by g_1, g_2 and g_3 contain each an involution of associated points.

The locus of the points P of V, for which one of the associated points Q lies in V consists of these straight lines and of the section c^4 of V with Δ^4. Now this locus is the section of V with the surface

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[1]) Vide ZEUTHEN, *Lehrbuch der abzählenden Methoden der Geometrie*, Teubner 1914.

REVIEW OF THE THEORETICALLY PREDICTED SYMMETRY OF RÖNTGEN-PATTERNS OF UNIAXIAL CRYSTALS, FOR PLATES PARALLEL TO THE BASAL FACE, AND TO THOSE OF THE FIRST AND SECOND PRISM

I. Tetragonal System.

Seriesnumber of the Class of Symmetry	*Indication of the Crystal-Symmetry*	*Elements of Symmetry in the considered Crystals:*	*Symmetry of the Röntgenpattern for a plate parallel to* $\{001\}$:	*Symmetry of the Röntgenpattern for a plate parallel to* $\{100\}$:	*Symmetry of the Röntgenpattern for a plate parallel to* $\{110\}$:	*Representative Crystalspecies:*
9	Tetragonal-bisphenoidal	$\overline{A}_4$ (also = A_2)	A single quaternary axis	A single horizontal plane of symmetry	A single horizontal plane of symmetry	No mineral known
10	*Tetragonal-pyramidal	A_4	A single quaternary axis	A single horizontal plane of symmetry	A single horizontal plane of symmetry	*Wulfenite*
11	Tetragonal-scalenohedrical	$\overline{A}_4$ (also = A_2) $2 A_2'$, $2 S_v''$	A quaternary axis; 2 × 2 planes of symmetry	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	*Urea, Potassiumhydrophosphate*
12	*Tetragonal-trapezohedrical	A_4; $2 A_2'$, $2 A_2''$	A quaternary axis; 2 × 2 planes of symmetry	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	*Nickelsulphate* ($6 H_2O$)
13	Tetragonal-bipyramidal	A_4; HS; C	A single quaternary axis	A single horizontal plate of symmetry	A single horizontal plane of symmetry	*Scheelite; Erythrite*
14	Ditetragonal-pyramidal	A_4; $2 S_v'$; $2 S_v''$	A quaternary axis; 2 × 2 planes of symmetry	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	*Penta-Erythrite*
15	Ditetragonal-bipyramidal	A_4; $2 A_2'$, $2 A_2''$, HS, $2 S_v'$, $2 S_v''$; C	A quaternary axis; 2 × 2 planes of symmetry	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	*Rutile; Cassiterite, Potassiumferrocyanide* (mimetic)

II. Trigonal System.

Seriesnumber of the Class of Symmetry.	*Indication of the Crystal-Symmetry:*	*Elements of Symmetry in the considered Crystals*	*Symmetry of the Röntgenpattern for a plate parallel to* $\{0001\}$:	*Symmetry of the Röntgenpattern for a plate parallel to* $\{10\overline{1}0\}$	*Symmetry of the Röntgenpattern for a plate parallel to* $\{\overline{1}2\overline{1}0\}$:	*Representative Crystalspecies.*
16	*Trigonal-pyramidal	A_3.	A single ternary axis	No symmetry at all	No symmetry at all	*Sodiumperjodate* ($3H_2O$)
17	Trigonal-rhombohedrical	A_3 (also = $\overline{A}_6$), C	A single ternary axis	No symmetry at all	No symmetry at all	*Phenakite; Dolomite*
18	*Trigonal-trapezohedrical	A_3; $3 A_2$	A ternary axis; three planes of symmetry	A single vertical plane of symmetry	The perpendic. to the plate is a single binary axis	*Quarz; Cinnabar*
19	Trigonal-bipyramidal	A_3; HS	A single senary axis	A single horizontal plane of symmetry	A single horizontal plane of symmetry	No mineral known
20	Ditrigonal-pyramidal	A_3, $3 S_v$	A single ternary axis	A single vertical plane of symmetry	The perpendic. to the plate is a single binary axis	*Turmaline*
21	Ditrigonal-scalenohedrical	A_3 (also = $\overline{A}_6$); $3 A_2$, $3 S_v'$; C	A single ternary axis	A single vertical plane of symmetry	The perpendic. to the plate is a single binary axis	*Calcite*
22	Ditrigonal-bipyramidal	A_3; $3 A_2$; HS; $3 S_v$	A senary axis; and 2 × 3 planes of symmetry	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	No mineral known

III. Hexagonal System.

23	*Hexagonal-pyramidal	A_6	A single senary axis	A single horizontal plane of symmetry	A single horizontal plane of symmetry	*Nephelite*
24	*Hexagonal-trapezohedrical	A_6; $3 A_2$; $3 A_2'$	A senary axis and 2 × 3 planes of symmetry	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	*Antimonylbariumtartrate + Potassiumnitrate*
25	Hexagonal-bipyramidal	A_6; HS; C	A single senary axis	A single horizontal plane of symmetry	A single horizontal plane of symmetry	*Apatite*
26	Dihexagonal-pyramidal	A_6; $3 S_v$; $3 S_v'$	A senary axis and 2 × 3 planes of symmetry	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary azis	*Zincite, Wurtzite*
27	Dihexagonal-bipyramidal	A_6; $3 A_2$; $3 A_2'$; HS; $3 S_v$; $3 S_v'$; C	A senary axis and 2 × 3 planes of symmetry	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	Two perpendic. planes of symmetry; the perpendic. to the photograph. plate is a binary axis	*Beryl*

It may be generally remarked here, that planes of symmetry perpendicular to the photographic plate, will be manifested in the Röntgenpattern by their resp. *intersections* with the plane of the photographic plate; and that in the case, where the perpendicular to the plate corresponds to the direction of a binary axis, this will appear in the pattern, as if a symmetry-centre in the photo were present. Binary axes in a plane parallel to that of the photographic plate are of course not revealed in the diffraction-pattern.

N.B. The symmetry-elements of the Crystals are indicated as follows: A_n = symmetry-axis of the first order, with a period of $\frac{2\pi}{n}$; $\overline{A}_n$ = symmetry-axis of the second order (axis of composed symmetry) of the period $\frac{2\pi}{n}$, *HS* = a horizontal plane of symmetry; S_v = vertical plane of symmetry; unequivalent axes and planes are discerned by accents; *C* = centre of symmetry. The optical axis is always supposed to be *vertical*; the cristallographical principal axis of the same direction is discerned as the *c*-axis. In the case of the trigonal crystals, the symbols of BRAVAIS are used; in the case of hexagonal and trigonal crystals both, the direction of the face $(10\overline{1}0)$ is supposed to be parallel to that of (100) in the tetragonal crystals, and just so that of $(\overline{1}2\overline{1}0)$ parallel to that of (010) in the case of tetragonal forms. In some trigonal crystals, the plates were cut parallel to $(01\overline{1}0)$ and $(2\overline{1}\overline{1}0)$, what does not involve any appreciable difference for the considered problem, but makes it necessary to compare more directly the corresponding patterns with those obtained from tetragonal crystals cut parallel to (110) and $(1\overline{1}0)$. The symmetry-classes indicated by * are those, whose crystals can appear in enantiomorphous forms. (Enantiomorphism).

of the points Q, which are associated to the points P of V, this is consequently a *surface of order seven*, Φ^7.

This order is also easily found from the number of intersections with a ϱ^4 of the complex; the latter intersects V in 4 points P, contains therefore 28 points Q, associated to it.

The joining lines of associated points apparently form a congruence (7,3).

§ 4. If the straight line l is one of the straight lines PQ, considered in § 1, a Φ^2 of the complex will intersect the straight line l in two associated points, consequently contain six points only, which are associated to points of l. The locus of those points is therefore a *twisted cubic* ϱ^3. The curve ϱ^7 has been replaced here by the figure composed of l and the ϱ^3 counted twice. The latter intersects l in two of the four points which l has in common with Δ^4; the two others are the double points of the involution lying on PQ.

Let us bring through PQ a plane V, in which PQ stands therefore for the straight line g_1. This plane intersects ϱ^3 moreover in a point R outside g_1; the joining lines of R with the two points on g_1 associated to it, must be the straight lines g_2 and g_3. We see therefore that the three intersections of g_1, g_2 and g_3 are mutually associated and that each plane V *contains one set of three associated points.*

A ϱ^4 of the complex passing through two associated points lying on g_1, intersects Φ^7 further in the 6 points associated to them and in the 14 points associated to its two other intersections with V. As the total number of intersections must be 28, the 6 points mentioned first are nodes of Φ^7. The three ϱ^3 belonging to g_1, g_2 and g_3 are therefore *nodal curves of* Φ^7.

A ϱ^4 passing through the three intersections of g_1, g_2 and g_3 intersects Φ^7 further in the 5 points associated to them and in the 7 points associated to the fourth intersection of ϱ^4 and V. From this it easily ensues that the five points mentioned are *triple points of* Φ^7.

§ 5. If P lies on Δ^4 one of the associated points coincides with P. If R is one of the others the locus of R may be inquired into.

A ϱ^4 of the complex intersects Δ^4 in 16 points, contains therefore the $16 \times 6 = 96$ points R associated to them; that locus is consequently a *surface of order* 24, Δ^{24}.

Δ^4 and Δ^{24} intersect in a curve of order 96; it will, however, degenerate:

1. in het locus of the points P, coinciding with *two* of the points associated to them. Δ^4 and Δ^{24} *touch* each other along this curve.

2. in the locus of the points P, coinciding with *one* of their associated ones while two more of the other points associated to them coincide as well.

§ 6. In order to find the first of these curves we investigate the locus of the points R, associated to the points of the section c^4 of V with Δ^4.

A Φ^2 of the complex intersects c^4 in 8 points, contains therefore $8 \times 6 = 48$ points R, so that the locus of R is a curve of order 24, ϱ^{24}.

The curve ϱ^{24} intersects V in 24 points, of which 2 lie on each of the three straight lines g, and these are associated to the intersections of g with the associated ϱ^3; there remain 18, which must lie on c^4, and in each of which the point P coinciding already with Q coincides now moreover with R.

The locus wanted is therefore a *curve of order* eighteen, ϱ^{18}.

§ 7. The ϱ^{24} found just now intersects Δ^4 in 96 points; 36 of them are lying in the just found intersections with c^4, the 60 remaining ones lie on Δ^4, coincide consequently with *one* of the associated ones while two others coincide on c^4. We see therefore that the second of the curves mentioned in § 5 is really of order 60.

§ 8. The Φ^2 of the complex passing through a point P of Δ^4, have a common tangent t in P. As they form a net two more points are necessary to determine one of them.

We now take these points infinitely near P, and in such a way, that they do not lie with t in *one* plane. The surface Φ^2 thus determined has two different tangent planes in P, must therefore be a *cone* which has P as vertex. Δ^4 *is therefore nothing but the locus of the vertices of the cones of the complex.*

§ 9. The involution I^8 considered here is a particular case of an I^8 investigated by Prof. Jan de Vries[1]). Three arbitrary pencils (Φ^2) had been given there. Through a point P passes out of each of them *one* Φ^2; these 3 Φ^2 will intersect moreover in 7 points outside P. If we associate these to P we get the I^8 meant.

The I^8 considered above is acquired by taking the 3 pencils as belonging to one and the same complex; in that case the three Φ^2

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[1]) These Proceedings volume XXI, p. 431.

passing through P determine a net and have the base-points of this net in common.

For the more general Γ^8 the proposition of § 1 does not hold good; consequently the joining lines of associated points form a complex of rays instead of a congruence of rays.

The locus of the coincidences is now a surface of order 8; the curve associated to a straight line l is of order 23, the surface associated to a plane V is also of order 23. The question arises how the results obtained above are connected with the properties of those more general Γ^8.

§ 10. If the 3 pencils (Φ^2) lie in the same complex ∞^1 pencils (A^2) may be introduced intersecting the three given pencils. If the Φ^2 of the complex are represented by the points of a tridimensional space, the (A^2) are represented by the generatrices of the ruled surface having the images of the given Φ^2 as directrices.

For a point P on the base-curve λ^4 of a (A^2) the three Φ^2 from the given pencils passing through P belong to (A^2), consequently they have λ^4 in common. *For such a point P the associated points Q become therefore indefinite,* if we start for the definition of the Γ^8 from the three pencils (Φ^2) instead of directly from the complex.

In order to find the locus of P, we observe that the Φ^2 of the three pencils (Φ^2) belonging to one and the same pencil (A^2) are projectively associated to each other, as immediately follows from the representation mentioned. The base-curves λ^4 are consequently sections of corresponding surfaces Φ^2 out of two projectively associated pencils; their locus is therefore a *surface of order four*, Ω^4.

§ 11. If starting from the more general Γ^8, the given pencils Φ^2 are allowed to change in such a way that they come to lie in the same complex, the occurrence of Ω^4 will apparently cause various degenerations.

As the points associated to a point P of Ω^4 are indefinite they may also be considered as coinciding with P, and consequently the surface Δ^8 of the coincidences of the general Γ^8 will degenerate into Δ^4 and Ω^4.

A straight line l intersects Ω^4 in 4 points, intersects therefore four λ^4, the ϱ^{23} associated in the general case to l degenerates consequently into the ϱ^7 found above and those four λ^4.

A plane V passing through l intersects ϱ^{23} in general in 15 points outside l, of these 12 lie now on Ω^4, which are associated by 3's to 4 points of l.

From the section of V with the associated surface Φ^{23} the section with Ω^4 is therefore separated thrice, and as this section must be counted once more as part of the section with Δ^8, Φ^{23} has degenerated into the surface Φ^7 found above and in the four times counted surface Ω^4.

§ 12. On each of the straight lines PQ considered in § 1 lies an involution of associated points, of which the double points are situated on Δ^4. If these are associated to each other an *involution on* Δ^4 is obtained. It has been deduced in a different way by STURM (Die Lehre von den geometrischen Verwandtschaften, Vol. III, p. 409). He proves among others that in this way to each plane section c^4 of Δ^4 a twisted curve ϱ^6 of order six and rank sixteen is associated.

Chemistry. — *"On the allotropy of the ammonium halides I."* By Dr. F. E. C. SCHEFFER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of June 26, 1915).

1. *Introduction.* In the literature, in particular in the crystallographical literature, there are a number of papers to be found which lead us to the conclusion that ammonium chloride and ammonium bromide can occur in two different crystalline forms. Thus STAS [1]) found that the transparent crystalline mass which deposits from the vapour of subliming ammonium chloride, comes off from the wall when cooled, and becomes opaque; he also states that the specific weight of the transparent and the opaque ammonium chloride are different. Though STAS does not enter into further details about these phenomena, these experiments would already be sufficient to suggest dimorphy here. It is remarkable that STAS has evidently succeeded in cooling the transparent ammonium chloride, which according to the above is metastable at the ordinary temperature, to room temperature without the conversion taking place, the more so because in the papers that have appeared later no indications are to be found for this possibility. GOSSNER [2]), who repeated STAS' sublimation experiment, says that generally conversion sets in already during the sublimation, and the clear crystals can only be preserved for a short time.

LEHMANN [3]) was the first to conclude to dimorphy; he tried

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[1]) STAS Untersuchungen über die Gesetze der chemischen Proportionen u. s. w. übersetzt von ARONSTEIN. S. 55 (1867).

[2]) GOSSNER. Zeitschr. f. Kryst. 38 110 (1903).

[3]) LEHMANN, Zeitschr. f. Kryst. 10 321 (1885).

to prove this by crystallisation experiments of a mixture of ammonium chloride, bromide, and iodide from aqueous solution. With a suitable choice of the concentrations he succeeded on cooling in obtaining a cubic kind of crystal, which is transformed on further cooling to the well-known skeletons, which the chloride and bromide of ammonium exhibit at the ordinary temperature. It is evident that only the appearance of a *transformation* can prove the dimorphy of the halogen salts; for ammonium chloride and bromide have the skeleton form at the ordinary temperature, whereas ammonium iodide crystallizes into cubi. From a solution which contains a mixture of the salts, both cubi and skeletons can deposit. According to LEHMANN the *transformation* must be explained in this way that mixed crystals of the skeleton type are converted to cubic mixed crystals, in which then at the same time interchange of substance with the solution will take place. That in mixtures of the three salts two kinds of mixed crystals occur, becomes also probable because of the very close crystallographic resemblance of NH_4Cl and NH_4Br, and from the limited miscibility of NH_4Cl and NH_4I, which GOSSNER [1]) observed.

According to KRICKMEYER [2]) NH_4Cl and KCl show limited miscibility. GROTH [3]) expressed the supposition in virtue of this isodimorphy that the crystalline form of the ammonium chloride, which can form at higher temperature, would be isomorphous with KCl. WALLACE [4]) points out in his treatise that if this supposition is correct, this would lead to a very remarkable conclusion. As KCl belongs to the pentagonikositetrahedrical class of symmetry, this would also have to be the case for the form of the ammonium chloride, which is metastable at the ordinary temperature, and which I shall call the β-form in what follows. As, however, α-ammonium chloride also belongs to the same class of symmetry, we should have two modifications with the same crystallographical symmetry. Then we should be obliged in my opinion to seek the difference between the two modifications in a different structure of the molecule. Ammonium chloride and bromide would then be very suitable examples for a test of Prof. SMITS' theory of the allotropy; according to this theory the phenomenon of allotropy is namely generally explained by the assumption of different kinds of molecules. If we consider that the above mentioned experiments of LEHMANN render it probable that NH_4Cl and NH_4Br can dissolve in NH_4I with formation of cubic mixed crystals, and

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[1]) GOSSNER, Zeitschr. f. Kryst. 40. 70 (1905).

[2]) KRICKMEYER, Zeitschr. f. physik. Chemie. 21. 72 (1896).

[3]) GROTH, Chem. Kristall. I. 167.

[4]) WALLACE, Centralblatt für Mineralogie u. s. w. 1910 S. 33.

that NH_4I probably crystallizes pentagonikositetrahedrically, we should arrive by the same train of reasoning as above at the conclusion that α- and β-ammonium chloride are both pentagonikositetrahedrical.

An entirely different indication for the existence of two modifications has been found by Prof. ZEEMAN and HOOGENBOOM [1]). In the research of the birefringency of the ammonium chloride cloud in the electric field it appeared that this can have a different sign and that also the reversal of sign of the refraction can be demonstrated. These phenomena are explained by the assumption that the refraction of positive and negative sign must be due resp. to the two ammonium chloride modifications.

The above mentioned experiments prove that ammonium chloride occurs in two modifications, but whether we have to do here with enantiotropy or monotropy cannot be inferred from the above.

WALLACE [2]), however, has shown of late that NH_4Cl and NH_4Br are enantiotropic. From cooling curves he found the points of transition resp. at **159°** and **109°**. By the aid of LEHMANN's Heating microscope he could directly observe the conversion; besides, dilatometric determinations furnished a confirmation of these results. For NH_4I no transition could be observed.

2. The question whether ammonium chloride shows allotropy is of importance in connection with JOHNSON's well-known experiment[3]), according to which dry and somewhat moist ammonium chloride have the same vapour pressure, though in the first case the partial dissociation of the vapour in ammonia and hydrochloric acid does not take place. Prof. ABEGG, in whose laboratory these experiments were carried out, considered this fact as in contradiction with our views on chemical equilibrium phenomena [4]). In the discussion of these experiments I proved before that JOHNSON's experiment leads to the conclusion that the thermodynamic potentials of the solid substance in dry and moist state are different [5]); I did not venture, then, however, to give an explanation of this difference in thermodynamic potential; especially as the occurrence of allotropy for NH_4Cl was not known to me then, and even though NH_4Cl were allotropic, the connection with JOHNSON's experiment would require a separate proof. Besides the possibility did not seem excluded

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[1]) ZEEMAN and HOOGENBOOM, These Proc. XIV, p. 558 and 786 XV, p. 178.

[2]) WALLACE l. c.

[3]) JOHNSON, Zeitschr. f physik. Chemie **61**. 457. (1908)

[4]) ABEGG, Zeitschr f. physik. Chemie **61**. 455 (1908).

[5]) SCHEFFER, Dissertatie Amsterdam 1909. Zeitschr. f. physik. Chem. **72**. 451. (1910).

to me that the entropy would undergo a modification through the presence of some water as catalyst[1]). Before the publication of my thesis for the doctorate Prof. WEGSCHEIDER led by slightly different considerations, had pointed out that the explanation of JOHNSON's experiment might among others be found by the assumption of two modifications of the ammonium chloride[2]). When now WALLACE's paper came under my notice, and I learned from it that ammonium chloride shows enantiotropy, I have come to the conclusion in connection with the above that I could investigate the possibility of the explanation which Prof. WEGSCHEIDER considered the most probable. First of all I have repeated WALLACE's experiments for this purpose; it appeared to me already at the first thermical determination that really NH_4Cl is enantiotropic, but that the temperature of transition had to deviate appreciably from the value given by WALLACE. In what follows I will begin with a description of the experiments which I have carried out to define the point of transition of ammonium chloride as accurately as possible.

3. *Thermic determination of the point of transition of ammonium chloride.*

A test tube with ammonium chloride crystals was heated in an oil bath at about 200°, and then placed on cotton wool in a wider tube. Observation of the temperature every half minute showed the temperature to remain constant at about 174°. If I placed a tube at room temperature in the oilbath of 200°, again in an air jacket, then the temperature-time-curve appeared to exhibit a horizontal part about 187°. Repetition of these experiments at lower temperature of the oil bath and with use of a second oil bath for the cooling curves produced but little change in the temporary constancy of the temperature. We must therefore deduce from these observations that ammonium chloride possesses a point of transition between **174°** and **187°**, which is found too low on cooling and too high on heating, through the conversion of the modifications proceeding too slowly at the point of transition to consume the supplied heat immediately and to supply the removed heat immediately again. The point of transition could not be defined more accurately in consequence of this retardation of the conversion. These experiments, however, lead me to the conclusion that the temperature of **159°**, which WALLACE gives for the point of transition, is indeed, considerably too low.

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[1]) KOHNSTAMM and SCHEFFER, These Proc. XVII p. 789, (1910/11).

[2]) WEGSCHEIDER, Zeitschr. f. physik. Chemie. **65**. 97 (1908).

4. *Vapour pressure measurements.*

It follows from the observations of the vapour pressure of solid ammonium chloride through extrapolation that the detection of the transition temperature through observation of a discontinuity in the vapour pressure line would require an exceedingly accurate pressure measurement; the pressure at 180° only amounts to a few millimeters of mercury.

I have, therefore, tried to find a discontinuity in the three-phase line SLG of the system $NH_4Cl - H_2O$. For if we measure the vapour pressures of the saturate solutions, the transition temperature will remain unchanged, at least if the solid substance does not absorb water in appreciable quantities. The vapour pressure measurements, performed by means of Cailletet tube and air manometer according to the well-known method, yielded no break which could be demonstrated with certainty when the accuracy was about $^1/_{20}$ atm. As I however want these vapour pressure measurements for the determinations of § 5, I have inserted some of the found pressures in table 1.

TABLE 1.

Temperature	Pressure (in atmospheres)	Temperature	Pressure (in atmospheres)
160.0	3.25	185.7	5.4
164.9	3.6	189.1	5.8
171.2	4.1	194.5	6.4
176.9	4.6	198.9	6.9
182.5	5.1	199.6	7.0

5. *Determinations of the solubility of ammonium chloride in water at temperatures between* 160° *and* 205°.

Another method for the determination of the transition point is found in the determination of the discontinuity in the liquid branch of the above mentioned three phase line SLG in the system $NH_4Cl - H_2O$. It is known that the liquid points can only be determined by approximation directly by means of fused tubes. In a liquid point the system can namely exist entirely as liquid phase which is just saturate with solid substance, the pressure being exactly equal to that of the vapour which might coexist with the liquid phase. If we observe in a tube the vanishing point of the crystals, we determine the liquid point of a mixture indicated by the concentration of the liquid at the disappearance of the last crystals; we must, therefore, then think the vapour as removed. It is clear that the weighed quantities must then be corrected for the quantity of substance which is found in the vapour phase at the vanishing point. For this, volume and pressure of the vapour must be known. In the observation of the vanishing point the position of the meniscus was for this purpose indicated on the tube by means of a writing-diamond. The volume of the vapour, which practically consists of water here, as the vapour pressure of NH_4Cl is negligible at all the observed temperatures, was then measured after the tube had been cut open, with water from a burette. The pressure could be read from table I and then the quantity of water in the vapour could be calculated by the aid of the laws of BOYLE and GAYLUSSAC. On account of the deviation from the gas-laws this calculation is of course not quite accurate, but the correction being small, this method of determination is, after all, accurate enough for this purpose. It is, of course, necessary to take the vapour space as small as possible.

First the tubes were filled with ammonium chloride and weighed; then from a burette, a definite quantity of distilled water was added and brought into the tube through the capillary connecting tube and stem by repeated heating and cooling. The tube (of combustion glass) was then fused to in the lighting gas oxygen flame, and weighed again. The determinations marked by crosses in table 2, were carried out in tubes of from 25 to 30 grams; these were weighed down to half milligrams. In later determinations the weight of the tubes of about 15 grams was determined down to tenths of milligrams. As the weighing of the tubes can easily give rise to errors on account of the large surface, I think that less value is to be attached to the determinations marked with crosses than to the others. In the second and third columns of table 2 the weighed quantity of substance is given; the fourth column gives the observed vanishing points, which were determined in an oilbath, electrically heated by 220 Volts of alternate current, which was regulated by the insertion of incandescent lamps. Uniformity of temperature in the oilbath was ensured by rapid stirring. The fifth column gives the quantities of water in the vapour at the vanishing point calculated according to the above given method; the sixth column contains the corrected quantity of water; the seventh the quantity of grams of NH_4Cl to 100 grams of water in the liquid saturate with gas and solid substance. Finally the eighth column gives the value for — $\log x$, in which x represents the number of molecules of NH_4Cl present in one mol. of the mixture. Hence x is given by:

$$x = \frac{\frac{g}{M_{NH_4Cl}}}{\frac{g}{M_{NH_4Cl}} + \frac{100}{M_{H_2O}}} = \frac{g}{g+297.0},$$

in which g represents the values of the seventh column.

To set forth the discontinuity in the solubility line under vapour

TABLE 2.

Vanishing points of the solid substance in NH_4Cl H_2O mixtures
$M_{NH_4Cl} = 53.50$; $M_{H_2O} = 18.016$.

N⁰.	Weight		t	Weight water in vapour	Weight water (corr.)	Grams of NH_4Cl to 100 grams of H_2O (g)	$log\,x$	$10^3 \frac{1}{T}$
	NH_4Cl	H_2O						
1	1942.8	1539.8	162.9	1.0	1538.8	126.2^{6}	0.5253^{4}	2.294^{1}
2 ×	1634.0	1271.0	165.65	3.5	1267.5	128.9^{1}	0.5190^{6}	2.279^{7}
3	2463.4	1853.7	169.5	0.9	1852.8	132.9^{5}	0.5097^{3}	2.259^{9}
4	2293.8	1696.0	172.0	1.9	1694.1	135.4^{0}	0.5042^{7}	2.247^{2}
5	2444.7	1748.0	176.1	1.7	1746.3	139.9^{9}	0.4943^{7}	2.226^{7}
6 ×	1638.0	1163.5	177.2	4.0	1159.5	141.2^{7}	0.4916^{9}	2.221^{2}
7	2087.1	1464.6	178.55	3.0	1461.6	142.7^{9}	0.4885^{5}	2.214^{6}
8	2189.5	1533.6	178.95	3.1	1530.5	143.0^{6}	0.4879^{9}	2.212^{6}
9 ×	1399.0	961 5	181.05	3.5	958.0	146.0^{3}	0.4819^{9}	2.202^{4}
10 ×	1424.0	973.0	181.75	4.5	968.5	147.0^{3}	0.4800^{0}	2.199^{0}
11	2479.5	1695.2	182.2	0.6	1694.6	146.3^{2}	0.4814^{2}	2.196^{8}
12 ×	1838.0	1246.0	183.05	3 5	1242.5	147.9^{3}	0.4782^{3}	2.192^{8}
13 ×	1917.5	1285.5	184.55	3.5	1282.0	149.5^{7}	0.4750^{5}	2.185^{5}
14 ×	1621.5	1070.0	187.3	4.0	1066.0	152.1^{1}	0.4701^{9}	2.172^{5}
15	2309.9	1520.2	187.9	1.2	1519.0	152.0^{7}	0.4702^{7}	2.169^{7}
16 ×	1525.0	998.5	189.1	5 0	993.5	153.5^{0}	0.4675^{8}	2.164^{0}
17	2169.6	1409.5	190.15	2.0	1407.5	154.1^{5}	0.4663^{8}	2.159^{1}
18	2336.1	1505 8	191.7	1.7	1504.1	155.3^{1}	0.4642^{4}	2.151^{9}
19	2510.4	1592.4	194.7	2.7	1589.7	157.9^{1}	0.4595^{2}	2.138^{1}
20	2421.1	1502.2	199.1	2.4	1499.8	161.4^{3}	0.4532^{9}	2.118^{2}
21	2556.6	1574.0	200.5	2.1	1571.9	162.6^{4}	0.4511^{9}	2.111^{9}
22	2246.2	1351.5	205.0	4.4	1347.1	166.7^{4}	0.4442^{3}	2.092^{0}

pressure as clearly as possible I have not considered the solubility as function of the temperature, but led by the theoretical expression for the solubility curve in its simplest shape:

$$\log x = \frac{a}{T} + b\,,$$

I have calculated the values of $\log x$ and $\frac{1}{T}$ (eighth and ninth columns of table 2), and drawn them as ordinate and abscissa in the graphical representation (fig. 1). The temperature range being small here I

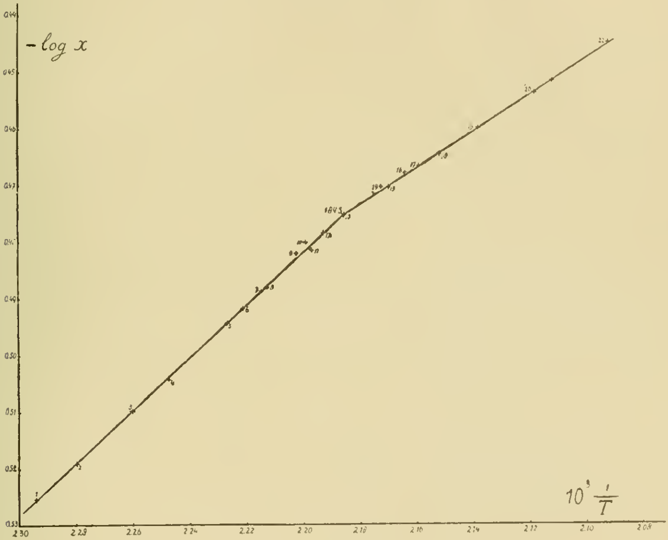

Fig. 1.

expected the above expression to account satisfactorily for the observations; the observations below and those above the transition point will present a straight line in this case. It appears from the graphical representation that really two straight lines can be drawn through the observed points so that the deviations occur irregularly on either side of these lines; at the same time in the tracing of these lines the probably smaller accuracy of the first determinations has been taken into account. I have calculated the values of a and b for both lines from the graphical representation; the equations of the lines drawn are:

$$-\log x = \frac{464.5}{T} - 0.5400 \text{ (below the transition point) and}$$

$$-\log x = \frac{327.8}{T} - 0.2412 \text{ (above the transition point).}$$

To get an idea of the extent of the experimental errors I have compared the values of g calculated according to the above expressions in table 3 with the values of the seventh column of table 2. It will be clear from the last column of table 3 that the agreement

TABLE 3.

N⁰.	t	Number of grams of NH_4Cl to 100 grams of H_2O.		Error
		calculated	found	
1	162.9	126.1^{5}	126.2^{6}	$+0.1^{1}$
2 ×	165.65	128.9^{5}	128.9^{1}	-0.0^{4}
3	169.5	132.9^{5}	132.9^{5}	0.0
4	172.0	135.6^{1}	135.4^{0}	-0.2^{1}
5	176.1	140.0^{3}	139.9^{9}	-0.0^{4}
6 ×	177.2	141.2^{4}	141.2^{7}	$+0.0^{3}$
7	178.55	142.7^{3}	142.7^{9}	$+0.0^{6}$
8	178.95	143.1^{7}	143.0^{6}	-0.1^{1}
9 ×	181.05	145.5^{2}	146.0^{3}	$+0.5^{1}$
10 ×	181.75	146.3^{1}	147.0^{3}	$+0.7^{2}$
11	182.2	146.8^{2}	146.3^{2}	-0.5^{0}
12 ×	183.05	147.7^{8}	147.9^{3}	$+0.1^{5}$
13 ×	184.55	149.4^{8}	149.5^{7}	$+0.0^{9}$
14 ×	187.3	151.7^{2}	152.1^{1}	$+0.3^{9}$
15	187.9	152.2^{1}	152.0^{7}	-0.1^{4}
16 ×	189.1	153.1^{9}	153.5^{0}	$+0.3^{1}$
17	190.15	154.0^{6}	154.1^{5}	$+0.0^{9}$
18	191.7	155.3^{3}	155.3^{1}	-0.0^{2}
19	194.7	157.8^{2}	157.9^{1}	$+0.0^{9}$
20	199.1	161.5^{2}	161.4^{3}	-0.0^{9}
21	200.5	162.7^{0}	162.6^{4}	-0.0^{6}
22	205.0	166.5^{4}	166.7^{4}	$+0.2^{0}$

is satisfactory; the maximum error in the value of g amounts to $5^0/_{00}$; for 14 of the 22 observations the deviation is even smaller than $1^0/_{00}$.

When we calculate the point of intersection of the two lines, we find **184.5°** for the transition temperature. In my opinion this value can only depart a few tenths of degrees from the real point of transition.

In these experiments the transition point could not directly be determined optically; I have thought only a few times that I could detect a difference in the appearance of the crystals above and below the transition point.

6. *Thermic determination of the transition point of ammonium chloride by means of catalysts.*

After the determination of the transition point from the solubilities in water I have resumed the original thermic determinations, and I have tried to find catalysts which can annul the retardation in the conversion at the point of transition. For this purpose I have looked for substances which are liquid at the transition point, and of which it could be expected that they react only little, if at all, to ammonium chloride. The number of available substances is not large; glycerine is very suitable for this purpose. A quantity of ammonium chloride was uniformly moistened in a mortar with a few drops of glycerine, and conveyed to a test tube. By placing this in an oilbath above the point of transition and then in a bath

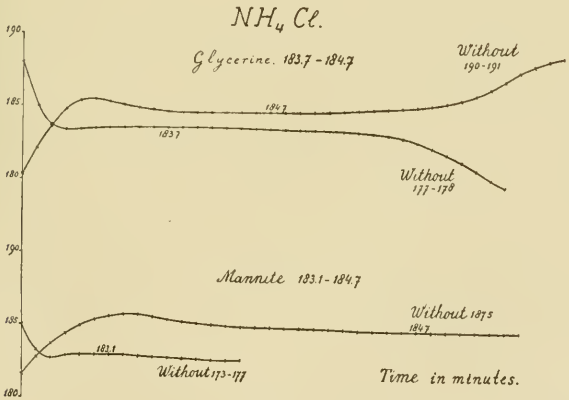

Fig. 2.

below this point I have determined a series of heating and cooling curves, the best examples of which are represented in the graphical representation (fig. 2). Descending we found **183°.7**, rising **184.°7.** At the same time it will appear from the graphical representation that the curves exhibit resp. a minimum and a maximum, which points to this that the conversion at first proceeds only slowly, but soon becomes constant so that the supplied resp. discharged heat and the thermal effect of the conversion compensate each other.

A second couple of curves, for which mannite acts as catalyst, presents only little more diverging values. Also the results of a few more substances used are reported in table 4.

TABLE 4.

Catalyst	Descending (max.)	Rising (min).
Glycerine	183.7	184.7
Mannite	183.1	184.7
Resorcin	183.3	185.4
Paraffin	179.9	185.75
Diphenylamine	179.95	186.3

It is clear that the catalysts counteract the retardation in the conversion of the solid substance in a more or less degree, and that this is particularly the case for glycerine and mannite, where the limits for the point of transition from 13° (see § 3) to 1°, resp. 1°.6 have contracted. Moreover it appears that the retardation in the conversion without catalysts is much smaller in case of heating than in case of cooling. If, however, we imagine that also when catalysts are used this difference in retardation continues relatively to exist, then the point of transition would be calculated at **184.5°** in the experiment with glycerine, at **184.4°** in that with mannite, in perfect harmony with the experiments of § 5.

7. Accordingly the experiments of § 5 and 6 yield the result that the point of transition of ammonium chloride has been fixed at **184.5°** with a possible error of a few tenths of a degree. The value given by Wallace (see § 1) is therefore more than 25° too low.

8. *Demonstration of the allotropy of ammonium chloride.* The transition from the β- into the α-form cannot be demonstrated by crystallisation of an aqueous solution under atmospheric pressure,

as the transition point lies too far above the boiling point, so that the β-crystals cannot be obtained metastable from these solutions either. I have, therefore, tried to make the transition suitable for demonstration by crystallisation from another solvent. The experiments of § 6 led me to surmise that glycerine would be suitable for this. If on an object glass we evaporise a solution saturated at the ordinary temperature to initial crystallisation, and if then we place the object glass under the microscope, we can clearly observe the cubi deposited in the heat. After some time a transformation then takes place, which propagates through the solid mass, and at the same time we see crystal skeletons of the known shape appear from the cubi. I have been able to demonstrate this transition by means of microscopic projection at the latest Physical and Medical Congress. The demonstration is still easier to carry out with ammonium bromide, as the point of transition lies at still lower temperature here, which I shall show in a following paper. The phenomena are entirely the same for ammonium chloride and bromide.

9. *Allotropy or isomery.* The phenomena which are explained by the assumption of more kinds of molecules, are expressed by a great number of names in the literature. Among these phenomena the occurrence of a substance in several solid phases will also often, if not always, have to be reckoned. In organic chemistry we have, namely, many examples of substances which can occur in two or more solid states, to which different molecular structure is assigned (tautomery, desmotropy). In § 1 I discussed an indication for the occurrence of two kinds of molecules also for ammonium chloride.

A rational collective name for the occurrence of more than one kind of molecules and more than one solid phase has however not yet been adopted, and yet this seems very desirable. The advantage lies in this that general thermodynamical relations (for homogeneous and heterogeneous equilibria) hold for both phenomena, which equations are therefore independent of the more subtle differences in structure of the molecules. Thermodynamically desmotropy, tautomery, isomery, metamery, allelotropy, pseudomery etc. etc. are namely perfectly equivalent, at least for so far as they refer resp. to homogeneous or heterogeneous states. If we consider which of the available denominations is suitable as a collective name, only allotropy and isomery present themselves for consideration in my opinion. The word isomery, however, is pretty generally current for the occurrence of molecules of equal molecular weight, which differ only in way of binding. There is no objection in my opinion to the use of allotropy as a collective name. This word is generally only used when elements occur in more than one solid state; that this word should also be used for compounds is only an advantage, for there is no reason whatever to assume an essential difference for the phenomenon for elements and compounds. Besides we find allotropy used already several times for compounds; moreover we find it already applied to non-solid states; thus oxygen is often called allotropic, when the occurrence of oxygen as ozone and ordinary oxygen is referred to.

Why then should not we generally indicate the occurrence of different kinds of molecules by allotropy? In this sense it was already used by Prof. SMITS in his theoretical considerations. Rationally the occurrence of two or more solid states is then to be called *phase-allotropy*, the occurrence of more kinds of molecules *molecular-allotropy*. Phase allotropy will then in virtue of the above often, if not always, find its ground in molecular allotropy [1]).

Nothing is known of structure and size of the molecules in solid state for ammonium chloride. In connection with the above this sufficiently justifies the choice of the title of this paper in my opinion.

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the University of Amsterdam.

Physics. — "*Isothermals of di-atomic substances and their binary mixtures. XVII. Preliminary measurements concerning the isothermal of hydrogen at* 20° *C. from* 60 *to* 90 *atmospheres*". By H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST. (Comm. 146*a* from the Physical Laboratory at Leiden).

(Communicated in the meeting of June 26, 1915).

1. *Introduction.* For a long time it has been the intention to extend the determination of isothermals of gases at low temperatures to pressures beyond the limit of 60 atmospheres, which had been fixed in the first stage of the Leiden investigations. In Communication 106 (April 1908) mention was made of a first step taken towards the realisation of that project.

On the basis of the data concerning the tensile strength of glass, published on that occasion, (about) fifteen manometer-tubes had been constructed, by which the divided open manometer (Comm. 44) could be extended in such a manner, that the entire height of mercury would correspond to a pressure of 120 atmospheres. These

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[1]) SMITS Zeitschr. f. physik. Chemie. 89 257 (1915).

high-pressure tubes with the boards to which they are attached were fitted to a wall of the working room, which also contains the standard-gauge of 60 atmospheres, in the same manner as the tubes of the latter. Originally it was intended (comp. Comm. 106) to fit up this wall with similar auxiliary apparatus as belong to the manometer-tubes of the 60 atmospheres-gauge, such as: pressure-connections to join the different manometer-tubes in series and to bring up the pressure, measuring rods suspended in cardanic rings beside the manometer-tubes used for measuring the height of the mercury columns, etc. It was further the intention to set up telescopes with which to take the readings on the new tubes in the same manner as with the standard-gauge of 60 atmospheres and finally to connect together all the tubes to one gauge of 120 atmospheres.

Want of room in the laboratory, however, prevented the execution of this plan; it would have been necessary to reserve the working-room completely for the gauges, which it was impossible to do. For this reason it was resolved in the measurements above 60 atmospheres to proceed by an indirect method.

For measurements in the pressure-range in question a standard-differential-manometer was constructed consisting of as many tubes for pressures above 60 atmospheres as would be necessary to supplement a pressure of about 60 atmospheres to the highest pressure to be measured. To obtain this differential gauge use is made of the same auxiliary apparatus, as serves for the measurements below 60 atmospheres, pressure-connections, taps, measuring-rods, telescopes, etc. but the tubes used for measuring pressures below 60 atmospheres are replaced by the desired number of high pressure tubes, which are mounted in the place of the former. The high-pressure tubes are joined to the system of pressure-connections and connected up in series in the same manner as with the divided open gauge and the pressures are regulated in such a manner, that in the upper space of the first tube of the series the pressure is about 60 atmospheres, and that the mercury-surface in the lower space of the last tube is subjected to the pressure to be measured. The pressure of about 60 atmospheres in the upper space of the first tube of the series is measured with a subsidiary manometer, which only serves as a pressure-indicator, the readings of which give the pressure in absolute measure by a calibration with the open standard gauge of 60 atmospheres.

If a pressure-indicator is available of sufficient accuracy for pressures of about 60 atmospheres, this method has the advantage, that the number of mercury-surfaces which have to be read becomes much smaller and that thereby the time required for a complete measurement is considerably shortened, which will as a rule increase the accuracy of a measurement, specially in view of the constancy of the room-temperature. The indicator used by us was the closed working manometer going from 20 to 60 atmospheres which was referred to in Comm. 78 and 97*a* and which we shall call M_{60}. Its accuracy at 60 atmospheres can be put at about $\frac{1}{4000}$.

At the time when Comm. 106 was published some progress had been made beyond the condition described in Comm. 100, not only with the pressure-measurement, but also with the arrangement of the further apparatus required for the higher pressures. This progress especially concerns a new auxiliary manometer, a closed hydrogen-manometer of very nearly the same model as M_{60}, but arranged for the pressure-range of 60—120 atmospheres. This manometer which we shall call M_{120} is represented diagrammatically in Plate I of communication 146*c*. M_{60} will similarly be found represented as *C* in Pl. I of Comm. 97*a* fig. 1. Both are constructed according to the system described in communication 50. M_{120} has a vessel twice as large a M_{60}.

When the pressure-cylinders in the apparatus of Comm. 50 were made, the MANNESMANN-process was not yet available. It was utilized, however, in the construction of M_{120} and the pressure-cylinder can thus stand a much higher pressure. There is moreover an improvement in the mounting of the manometer, which consists principally in the mercury entering the cylinder from below, as in the closed manometers described in Comm. 50. The mounting is for the rest in every respect similar to that of the pressure-cylinder, represented in fig. 3 Plate I Comm. 97*a*.

The measuring tube of the manometer had been calibrated with great care by Dr. C. BRAAK. We completed the manometer and filled it with distilled hydrogen (Comm. 94*f*, XIV). For its further arrangement and the method of using it in the experiments we may refer to previous communications.

By means of the completed apparatus it was possible to carry out the calibration of M_{120} with the standardmanometer and obtain data in connection with the question which interested us more particularly as to whether AMAGAT's observations which only start at 100 atmospheres would join on properly to accurate measurements with the open gauge. SCHALKWIJK's measurements with the aid of the same open gauge and the accurate piezometers of Comm. 50 had given rise to some doubt on this point (comp. Comm. 70 cont. towards the end). But as those measurements had not gone beyond

60 atmospheres, it was quite possible, that the extrapolation on which the above conclusion was based would turn out to be impermissible.

It had been our intention to carry the calibration of a working-manometer for pressures above 60 atmospheres and the determination of the isothermals of hydrogen at 20° C. up to 100 atmospheres. But when we had reached 90 atmospheres the connections in the pressure-system turned out less perfectly tight as was desirable. The mercury-surfaces were not completely still and to attain this it appeared necessary to affect certain improvements. But it was not till 1915 that these were carried out (comp. next Comm. 146*b*). Soon after the measurements mentioned above which were made in 1911, our work was interrupted by the departure of one of us and remained thus confined to a few preliminary determinations which do not extend beyond 90 atmospheres.

2. *Arrangement of the divided open gauge for measurements from 60 to 100 atmospheres.* The connections of the apparatus, already roughly indicated in section 1, are shown in the Plate belonging to Comm. 146*c* (these Proceedings below p. 472).

The figure differs from the earlier representation of the gauge by the manner in which the tubes of the open gauge which had now to serve for the measurement of 60 to 100 atmospheres are joined up: the same arrangement has been used in the measurements of the next communication. As will be seen, the first five tubes have been left intact, while the remaining tubes were replaced by tubes of greater wall-strength, destined for pressures from 60 to 100 atmospheres and tested to a pressure double of what they are intended to be used at.

This arrangement has the advantage that the first five tubes which go up to 20 atmospheres remain available as a separate open gauge, and this is necessary, because they are not only used as a standard-manometer, but also regularly as working-manometer for the range below 20 atmospheres and in this respect supplement the manometer which we have described in previous communications, going from 20 to 60 atmospheres, which above we called M_{60}. In the open gauge up to 20 atmospheres, M_{60} and M_{120} we thus possess a set of three manometers which embrace the whole range of pressure, through which the isothermals at low temperatures are measured in the Leiden-Laboratory at the present time.

The steel capillary on the left of tube B_5 which normally is coupled to the T-piece T_5 is now connected to a tube which through the stop-cock K_{18} puts B_5 into communication with the manometer M_{60}. To begin with, when the pressure is first admitted, the stop-cocks K_6 K_{19}, K_{22}, K_{23}, K_{27}, K_{28}, K_{32}, K_{34}—K_{37} are all open and the pressure is raised to about 60 atmospheres, when the mercury in M_{60} will rise very nearly to the top, whereas the mercury surfaces in the open gauge will remain where they are. K_{36} is then closed and the pressure is further raised, whereby the mercury in the manometer-tubes goes up in the usual way and thus indicates the excess of the pressure above the pressure of about 60 atmospheres, which is read on M_{60}. In this manner the tubes B_5 etc. are put in series behind M_{60} as indicated in section 1. Further details of the arrangement will be sufficiently clear from an inspection of the Plate without any further description.

If it is desirable to be able to use the two parts of the open gauge simultaneously, viz. the first five tubes as open gauge up to 20 atmospheres and the next ten as differential manometer from 60 to 100, or also to connect them up into a single open gauge from 0—60 atmospheres, this is easily attained by means of a side connection to the pressure-cylinder with T-piece and two stop-cocks at the branching-point, as was actually the case in our experiments.

With the above arrangement of the manometer it was impossible to go beyond 100 atmospheres. In order to continue the measurement in a similar way, the open gauge of 20 atmospheres remaining available, it will be necessary to have a new index-manometer on which 100 atmospheres may be read to replace M_{60}, with the addition of five suitable tubes to be joined up as a differential manometer for the difference between 100 and 120 atmospheres.

3. *The normal volume.* As mentioned above, the reading-tube of the manometer had been carefully calibrated. The comparison with the open standard-gauge could therefore serve at the same time as a determination of the isothermal of hydrogen at 20° C.

It was even possible to determine accurately the normal volume before and after the compression, because the vessel of the manometer (of the pattern of Comm. 50) is provided at its lower end with a small U-tube, also calibrated and containing the mercury which closes the tube, when it is not immersed in the mercury of the pressure-cylinder.

At the same time in our experiments this was not done. In a first determination of the isothermal of hydrogen from 60 to 100 atmospheres we thought ourselves justified in using an indirect determination of the normal volume, obtained by calculation from a reading of M_{120} at a pressure which was also read on M_{60} and therefore accurately known through the direct comparison with the open standard-gauge. For this calculation the formula is available which represents SCHALKWIJK's observations within the limits of their accuracy (Comm. 70).

Three measurements were made yielding the following data. The deviations from the mean are not higher than $\frac{1}{3300}$. The result may certainly be called satisfactory, considering that M_{60} gives the pressure in this case with an accuracy of $\frac{1}{4000}$, as was confirmed moreover by a special comparison with the open gauge of 0—60, and that the reading of the volume in M_{120} was not more accurate than to about 1 part in 10000. The mean was therefore taken as the normal volume.

TABLE I.

Date	V_{20}	p	Normal vol.
13 Febr. 1911	1.76969 c.M^3	62.504 atm.	99.568 c.M^3
21 „ „	1.76633 „	62.802 „	99.601 „
22 „ „	1.76017 „	63.039 „	99.618 „
		Mean	99.596 „

4. *Results.* Only one series of measurements was made. The calculation for M_{60} and for the open gauge were exactly as formerly. The only point to be mentioned is, that the corrections for the weight of the air-columns of the open gauge were calculated using the densities as given in the tables which BRINKMAN deduced from AMAGAT's observations. (Comp. also Comm. 146*c*). Table II (p. 468) gives the results of the measurements.

The deviations from the values which would follow from SCHALKWIJK's formula are all with the exception of the first in the same direction. Except in the doubtful observation corresponding to the density 80, the deviation is only about 1 in 1500, the mean positive deviation (leaving out of account the observation at $d_A = 80$) 0.0003 falls on the limit of what may be considered as established, considering the degree of accuracy of the observations. The fifth column of Table II contains for the highest pressures the values according to the formula which was calculated from the series in Comm. 70 derived from AMAGAT's observations and given by SCHALKWIJK at

TABLE II.

Isothermals of hydrogen at 20° C.

d_A	p	$pv_A(W)$	$pv_{A.\text{Schalkwijk}}$	$pv_{A.\text{ Amagat}}$
60.120	67.101	1.11610	1.11625	
64.059	71.729	1.11966	1.11936	
67.507	75.797	1.12281	1.12211	
70.531	79.344	1.12494	1.12454	
73.853	83.266	1.12746	1.12723	
77.470	87.580	1.13043	1.13017	1.13227
[79.852	90.509	1.13349	1.13213	1.13425]

the end of Comm. 70. No great value can be ascribed to the extrapolation by means of this formula, which is valid for pressures above 100 atmospheres from 100 down to 60 atmospheres, but in the neighbourhood of 90 atmospheres the formula probably represents correctly to one or two parts in a thousand what would follow from Amagat's observations.

Leaving out of account the observation at 90 atmospheres on the ground of a priori doubt as to its accuracy, although from the next communication it will appear, that it is really affected by a much smaller error than the others and that it would lead to a different conclusion, our results would seem to show, that an extrapolation above 60 atmospheres with Schalkwijk's formula calculated for 4 to 60 atmospheres, although not giving the same accuracy in that region, is still sufficiently accurate to support the suggestion, that Amagat's value at 100 atmospheres is too high. The error would however be less than $\frac{1}{500}$, the amount deduced from Schalkwijk's formula.

Physics. — "*Isothermals of di-atomic substances and their binary mixtures. XVIII. The isothermal of hydrogen at* 20° *C. from* 60—100 *atmospheres.*" By H. KAMERLINGH ONNES, C. A. CROMMELIN and Miss E. I. SMID. (Communication 146*b* from the Physical Laboratory at Leiden).

(Communicated in the meeting of June 26, 1915).

1. *Introduction.* The measurements communicated in this paper are a revision and extension of those of the preceding communication. They are to be looked upon as a first part of a more accurate investigation to obtain a bridge between the accurate isothermal at 20° C. and between 4 and 60 atmospheres, determined by SCHALKWIJK[1]), and AMAGAT'S isothermals[2]), which only begin at 100 atmospheres.

Previous determinations by KAMERLINGH ONNES and HYNDMAN[3]) were made with the same ultimate aim in view. They were made with the piezometers for low temperatures and gave the same values as SCHALKWIJK'S measurements with the piezometers for ordinary temperature. On this ground measurements at 0° C. with the same piezometers for low temperatures could be undertaken with confidence. In the paper by KAMERLINGH ONNES and HYNDMAN quoted above a determination of the isothermal for 0° C. was published which was replaced by a more accurate one in a later communication[4]). It will be necessary to repeat the latter investigation and extend it to 100 atmospheres in order to obtain the desired connection with AMAGAT'S work. In addition it will be necessary to undertake a determination with SCHALKWIJK'S piezometer IV, provided with a vessel of twice the volume, and thus extending from 60 to 120 atmospheres; as a continuation of work with a somewhat different object, viz. the investigation of the isothermal of 20° C. arranged to reach a higher accuracy. For it will now also be our object to know this isothermal from 60 to 120 atmospheres with an accuracy of 1 in tenthousand.

In the mean time, while this investigation of the highest accuracy is still in abeyance, the necessary calibration of the working mano-

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[1]) J. C. SCHALKWIJK, These Proceedings 4, p. 107, 1901, Comm. 70 (cont.), Dissertation, Amsterdam, 1902.

[2]) E. H. AMAGAT. Ann. de chim. et de phys. (6). 29. p. 68, 505, 1893

[3]) H. KAMERLINGH ONNES and H. H. F. HYNDMAN, These Proc. 4. p. 761, 1902, Comm. 78.

[4]) H. KAMERLINGH ONNES and C. BRAAK, These Proc. 10, p 413, 1907, Comm. 100*a* and 100*b*. C. BRAAK, Dissertation, Leiden, 1907.

meter M_{120} with the open standard-gauge (as carried out in the preliminary measurements of the preceding communication) afforded an opportunity for measuring the isothermal of hydrogen at 20° C. up to 100 atmospheres, with an accuracy of 1 in 3000 or 4000, as required in the investigations with piezometers for low temperatures which will go up to 100 atmospheres and first of all in the investigation of the isothermal of 0° C. to 100 atmospheres mentioned above. The calibration of M_{120} also served as a link in the comparison of a pressure-balance of SCHAEFFER and BUDENBERG with the open standard-gauge which will be dealt with in the next communication 146*c*.

2. As regards the experimental method we can be short, as it is fully described in the preceding and in the next communication, the latter of which also containing a plate. We only mention, that we considered it advisable to compare once more the closed manometer M_{60} at a few pressures with the open gauge, seeing that several years had elapsed since the last comparison and that on one occasion a small change of the normal volume had been noticed.

Table I contains the results of this comparison, O. M. standing for "open manometer".

TABLE I. Comparison M_{60} with O. M.

Date	Series	N⁰.	O. M. in int. atm.	M_{60} in int. atm.	O. M.—M_{60} abs.	O. M.—M_{60} in $^0/_0$
29 Jan. 1915	II	1	24.100	24.103	— 0.003	— 0.013
29 Jan.	II	2	24.103	24.104	— 1	— 4
29 Jan.	III	2	39.955	39.957	— 2	— 5
30 Jan.	IV	2	60.151	60.142	+ 9	+ 15

In view of the accuracy of the two instruments it will be seen, that the correspondence which is obtained must be called completely satisfactory.

The method differed from that of the preliminary determination of the preceding communication by the normal volume of M_{120} being directly measured, in order to obtain a determination of the isothermal as independent as possible.

The results of these measurements were as follows:

Measurement I: 102.875 cc.
,, II: [102.817] ,,
,, III: 102.874 ,,

In taking the mean the second measurement was given half the weight of the other two, on the ground that it does not agree well with the others and that an irregularity must have occurred in it, as was also clearly shown by a discussion of the observed temperature, pressure and barometer in connection with each other. The mean was thus taken at 102.863 cc.

3. *Results.* These are collected in Table II. The pressures are given in international atmospheres (75.9488 cms. mercury at Leiden), in the densities (d_A) the normal density and in the volumes (v_A) the normal volume is taken as unit.

TABLE II.

Isothermal of hydrogen 20° C.

p	d_A	$p\,v_A$
65.247	58.500	1.11533
73.079	65.205	1.12075
77.363	68.826	1.12404
81.188	72.059	1.12670
85.133	75.374	1.12948
88.377	78.074	1.13198
92 677	81.660	1.13493
96.490	84.817	1.13765
100.336	87.979	1.14047

As regards the representation of these observations by a series with ascending powers of d_A[1]) the question arose as to whether they could be represented by SCHALKWIJK's formula for 4 to 60 atmospheres

$$pv_A = 1.07258 + 0.6671 \times 10^{-3}\, d_A + 0.993 \times 10^{-6}\, d_A{}^2$$

in other words, whether SCHALKWIJK's formula, which holds up to 60 atmospheres, could be extrapolated as far as 100.

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[1]) H. KAMERLINGH ONNES, These Proceedings 4, p. 175, 1901. Comm. N°. 71.

Table III contains the results of a comparison of our observations with SCHALKWIJK's formula:

TABLE III. Comparison with SCHALKWIJK's formula.

$pv_A(W)$	$pv_A(R)$	$W-R$ abs.	$W-R$ in %
1.11533	1.11499	+ 0.00034	+ 0.03
2075	2028	47	4
2404	2317	87	8
2670	2578	92	8
2948	2847	101	9
3198	3068	130	12
3493	3364	129	12
3765	3627	138	12
4047	3892	155	14

4. *Discussion.* As will be seen from Table III, the deviations from SCHALKWIJK's formula follow a very distinct systematic course; near 60 atmospheres they are still small, but at higher pressures they become much larger and largely exceed the limits of our accuracy.

In deducing a new formula we have assumed for A_{A0} 1) at 0° C. the value given by KAMERLINGH ONNES and BRAAK $A_{A0} = 0.99942$, which gives at 20° $A_{A20} = 1.07261$ and calculated B_A and C_A by the method of least squares from all the observations from 4 to 100 atmospheres, viz. those of SCHALKWIJK and those of this paper; the formula thus represents the isothermal of hydrogen of 20° from 4 to 100 atmospheres.

Table IV gives the deviations from this formula of SCHALKWIJK's observations, those of the preceding and those of the present communication.

The observations of the preceding communication have not been used in the calculation of the constants of the formula. They are however given in the Table. It has to be mentioned, that in the preceding communication the normal volume was calculated by means of SCHALKWIJK's formula, whereas now it seemed preferable to determine it with our own more final one. The figures are

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1) For the notation used for the virial-coefficients comp. Comm 71.

TABLE IV. Isothermal of hydrogen 20° C.
4—100 atm.

$$pv_A=1.07261+0.65712\times10^{-3}\ d_A+1.2926\times10^{-6}\ d_A$$

	pv_A (W)	pv_A (R)	$W-R$ abs.	$W-R$ in %
SCHALKWIJK.	1.07677	1.07676	+ 1.00001	0.00
	7797	7811	− 14	− 1
	7982	7970	+ 12	+ 1
	8160	8125	+ 35	+ 3
	8141	8138	+ 3	0
	8321	8295	+ 26	+ 2
	8383	8393	− 10	− 1
	8770	8719	+ 51	+ 5
	9023	9012	+ 11	+ 1
	9125	9108	+ 17	+ 2
	9318	9343	− 25	− 2
	9491	9517	− 26	− 2
	9636	9618	+ 18	+ 2
	1.10093	1.10110	− 18	− 2
	0647	0650	− 3	0
	1157	1186	− 29	− 3
K. ONNES, DORSMAN, HOLST	1.11636	1.11676	− 0.00040	− 0.04
	1992	1998	− 6	− 1
	2307	2284	+ 23	+ 2
	2520	2535	− 15	− 1
	2772	2816	− 44	− 4
	3069	3123	− 54	− 5
	3375	3329	+ 46	+ 4
K. ONNES, CROMMELIN, MISS SMID.	1.11533	1.11547	− 0.00014	− 0.01
	2075	2096	− 21	− 2
	2404	2396	+ 8	+ 1
	2670	2667	+ 3	0
	2948	2948	0	0
	3198	3179	+ 19	+ 2
	3493	3489	+ 4	0
	3765	3765	0	0
	4047	4042	+ 5	0

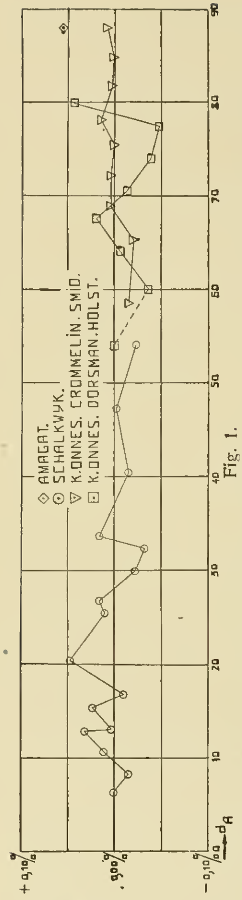

Fig. 1.

thus somewhat different to what would follow from Table II of the previous paper.

The deviations are graphically represented in fig. 1. It is very striking, how much the accuracy of the measurements has been increased since previous determinations. The circumstances under which they were carried out (very constant room-temperature, entire absence of leakages, etc.) were extremely favourable and, as great care was bestowed on the measurements, it appears that they have reached the full measure of accuracy of which they are capable.

The accuracy of $\frac{1}{5000}$ to $\frac{1}{10000}$, which would follow from the excellent agreement of our results with the formula can only be a relative accuracy in view of the uncertainty of the normal volume (see above). It must therefore be ascribed to an accidental concurrence of favourable circumstances, that the agreement with SCHALKWIJK's observations is so very close. As the matter stands, the portion of the isothermal determined by him is continued without any discontinuity by that of our experiments.

The figure also contains the value of pv_A for 20° C. and 100 atmospheres, which would follow from AMAGAT's observations according to the principles developed in Comm. 71 and which has been calculated by a formula given by SCHALKWIJK. The deviation of this value from that given by our formula is only 1 in 1000. This accordance with AMAGAT's observations may be called excellent, especially when we consider, that the calculation is as a matter of fact of the nature of an extrapolation, albeit one which exceeds the limits of the observation by very little only, as in AMAGAT's work the isothermal of 0° C. is the only one which goes down to 100 atmospheres. We can therefore now set aside the supposition, made before, that AMAGAT's value at 100 atmospheres might be too high by 1 in 500. This supposition was based on SCHALKWIJK's determinations up to

60 atmospheres and the measurements of the preceding paper going up to 90 atmospheres had not been able to refute it, although they tended to show, that the polynome of three terms by which SCHALKWIJK's pv_A had been represented using least squares did not hold accurately at the higher pressures. The agreement of 1 in 1000, with AMAGAT now obtained justifies the expectation that a determination of the isothermal of 0° C. at 100 atmospheres made with the degree of accuracy which we have now reached, will completely confirm AMAGAT's direct observation at this point. Our results are thus well qualified to confirm the high value of AMAGAT's excellent work.

It appears that in the series

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{{v_A}^2} + \frac{D_A}{{v_A}^4}$$

the term $\frac{D_A}{v^4}$ may be neglected. The value of B_A which follows from our results is in good agreement with the values calculated by KAMERLINGH ONNES and BRAAK and by SCHALKWIJK from their determinations of isothermals. If the various B_A-values are represented as a function of the temperature, they show only small deviations from the curve which may be drawn through them. The B_A-values according to AMAGAT are very considerably higher.

Whereas B_A thus agrees well with what was to be expected in connection with previous observations, it is otherwise with C_A. Judging by the C_A-values of KAMERLINGH ONNES and BRAAK at low temperatures and those according to AMAGAT at ordinary and higher temperatures, at 20° a value of C_A of about $0{,}6 \times 10^{-6}$ would be expected, whereas we find a value of C_A which is more than twice as high. It is less astonishing, that SCHALKWIJK's C_A viz. $0{,}993 \quad 10^{-6}$ is also considerably higher than what had to be expected, because at the highest density reached by him the value of the term $C_A {d_A}^2$ is no more than about 0,003, so that only a very small accuracy could be expected here; in our observations on the other hand the term $C_A {d_A}^2$ rises at the highest density to nearly 1°/₀ of pv_A, so that the accuracy, although still only small, might be expected to be many times higher.

We have in vain looked for errors in our observations, which might account for this unexpectedly high value of C_A. As mentioned above the observations were somewhat imperfect as regards the normal volume, for the rest they left nothing to be desired. Neither could the supposition of a small error having crept in the calibration of the top of the manometertube give an explanation, unless this error were supposed to have been of an amount entirely excluded by the measurements themselves. Naturally it might be questioned, whether the term in v_A^{-3} left out can represent the course of the isothermals in this region with an accuracy corresponding to the accuracy of the observations. The observations in this region are much more accurate than for the rest of the isothermals, the study of which as a whole led to the selection of the polynome in the given form for the purpose of representing the complete net of isothermals. The circumstance, that the deviations in the range below 60 atmospheres show a systematic change, may possibly be a sign, that the development which was chosen is actually not quite sufficient for the present purpose.

In a subsequent paper our observations will be discussed in connection with the further, fairly numerous observational data concerning the equation of state for hydrogen.

Physics. — "*Comparison of a pressure-balance of* SCHÄFFER *and* BUDENBERG *with the open standard-gauge of the Leiden Physical Laboratory between* 20 *and* 100 *atmospheres, as a contribution to the theory of the pressure-balance.*" By Dr. C. A. CROMMELIN and Miss E. I. SMID. (Comm. N°. 146*c* from the Physical Laboratory at Leiden).

(Communicated in the meeting of June 26, 1915).

1. *Introduction. Object of the investigation.* The measurements undertaken to extend the determination of the isothermal of hydrogen at ordinary temperature from 60 to 100 atmospheres, which are described in the preceding communication, afforded a welcome opportunity for carrying out a comparison planned a long time ago of the pressure-balance of SCHÄFFER and BUDENBERG with the open manometer of the Physical Laboratory at Leiden.

In the isothermal-determinations of gases under high pressure undertaken at Amsterdam by Prof. KOHNSTAMM with the apparatus belonging to the VAN DER WAALS-fund the pressure-measurements are based on the indications of a pressure-balance by SCHÄFFER and BUDENBERG, and the unit in which the volume of the gas in the observations under high pressures is expressed is also dependent upon the indications of a pressure-balance of that kind.

In fact this "normal volume" is derived by KOHNSTAMM and WALSTRA [1]) from the volume which corresponds to the pressure given by the pressure-balance according to the isothermal of hydrogen as determined by SCHALKWIJK [2]) at Leiden by means of the open manometer of KAMERLINGH ONNES [3]). In order to reduce the observed pressures and volumes in the investigations by KOHNSTAMM and WALSTRA to real pressures and volumes, which are required for the deduction of the equation of state, an investigation as to the real pressure, corresponding to a definite indication of the pressure-balance, is thus indispensable.

As the open manometer in question allows absolute pressure-measurements up to 120 atmospheres of great accuracy, a calibration of the small pressure-balance, used in the experiments of KOHNSTAMM and WALSTRA, would at any rate yield the normal volume belonging to the measurements at lower pressures.

Independently of the absolute calibration itself of the pressure-balance in the region explored, the comparison of this balance with the open gauge was also of great value for forming an estimate of the accuracy of the determination of the very high pressures. The desirability of such comparison was insisted upon by KOHNSTAMM and WALSTRA not long ago.

Of the theory of the pressure-balance only little is known and even that has not been at all adequately tested by experiment. Worst of all the experiments made so far do not confirm the theory. We are chiefly referring to E. WAGNER'S[4]) investigation, whose calculations about an AMAGAT-gauge are also mutatis mutandis applicable to a pressure-balance. WAGNER calculates the force which the cylinder of an AMAGAT-gauge experiences owing to the viscosity of the oil which flows through the narrow interspace between piston and cylinder and finds that this force cannot always be neglected in the practice of accurate measurements. In order to calculate the true pressure from the indications of the gauge a correction has to be applied to the latter, but since in the expression for the force, besides constants of the instrument, only the pressure occurs as a

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[1]) PH. KOHNSTAMM and K. W WALSTRA. These Proceedings 16. p. 754, 822. 1913 and 17 p. 203. 1914 and K. W. WALSTRA, Dissertation Amsterdam 1914, where also a description of the pressure-balance will be found.

[2]) J. C. SCHALKWIJK. These Proceedings 3. p. 421, 481 1901. Comm. 67 and Dissertation, Amsterdam, 1902.

[3]) H. KAMERLINGH ONNES. These Proceedings 1. p. 213. 1898. Comm. 44.

[4]) E. WAGNER, Dissertation. München, 1904 and Ann. d. Phys. (4) 15 p. 906, 1901. Comp. also G. KLEIN, Dissertation Techn. Hochsch. Berlin, 1909.

factor, the correction can be made to the sectional area on which the pressure acts; the area thus corrected, the "functional" area, is therefore according to WAGNER's theoretical deductions a constant for the instrument and naturally differs a little from the real area. WAGNER determined the functional area of his AMAGAT-gauge by means of experiments at low pressure, he also measured the real area and found the two exactly equal! This result is in contradiction with the theory, and, assuming WAGNER's experiments to be trustworthy, this would indicate, that the theory is not so simple and that there are possibly other factors which might influence the functional area, in which case it might very well happen that the functional area would turn out to be dependent on the pressure.

Before this matter can be cleared up, i.e. before a revised theory of the pressure-balance can be tested by experiment, it will be necessary to study the instrument as fully as possible from an experimental point of view, i.e. to compare its indications over as wide a range of pressures as possible with those of a standard-manometer and on the other hand to make very accurate measurements of the dimensions of its various parts. On the basis of these data it will then perhaps be possible to build up a more exact theory.

If it appeared that the functional area in accordance with WAGNER's theory were independent of the pressure over the whole range of comparison, one would be justified in extrapolating beyond the region, where the comparison with the open gauge is possible (i.e. above 120 atmospheres), and thus in calculating the actual pressure at 250 atmospheres from the indication of the balance with the same functional area as was found say at 100 atmospheres; the large pressure-balance of the VAN DER WAALS-fund which has a range from 250 to 5000 atmospheres could then be compared with the small balance at 250 atmospheres and in this manner the pressures on the isothermals of hydrogen measured by KOHNSTAMM and WALSTRA with both instruments could be corrected using the functional area thus determined.

So far we have not gone beyond 100 atmospheres with the comparison, as it was made in connection with the determination of the isothermal of 20° C. dealt with in the preceding communication. The range from 60 to 100 atmospheres gave sufficient data for the purposes of the investigation: they show the desirability of a further systematic investigation of various questions in connection with the theory of the pressure-balance; but this investigation can be carried out, independently of the apparatus in the possession of the laboratory. We resolved to defer the continuation of the measurements, which become more an more difficult as the pressure rises, until the above investigation should have been carried out.

2. *Experimental method.* A simultaneous reading of the open gauge and the pressure-balance turned out to be practically impossible. In fact in the pressure-balance the pressure in the oil-passages is only constant, while the piston with its weights is turning freely, and this motion does not continue longer than a few minutes at the utmost; when the rotation has come to a stop and the piston is again set in motion by hand, there are always, however carefully the operation is conducted, small vertical forces exerted on the piston which are propagated in the tubes as pressure-impulses and disturb the pressure-equilibrium. On the other hand the various readings on the open gauge require much more time than the two or three minutes which the pressure-balance, while left to itself, allows; in fact, when all the tubes are at the proper pressure, a complete reading carried out by two cooperating observers requires about three quarters of an hour.

A simultaneous reading of pressure-balance and open gauge being therefore attented with practically unsurmountable difficulties, we resolved to carry out the comparison through the intermediary of the two closed hydrogen-manometers of the Leiden-Laboratory M_{60} and M_{120}, the former of which has a range from 20 to 60 atmospheres, the latter from 60 to 120. We already will mention here, that this procedure did not impair the accuracy aimed at in any respect, as will moreover appear from the discussion in the next section.

The accompanying plate shows the open manometer *O. M.*, the two closed manometers M_{60} and M_{120} and the pressure-balance *D. B.* with its oil-forcing pump *O. P.* besides the connections and stopcocks by which the various apparatus are joined up together. The construction and method of working of the various gauges having been repeatedly described and represented need not be gone into on this occasion ¹).

A small complication arose in connection with the transmission

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¹) Open manometer: H. Kamerlingh Onnes. These Proceedings I. p. 213. 1898. Comm. 44, and J. C Schalkwijk Dissertation, Amsterdam 1902. H. Kamerlingh Onnes, C. Dorsman and G. Holst These Proc. Supra Comm. 146a. Manometer M_{60}: H. Kamerlingh Onnes and H. H. F. Hyndman, These Proceedings 4 p. 761. 1902, Comm. 78. § 17, H. Kamerlingh Onnes and C. Braak. These Proceedings 9 p. 754. 1906. Comm. 97a, § 3. Manometer M_{120}: These Proceedings Supra. Comm. 146a, 146b. Pressure-balance: Ph. Kohnstamm and K. W. Walstra l.l. c.c.

of the pressure from the oil-passages of the pressure-balance to the tubes of the Leiden-manometers, in which compressed air is always used for transmitting the pressure. This transmission was at first carried out by means of the steel tube D_1 with its level-gauge P_3. The level of the oil in it could be easily kept up at the desired height by the aid of the oil-pump *O. P.* When this arrangement had been in use for some time, it appeared that small changes of pressure in the oil of the pressure-balance, produced by the addition of small weights on the piston, were but very slowly and gradually transmitted to the manometers M_{60} and M_{120}; it was therefore desirable to transmit the pressure in the oil of the pressure-balance to the mercury of the closed gauges by means of tubes exclusively filled with liquid, eliminating all air connections. This arrangement could be easily applied to M_{120} by screwing a steel tube with a level-gauge P_1 to the tap K_{23} (the object proper of which is to fill the manometer with mercury, when being mounted). Beyond this gauge P_1 a second gauge P_2 was mounted and the latter was in connection with the oil-passages. Between the mercury in the lower half of P_1 and the oil in the upper half of P_2 the pressure was transmitted by means of glycerine.

Our procedure was to bring up the pressure at first in the usual manner with compressed air; if the stop-cock K_{20} was then opened and K_{27} and K_{28} closed, the pressure-transmission exclusively by means of liquids was realized. The pressure was further raised by means of the oil-pump. This arrangement completely answered our expectations: pressure-changes of $\frac{1}{10000}$ in the oil of the pressure-balance were now instantaneously indicated on M_{120}.

3. *Accuracy.* An opinion as to the accuracy which may be expected may be formed by giving some data respecting the absolute and relative accuracy of the indications of the various instruments.

The open manometer, when free of leakages and with a room-temperature which is carefully kept constant, gives with certainty an accuracy (absolute) of 0.01 °/₀.

The manometer M_{60}, if the reading is certain to 0.1 mm. — which is undoubtedly to be attained — guarantees

at 20 atmospheres an accuracy of 0.008 °/₀
,, 60 ,, ,, ,, ,, 0.020 °/₀

For the manometer M_{120} the following figures hold:

at 65 atmospheres an accuracy of 0.007 °/₀
,, 100 ,, ,, ,, ,, 0.016 °/₀

The accuracy given for the two closed manometers is not only a relative one, but for a large number of points an absolute one as well, seeing that both instruments have been directly compared with the open manometer at those points. As to the pressure-balance, neither with respect to the absolute nor to the relative accuracy was anything known with certainty at the beginning of our investigation. It had only been found, that the sensitivity of adjustment in the neighbourhood of a definite pressure is very high and certainly amounts to 0.02°/₀ or even 0.01°/₀. As an instance, the pressuretransmission through liquids being used, and the pressure-balance being loaded with 65 kilogrammes, the addition of 10 grammes to that load could be observed on M_{120} with absolute certainty. The data regarding the accuracy of the pressure-balance which we have now obtained by our investigation will be given further down, when the results are discussed.

4. *The calculations.* The reduction of the indications of the open manometer is very simple in principle; the various corrections, however, require some care, if an accuracy of 0.01 °/₀ is to be guaranteed. These corrections have all been fully discussed by SCHALKWIJK in his Dissertation, so that we may confine ourselves to a few remarks. The correction for the weight of the columns of compressed air, which transmit the pressure from each tube to the next, becomes considerable at the higher pressures. Instead of air hydrogen might be used[1]), which would yield a double advantage: in the first place the correction thereby becomes ten times smaller and secondly the isothermal for hydrogen at 20° is at present very accurately known up to 100 atmospheres[2]), so that the correction can be calculated with great accuracy. It is true, that this method requires very pure hydrogen being available, in order to be certain of the specific gravity, but at the present time hydrogen prepared in the cryogenic laboratory by distillation is so absolutely pure, that an influence on the specific gravity of traces of admixed air, which is relatively large, need not be feared. We have ascertained, however, that for pressures up to 100 atmospheres it is not yet necessary

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[1]) This method was recommended by H. KAMERLINGH ONNES in 1898; comp. These Proceedings 1, p. 213, 1898, Comm. N⁰. 44.

[2]) J. C. SCHALKWIJK, These Proceedings 3, p. 421, 481, 1901. Comm. N⁰. 67. These Proceedings 4, p. 23, 29, 35 1901, Comm. N⁰. 70, Dissertation, Amsterdam, 1902 H. KAMERLINGH ONNES, C. A. CROMMELIN and Miss. E. I. SMID, These Proceedings supra. Comm. N⁰. 146b. For the temperature correction compare the empirical equation of state of H. KAMERLINGH ONNES in the paper by J P. DALTON. These Proceedings 11, p. 863, 1909. Comm. N⁰. 109a.

to introduce this complication and we have therefore preferred to calculate the corrections for air.

For this purpose AMAGAT's[1]) isothermals are available which have been represented in different ways by equations by BRINKMAN[2]) and by KAMERLINGH ONNES[3]): from these equations tables of correction were drawn up. The corrections calculated by the two methods agree to 0.5 mm. even at 100 atmospheres. As will appear further down the results prove, that in this manner the correction is approximated with sufficient accuracy.

The correction for the compression of the mercury remains small, it is true, even at 100 atmospheres, but still comes into account. For this correction we have also calculated a table, based on the compressibility of 0.00000392 according to AMAGAT.

There was no need for a correction for the flow of the mercury through the tubes, fully discussed by SCHALKWIJK, as the mercury did not move at all. Thanks to the steel connecting tubes being *soldered* to the glass tubes, to the fibre-washers and to all the couplings being immersed in oil[4]) we succeeded in obtaining the open manometer completely free of leakages even at 100 atmospheres, while at the same time the room-temperature was kept constant so successfully (owing to steam-heating, improved illumination by metal-wire lamps, which give very little heat etc.) that even with the very lengthy readings at the higher pressures there was hardly any sign of flow in the tubes.

The corrections for capillary depression have not been applied. A discussion showed, that the algebraic sum of these corrections would have no influence on the accuracy aimed at, especially if by tapping the tubes care was taken to obtain well-shaped convex menisci[5]). As a matter of fact the correction would have been very difficult, seeing that with the illumination used the height of the menisci could not be determined with the telescopes which served for reading the mercury-surfaces.

The further corrections do not require any special mention. The method of reducing the indications of the manometers M_{60} and M_{120} do not call for any remarks either. As regards the load on the

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[1]) E. H. AMAGAT, Ann de chim. et de phys. (6) 29, Juni and Augustus 1893.

[2]) C. H. BRINKMAN, Dissertation, Amsterdam, 1904.

[3]) Zie J. P. DALTON, These Proceedings 11, p. 874, 1909 § 2 Comm. N⁰. 109c.

[4]) The oil-vessels in question are not shown in the somewhat diagrammatic figure. For some of the improvements mentioned here compare H. KAMERLINGH ONNES, These Proceedings 8, p. 75, 1905, Comm. N⁰. 94*b*.

[5]) Here again the results prove the reasoning to have been correct.

pressure-balance, it has to be kept in mind, that it consists of the total weight of piston and imposed weights, with the addition of the atmospheric pressure multiplied by the functional section.

The pressure of the atmosphere at Leiden is taken as equivalent to 75,9488 cms. mercury, one atmosphere being equal to 1,0336 kilogrammes.

5. *Measurements and results.* As explained in § 2 the measurements consisted in (1) a comparison of M_{60} and M_{120} with the open manometer, (2) a comparison of the pressure-balance with M_{60} and M_{120}.

We will first discuss the *measurements between* 20 *and* 60 *atmospheres carried out by means of* M_{60}.

Before undertaking the comparison of M_{60} with the pressure-balance we made sure by means of a comparison of M_{60} with the open manometer (fully described in the preceding communication), that the indications of the closed manometer still deserve the confidence which had always been given them in recent years. As shown in that communication the result of this comparison was, that since the last comparison[1]) a few years ago the closed manometer had not undergone any change.

The comparison of M_{60} with the pressure-balance was carried out as follows. The pressure having been adjusted at a chosen value, the pressure-balance was set in rotation and we waited, until the mercury-surface in M_{60} did not change any more. The pressure was in this case transmitted from air to oil and as the pressure-impulses which are due to the setting and keeping in motion of the pressure-balance are only very tardily propagated to M_{60}, it appeared possible to turn the pressure-balance without any modification of the position of the mercury-column being noticeable. A reading was taken, when the mercury-surface had been constant for a considerable time.

Table I gives the results of two series of measurements. For the measurements of June 22 the pressure-balance was once more carefully centred, as we thought that the adjustment had not been quite perfect.

The observations marked with an asterisk were calculated by means of SCHALKWIJK's isothermal and in these observations the manometer has thus not merely been used as an indicator. The concordance between the two kinds of observations appeared, however, to be so excellent, that it was considered unnecessary to establish

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[1]) These Proceedings supra, Comm N'. 146*b*, § 3.

the pressure by direct measurement with the open manometer for the points in question.

We now proceed to the *measurements from* 60 *to* 100 *atmospheres carried out by means of* M_{120}.

In this case we could not check the readings by means of the isothermal and the calibration, as the comparison of a few years ago[1]) did not appear to have fully given the desired accuracy; this was the reason, why it was repeated together with the present determinations and replaced by a new calibration[3]). In this region we have therefore made the comparison at a larger number of

TABLE I. Comparison pressure-balance with M_{60}.[2])

Date	N⁰.	Weights on pressure-balance in kilogrammes	Pressure according to M_{60} in kilogrammes per cm²., diminished by atm. pressure	Reciprocal functional section in cm^{-2}.	Functional section in cm².
6 Febr. 1915	I	21.650	21.729	1.0036	0.9964
	IX*	25.650	25.744	36	64
	II*	31.410	31.520	35	65
	VIII*	36.000	36.121	33	67
	III	41.760	41.895	32	68
	VII*	46.050	46.188	30	70
	IV*	50.130	50.269	28	72
	VI*	55.710	55.848	25	75
	V	61.300	61.445	24	76
22 June 1915	VIII*	25.000	25.089	1.0035	0.9965
	I*	30.000	30.086	28	72
	VII*	35.000	35.092	26	74
	II	40.000	40.114	28	72
	VI*	45.000	45.098	22	78
	III*	50.000	50.120	24	76
	V*	55.000	55.112	20	80
	IV	60.000	60.112	19	81

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[1]) These Proceedings Supra Comm. 146*a*.

[2]) The arrangement of the tables is somewhat different from that in the original Dutch publication.

[3]) These Proceedings Supra Comm 146*b*.

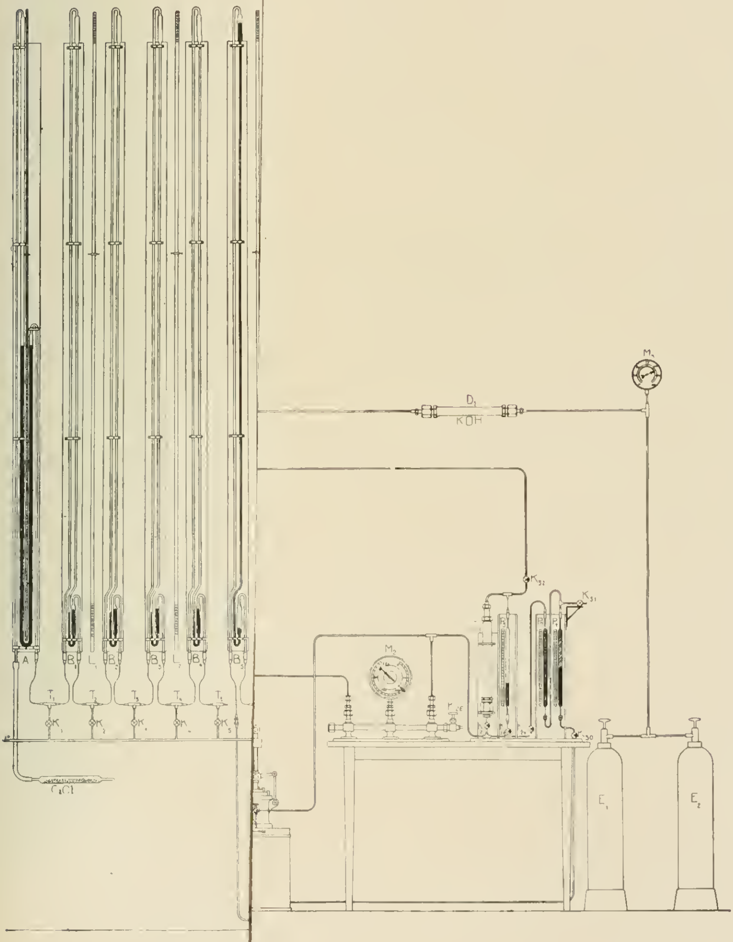
TABLE II. Comparison pressure-balance with M_{120}.

Date	N⁰.	Weights on pressure-balance in kilogrammes	Pressure according to M_{120} in kilogr. per cm^2., diminished by atm. pressure	Reciprocal functional section in cm^{-2}.	Functional section in cm^2.
27 March 1915	I	67.000	67.143	1.0021	0.9979
	II	71.050	71.210	22	78
	III	75.000	75.147	19	81
	IV	79.650	79.865	27	73
	V	83.500	83.729	27	73
	VI	87.550	87.795	28	72
	VII	91.050	91.291	26	74
	VIII	95.550	95.790	25	75
	IX	99.500	99.815	31	69
	X	103.500	103.884	37	63
29 March 1915	X	67.200	67.329	1.0019	0.9981
	IX	71.100	71.236	19	81
	VIII	75.100	75.248	19	81
	VII	79.600	79.776	22	78
	VI	83.050	83.329	33	67
	V	87.550	87.745	22	78
	IV	91.050	91.292	26	74
	III	95.450	95.694	25	75
	II	99.350	99.667	32	68
	I	103.350	103.686	32	68
24 June 1915	II	75.000	75.187	1.0025	0.9975
	VII	80.000	80.216	27	73
	III	85.000	85.234	27	73
	VIII	90.000	90.271	30	70
	IV	95.000	95.298	31	69
	IX	100 000	100.362	36	64

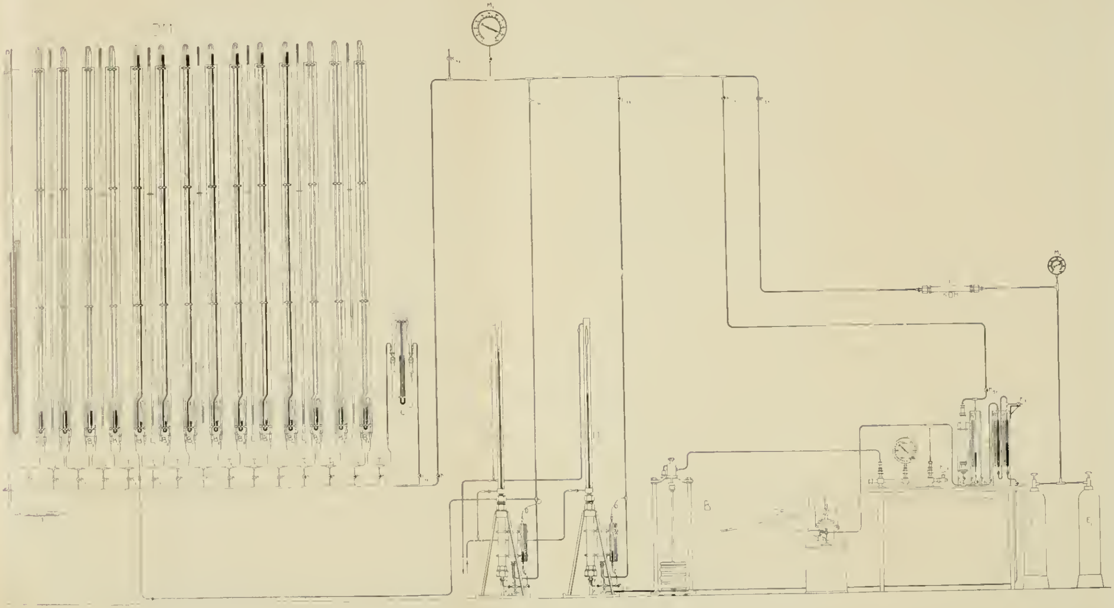
TABLE II continued. Comparison pressure-balance with M_{120}.

Date	N°.	Weights on pressure balance in kilogrammes	Pressure according to M_{120} in kilogr. per cm^2. diminished by atm. press.	Reciprocal functional section in cm^{-2}.	Functional section in cm^2.
23 April 1915	I	67.000	67.174	1.0026	0.9974
	II	71.000	71.212	29	71
	III	75.000	75.217	29	71
	IV	79.000	79.239	30	70
	V	83.000	83.268	32	68
	VI	87.000	87.263	30	70
	VII	91.000	91.294	32	68
	VIII	95.000	95.338	35	65
	IX	99.000	99.383	38	62
	X	103.000	103.406	39	61
24 April 1915	X	67.000	67.174	1.0026	0.9974
	IX	71.000	71.180	26	74
	VIII	75.000	75.229	30	70
	VII	79.000	79.259	32	68
	VI	83.000	83.272	32	68
	V	87.000	87.278	32	68
	IV	91.000	91.313	34	66
	III	95.000	95.328	34	66
	II	99.000	99.395	39	61
	I	103.000	103.423	41	59
18 June 1915	III	70.000	70.185	1.0026	0.9974
	IV	80.000	80.263	32	68
	V	90.000	90.295	32	68
	VI	100.000	100.390	39	61
18 June 1915	X	70.000	70.181	1.0025	0.9975
	IX	80.000	80.256	32	68
	VIII	90.000	90.301	33	67
	VII	100.000	100.360	36	64
19 June 1915	III	70.000	70.179	1.0025	0.9975
	IV	80.000	80.247	30	70
	V	90.000	90.286	31	69
	VI	100.000	100.375	37	63

C. A. CROMMELIN and e Leiden Physical Laboratory between 20 and 100
atmospheres, as a contrib



C. A. CROMMELIN and Miss E. I. SMID: "Comparison of a pressure-balance of Schäffer and Budenberg with the open standard-gauge of the Leiden Physical Laboratory between 20 and 100 atmospheres, as a contribution to the theory of the pressure-balance of S. and B".



points. After the completion of the investigation described in the preceding communication the various points could be each separately checked by a comparison with the isothermal deduced from the points combined. If the manometer had been filled with a different gas or an arbitrary mixture of gases, it would have served its purpose as an intermediary between pressure-balance and open manometer equally well.

Table II contains the results of the comparison of the pressure-balance with M_{120}, extending over the range from 60 to 100 atmospheres. The measurements of March 27 and 29 and June 24 were made with the air-liquid transmission of pressure, as had been those with M_{60}, whereas in those of April 23 and 24 and June 18 and 19 use was made of the liquid system mercury-glycerine-oil which was arranged later on as described in one of the preceding sections.

6. *Discussion.* The results of all the measurements as contained in the above tables lead to the following conclusions:

1. The functional section is not independent of the pressure, but as the pressure rises above 20 atmospheres it increases, goes through a greatest value at about 70 atmospheres and then diminishes with greater rapidity as far as the comparison reached. The greatest deviation is 0.0020.

2. When the determinations were repeated, the same value was not always found for the functional section, the greatest deviation being about 0.0005 in this case.

3. The functional section differs from the geometrical section as given by SCHÄFFER and BUDENBERG (1 cm^2) by about 0.0030.

4. The sensitivity of the pressure-balance $\frac{1}{10000}$ thus far exceeds its accuracy. If the latter is to be raised to the value of the sensibility, the theory of the instrument will have to be developed and means will have to be found to obtain constant results within the limits of the sensibility. Probably in order to attain this accuracy a pressure-balance will always directly or indirectly have to be compared with an open manometer.

5. Pressures which have been measured with a SCHÄFFER and BUDENBERG pressure-balance which has not been calibrated cannot at present be estimated at a higher accuracy than about $\frac{1}{400}$, provided that the error in the area of the piston is not larger than 0,1 $^0/_0$.

In conclusion we wish to thank Professor KAMERLINGH ONNES and Professor KOHNSTAMM for their sustained interest in our work.

Physics. — "*The specific heat at low temperatures. II. Measurements on the specific heat of copper between* 14 *and* 90° K." By W. H. Keesom and H. Kamerlingh Onnes. Communication N°. 147*a* from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes).

(Communicated in the meeting of June 26, 1915).

§ 1. In Comm. N°. 143 (Oct. 1914, These Proceedings Dec. 1914) § 6 we published a series of measurements on the specific heat of copper between 15 and 22° K. We have since made some improvements in the experimental arrangement, particularly as regards the resistance measurement for the purpose of the determination of the temperature increase in the calorimetric experiment. The determination of the "sensitivity" of the Thomson-bridge arrangement (cf. Comm. N°. 143 § 2) was made this time by shunting the standard resistance of 1 Ω (cf. Comm. N°. 143 Fig. 5) by a known resistance and reading the resulting galvanometer deflection. Irregularities as mentioned in Comm. N°. 143 § 4 note 1 did not occur now.

At a new calibration of the thermometer wire Au_{c3} it appeared not to have remained so constant, especially at liquid hydrogen temperatures, as at the time of the measurements of Comm. N°. 143 we concluded from determinations in liquid hydrogen on two different days (table I Comm. N°. 143), and also from the comparison of the result of a control measurement [1]) at the boiling point of oxygen on May 25 with the results of the measurements of May 18 1914. See table I.

Hence the resistance of the gold wire Au_{c3} [2]), which is enclosed in enamel between metal, appears to show small differences when brought to the same temperature at different times. This behaviour agrees with what has been experienced with wires sealed in glass: cf. Kamerlingh Onnes and Holst, Comm. N°. 141*a* § 4.

At liquid oxygen temperatures the differences are, however, so small, that for the calorimetric determination at these temperatures they are unimportant. At liquid hydrogen temperatures account has to be taken of these changes.

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[1]) This control measurement, which was not mentioned in Comm. N°. 143, gave:

	T	$W_{Au_{c3}}$
May 25 '14	90.45	3.6616

[2]) The preliminary treatment consisted in (cf. Comm. N°. 143 § 3 : glowing before the winding, then 6 times cooling in liquid air and allowing it to return to room temperature, likewise 2 times in liquid hydrogen.

TABLE I. Resistance of Au_{c3}.

N⁰.		T	W	Standard-thermometer	$\frac{W}{W_{\text{May '14}}}$
27 Febr. '15	II	14.10	0.6164	H_2 vapour pressure apparatus	1.0034
	III	16.97	0.6437		34
	I	20.41	0.6952		33
25 Febr. '15	II	56.94	2.0822	$Pt_{I'}$	
	III	60.65	2.2582		
	IV	68.65	2.6385		[1.0033] 2)
	V	77.93	3.0779		1.0010
	VI	86.41	3.4759		
	I	90.28	3.6550		0.9999
30 April '15	II	14.49	0.6188	$Pt_{I'}$ 1)	1.0023
	IV	16.97	0.6432		25
	III	18.49	0.6633		24
	I	20.49	0.6954^5		15
12 May '15	II	60.69	2.2580	$Pt_{I'}$ with changed zero resistance, calculated from the resistance of Pt_{1_2} at points III and IV.	
	III	68.77	2.6429		[1.0027] 2)
	IV	77.84	3.0718		1.0004
	I	89.89	3.6360		0.9997
	V	89.89	3.6368		0.9999

This was done for the measurements treated in this paper by determining for each series of measurements in liquid hydrogen a point of the scale of Au_{c3} with the aid of the temperature derived from the pressure of the liquid hydrogen bath 3).

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1) Checked by comparison with the temperatures calculated from the pressure of the bath.

2) It has appeared since that at this temperature the calibration of the auxiliary thermometers used in the measurement of May '14 was less accurate.

3) In table I it appears from the measurements of April 30 '15 that even in a single series of measurements at hydrogen temperatures small changes in Au_{c3} may occur. With a view to this fact we intend in future measurements to determine each time at least two points of the scale of Au_{c3}, viz. one at the boiling point and one at the melting point of hydrogen.

§ 2. *Heat capacity of the core K_{III}.* With a view to the irregularities which had occurred in the measurements of 1914 (Comm. N°. 143 § 4) this heat capacity was determined once more. In these measurements at a pressure of 75.6 cms. of the hydrogen bath, which corresponds to $T = 20.31$, $W_{Au_{t3}}$ was found equal to 0.6940 Ω, whereas according to the calibration of Febr. 27, '15 this resistance corresponds to $T = 20.34$. The difference between these two values of T corresponds to a displacement of the curve, which represents the heat capacity of K_{III} as a function of the temperature to an amount of 0.3 °/₀ of the heat capacity at 15° K., and to an appreciably smaller amount at 20° K. As this is far within the limit of accuracy reached in the measurements the calibrations of 25/27 Febr. '15 could be used for the calculation of the temperatures.

TABLE II. Heat capacity of the core K_{III}.

N⁰.		Mean temperature	Temperature increase	Heat capacity in joules/degree K.
27 Jan. '15	II	14.81^5	1.018	0.714
	III	15.07	1.174	0.732
	IV	15.87	1.227	0.822
	V	18.02	1.171	1.082
	VI	20.56	0.895	1.419
	1	20.86^5	1.005	1.488
	VII	25.40	0.856	2.29
	VIII	30.33	0.939	3.32^5
	IX	39.91	0.856	6.23
	X	49.91	0.736	9.43
28 Jan. '15	I	60.13	1.024	12.66
	II	61.04	0.993	12.73
	III	70.40	0.834	15.27
	IV	80.58	0.718	17.44
	V	81.10	0.701	17.95
	VI	89.01^5	0.768	19.45
	VII	89.57^5	0.758	19.49

The heat capacity appears to be a little smaller in the region of the liquid hydrogen temperatures in these measurements than at those of 1914, *viz.* 0.023 joules/degree at 15° K., and 0.038 joules degree at 20° K.[1])

This difference can be explained by the fact that for the measurements of 1915 on K_{II} for the wires which carry the heating current a little less platinum had been used. This circumstance was taken into account as far as possible.

§ 3. *Atomic heat of copper.*[2]) For the measurements the same block of copper was used as for those of Comm. N°. 143 § 6: electrolytic copper of Felten and Guillaume, 596,0 grammes.

As a check on the purity of the copper after the measurements a strip was cut from the block; the strip was filed to a rectangular section, then rolled and annealed. The resistance was then measured at room temperature and in liquid hydrogen[3]).

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[1]) The measurements of 1914 being corrected for the change of Au_c3.

[2]) The atomic heat of copper has already been measured between 23 and 88° K. by W. Nernst, Ann. d. Phys. (4) 36 (1911), p. 395.

[3]) We took advantage of this opportunity to test at the same time the purity of the lead which we had used for the measurements on this metal of Comm. N°. 143, and to investigate the influence of the treatment of the metal on the decrease of the resistance. The results are collected in the following table.

	$\frac{W_{20.36^\circ K}}{W_{11.8^\circ C}}$	$\frac{W_{17.0^\circ K}}{W_{11.8^\circ C}}$	$\frac{W_{14.93^\circ K}}{W_{11.8^\circ C}}$	$\frac{1}{W_{0^\circ C}} \cdot \frac{dW}{dT}$ at 10° C.
Copper filed	0.01287		0.01229	0.00426
„ rolled	0.02359	0.02311	0.02295	420
„ „ and annealed	0.01042		0.00982	430
Lead cut	0.02827		0.01229	411
„ rolled	0.02828		0.01222	410

These data lead to the following conclusions regarding the influence of the treatment of the metal on the change of the resistance with change of temperature:

For *copper* rolling diminishes the decrease of the resistance between room temperature and the boiling point of hydrogen in a large degree.

By subsequent annealing the influence of rolling the copper is not only annulled, but the decrease of the resistance between the temperatures mentioned above is now even greater than that of copper which has not been rolled and annealed; apparently annealing has also annulled the influence of previous mechanical treatment (filing), probably in consequence of the fact that the metal has united again to larger crystals.

The temperature-coefficient at hydrogen temperatures undergoes only a small change by the manipulations mentioned above.

The change of the resistance of *lead* suffers no or only a small change by rolling.

$$\frac{W}{W_{11.8^\circ \mathrm{C.}}} = 0.0104 \text{ at } 20.4^\circ \text{ K.}$$

$$= 0.0098 \text{ at } 14.9^\circ \text{ K.}$$ [1]

The temperature coefficient at 10° C. was also determined by measurements at 0 and 20° C.:

$$\frac{1}{W_{0^\circ \mathrm{C.}}} \cdot \frac{dW}{dT} = 0.00430 \text{ at } 10^\circ \text{ C.}$$

These values point to a high degree of purity, which is certainly sufficient for the measurements on the atomic heat [2].

In the measurements in hydrogen at a pressure of the bath of 75.2 cms, to which belongs $T = 20.30$, Au_{c3} was found equal to 0.6932 Ω. According to the calibration of Febr. '15 this resistance corresponds to $T = 20.29$. The agreement between these values of

TABLE III. Atomic heat of copper.

N⁰.		Mean temperature	Temperature increase	Heat capac. of copperblock + core in joules/ degree K.	Atomic heat in cal$_{15}$/ degree K.		θ
					C_p	C_v	
16 Dec. '14	II	14.51	1.206	2.246	0.0396		330
	III	15.59^5	0.955	2.791	506		326
	IV	17.17	1.047	3.691	687		325
	V	20.19^5	1.065	5.959	0.1155		321
	I	20.74^5	0.880	6.255	1217		324
	VI	25.37	0.918	11.42	234		319
	VII	29.73	0.667	18.01	377		317
	VIII	40.22	0.822	40.55	870		315
	IX	50.04	0.672	66.38	1.434		315
15 Jan. '15	I	59.75	0.537	94.42	2.06		310.5
	II	60.33	0.540	95.40	2.08		312
	III	69.66	0.598	118.2	2.59	2.58	313
	IV	80.32	0.588	137.7	3.05^5	3.04	317
	V	88.86	0.532	151.85	3.37	3.35	321
	VI	89.38	0.522	154 8	3.44	3.42	316.5

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[1] Cf. also H. KAMERLINGH ONNES and B. BECKMAN. Comm. N⁰. 129*a*, Table VII.

[2] Cf for instance W. MEISSNER, Ann. d. Phys. (4) 47 (14 Sept. 1915), p. 1001. [Added in the translation].

7 is sufficient to calculate the temperatures from that calibration.

In Fig. 1 [1]) the results of our measurements are represented. In the upper lefthand diagram the region up to 25° K. is represented on a larger scale.[2])

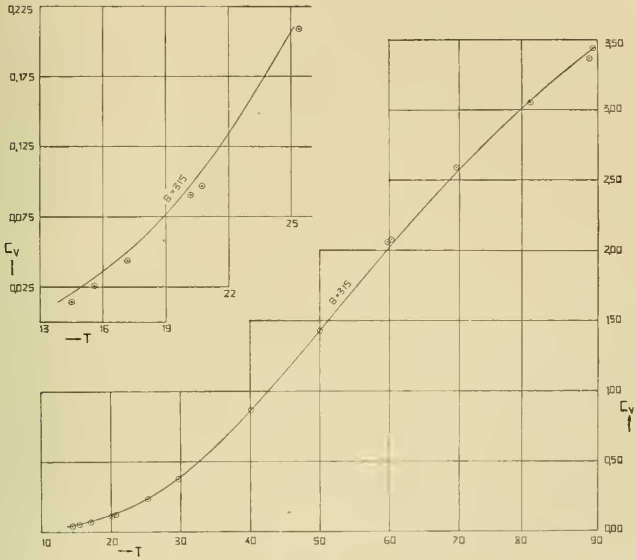

Fig. 1.

The curve has been calculated from Debije's formula [3]) with $\theta = 315$. Debije's formula appears again to be capable of representing the atomic heat over a large region — the ratio of the largest to the smallest value of the measured atomic heats amounts to more than 80 — with a good approximation.

In table IV we have compared the atomic heats of copper in the region of the liquid hydrogen temperatures with the T^3-law derived by Debije for low temperatures:

$$C_v = 464.1 \left(\frac{T}{\theta}\right)^3$$

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[1]) In Fig. 1 the vertical line which indicates $T = 80$ has been drawn inaccurately; it has to be moved 1.25 mm. to the right. [Note added in the translation].

[2]) At 88 K. our results agree fairly well with those found by Nernst l.c., at the lower temperatures (33° – 23° K.) our values are smaller

[3]) P. Debije. Ann. d. Phys. (4) 39 (1912), p 789.

TABLE IV. Copper.

No.	T	C_v	θ	C_v calc. ($\theta = 325.1$)	Obs.—Calc.	in %
16 Dec. '14						
II	14.51	0.0396	329.6	0.0412	— 0.0016	—4.0
III	15.59^5	506	326.3	512	— 6	— 1.2
IV	17.17	687	324.6	684	+ 3	+0.4
V	20.19^5	0.1155	321.1	0.1112^5	+ 42^5	+3.7
I	20.74^5	1217	324.1	1206	+ 11	+0.9
			mean 325.1			

In these measurements, which are more accurate than those of July '14 (Comm. N°. 143 § 6), a small deviation from the T^3-law shows itself. The deviation is in the sense that at decreasing temperature the atomic heat *decreases more rapidly* than follows from the T^3-law.

The deviation becomes still more apparent, if one compares the atomic heat over the whole region of the measurements of this paper with Debije's general formula for the atomic heat, cf. fig. 1 and the values of θ in table III.

In the liquid hydrogen region and above it, up to 40° K., the values of θ decrease continually (fig. 2). In this respect the

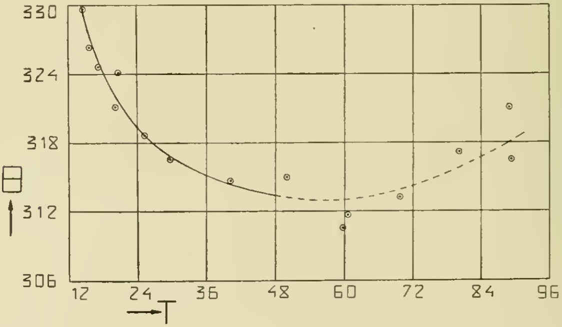

Fig. 2.

behaviour of copper differs from that of lead. For the latter metal the values of θ increase with increasing temperature in the liquid hydrogen region, and begin to decrease beyond about 30° K.[1])

§ 4. Table V contains values of the energy U, which are derived

TABLE V. Copper.

T	U in cal_{15}.	$\frac{U}{T}$	θ_u
20	0.557	0.0278^5	322
30	2.86	0.0952	320
40	8.94	0.223	317
50	20.31	0.406	316^5
60	37.8	0.629	315
70	61.1	0.873	314
80	89.4	1.118	314
90	121.7	1.352	315

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[1]) Our results point further to an increase of θ for copper above 70° K. It is true, that the increase hardly exceeds the degree of accuracy reached in our measurements, but meanwhile it finds a confirmation in the results obtained by SCHIMPFF, ZS. physik. Chem. 71 (1910), p. 257, by RICHARDS and JACKSON, ZS. physik. Chem. 70 (1910), p 414, by KOREF, Ann. d. Phys. (4) 36 (1911), p. 49, R. EWALD Ann. d. Phys. (4) 44 (1914), p. 1213 and by ROLLA. Gazz. chim. 44 I (1914), p. 646, at temperatures between that of liquid air and room temperature or 0° C. respectively. A curve which is drawn through our results below 90° K., and which represents the observations mentioned above as follows:

Interval of Temperature	c_p from curve	c_p observed	Obs.—Calc.	
83—290° K.	0.0790	0.0786	—0.0004	SCHIMPFF.
194 - 290	0.0879	0.0880	+ 1	
85—293	0.0794	0.0789	— 5	RICHARDS and JACKSON.
83.5—190	0.0710	0.0720	+ 10	KOREF.
196.5 - 273.1	0.0873	0.0878	+ 5	
82.0—191.1	0.0708	0.0722	+ 14	EWALD.
197.9—273.1	0.0874	0.0881	+ 7	
82—191.5	0.0709	0.0720	+ 11	ROLLA.
198.2—273.1	0.0874	0.0860	— 14	

gives i. a. the following values of C_p :

by graphical integration from a curve which has been drawn through the experimental points of fig. 1, with an extrapolation below 14° K. on the basis of the assumption that the T^3-law is the ultimate limiting law.

The last column gives the values θ_u calculated from $x = \frac{\theta_u}{T}$, x being derived from DEBIJE's formula for the energy:

$$U = 9\,Nk\,T\,\frac{1}{x^3}\int\limits_0^x \frac{\xi^3 d\xi}{e^\xi - 1}$$

The change of θ_u with T has the effect of making the values of θ, which are derived directly from the atomic heats, differ somewhat from those of θ_u.

For copper θ_u appears to decrease with increasing temperature in the region of 20 to 70 K., the rate of decrease being more rapid at the lower than at the higher temperatures of this region.

§ 5. The values of θ_u found in § 4 (and also those of θ, § 3) are smaller than those following from the formula given by DEBIJE l.c., which with the value found by MILLIKAN for the AVOGADRO number (cf. Suppl. N° 36*b*, March '14) changes to:

$$\theta = \frac{3{,}657.10^{-3}}{M^{1/3}\varrho^{1/6}\varkappa^{1/2}}\,\frac{1}{[f(\sigma)]^{1/3}},$$

v.z.. for 18 C.: $\theta = 333$, for $-$ 191° C.: $\theta = 344$ [1].

In LINDEMANN's formula [2]):

$$\theta = k_L \frac{h}{k}\,\frac{T_s{}^{1/2}}{M^{1/2}\,v_M{}^{1/3}}$$

one finds for Cu from $\theta = 315$: $k_L = 2.72.10^{12}$

whereas for Pb from $\theta = 88$ follows: $k_L = 2.81.10^{12}$, where for v_M the values at $T = 0{,}2\ T_s$ have been used.

$T\ = 120$, 160, 200 240, 280,

$C_p = 4.22$, 4.85. 5.28, 5.60, $5\,80^5$, from which we find:

$\vartheta\ = 331$, 343, 336

On the contrary the results of E. H. and EZER GRIFFITHS, Phil. Trans. 214 A (1914), p 319, cannot be reconciled so easily with ours as can be seen from the fact that they give: at 138° K. $\vartheta = 278$, at 149.5° K. $\vartheta = 285$

[1] Calculated from: 18 C.: $\varrho = 8{,}94$, $\varkappa = 0.74.10^{-12}$, $\sigma = 0{,}35$

$-$191° C.: 9,02, $0{,}69.10^{-12}$, 0,35.

The value of $\varkappa$ at 18° C. has been taken from E. GRÜNEISEN Ann. d. Phys. (4) 25 (1908), p. 848, the change of with temperature from E. GRÜNEISEN, Ann. d. Phy.. (4) 33 (1910). p. 1264.

σ has been assumed to change inappreciably with the temperature according to E. GRÜNEISEN, Ann. d. Phys. (4) 33 (1910), p. 1272.

[2]) F. A. LINDEMANN, Physik. ZS. 11 (1910), p. 609.

As Lindemann's formula can be deduced[1]) from the principle of similarity, applied to solid substances, the data mentioned for k_L can serve at the same time as a comparison of these two metals with respect to that principle. In this comparison the change of θ with the temperature has, however, not been taken into account.

Physics. — "*Further experiments with liquid helium. O. On the measurement of very low temperatures.* XXV. *The determination of the temperatures which are obtained with liquid helium, especially in connection with measurements of the vapour-pressure of helium.*" By H. Kamerlingh Onnes and Sophus Weber. (Comm. 147*b* from the Physical Laboratory at Leiden).

(Communicated in the meeting of June 26, 1915).

1. *Introduction.* In this paper will be given some new determinations of vapour-pressures of helium based on more accurate temperature-measurements, as also a contribution to the knowledge of the correction for the thermal molecular pressure, which has to be applied with constant volume-thermometers for low temperatures with gas under diminished pressure, if the manometer is kept at the ordinary temperature.[2])

This correction was discussed in Comm. 124*b* (Dec. 1911); an estimate of its magnitude, which was necessary to form a judgment of the value of the temperature-determinations, showed that its influence would only exceed the limits of accuracy then given, viz. 0.1 of a degree, in the measurement of the lowest temperatures.

The present determinations of the boiling point of helium made with the aid of a helium thermometer with mercury-manometer arranged for more accurate measurements have enabled us to test the accuracy of the temperature-determination in the previous series of experiments with liquid helium, in which this point had also been determined. It appears that the difference of the previous results from the present can be explained by the correction for the thermal molecular pressure. This correction remains below the value, then given for the limit of accuracy. As to the correction at the lowest temperatures which were measured, this also appears to have about the estimated magnitude. The previous measurements are thus as a whole confirmed.

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[1]) H. Kamerlingh Onnes, Comm. N°. 123 (June '11).

[2]) Compare for a different arrangement the conclusion of § 7, Comm. Suppl. 34 (Sept. 1913), where the investigation contained in the present communication was also announced.

We have now for the first time made measurements with a helium thermometer in which a heated-wire manometer according to KNUDSEN serves as manometer (comp. § 7 Comm. Suppl. 34). With this thermometer it will be possible to go to still lower temperatures than heretofore. In these measurements the correction for the thermal molecular pressure became even now of paramount importance. We succeeded in calculating a formula for this correction, albeit with the aid of a hypothesis regarding the effective molecular free path which leads to a semi-empirical relation.

The new constant in this formula which is a characteristic constant for helium could be chosen such, that for all our measurements with the thermometer with hot-wire-manometer a satisfactory agreement was obtained with the thermometer with mercury-manometer.

2. *Survey of the difficulties inherent in the determinations of the lowest temperatures.* All measurements of temperature in the helium-region will ultimately have to be reduced to readings on a helium-thermometer supposed to be filled with helium in the AVOGADRO-condition. Hence the importance of knowing, how to arrive at accurate determinations with a helium-thermometer, even at very low pressures. For measuring those temperatures, at which the vapour-pressure of helium approaches a very small value, no other helium-thermometers but those with gas at very low pressure can be used, as the pressure in the thermometer must in any case remain below the vapour-pressure corresponding to the temperature to be measured.

Various circumstances thus render it difficult to raise the accuracy to the level which would be permitted by the high degree of constancy of the temperature of the helium-bath which can be attained when the experiment is not unduly prolonged.

It will be necessary to take care that the following conditions are fulfilled.

1. The dead space, or rather that part of the dead space the temperature of which is uncertain, must be made as small as possible.

2. The adjustment of the equilibrium must take place in a sufficiently small time in order to prevent the temperature-changes of the helium-bath affecting the measurements.

3. The deviations of the equation of state for the thermometric gas from the AVOGADRO-condition must not come too much into account.

4. The correction for the thermal molecular pressure must not become too large and this pressure must not reach a region, for which the correction is less accurately known.

It will be seen that these requirements cannot all be fulfilled at the same time. A small value of (1) goes together with a large value of (2) and similarly a minimum of (3) corresponds to a maximum of (4).

All we can do therefore is choosing the construction of the thermometer such that in the intended measurements an optimum is attained as regards satisfying the mutually conflicting requirements.

A calculation of the order of magnitude of each of the aforementioned disturbances, uncertainties or corrections will in general sufficiently enable us to reach our object.

It is clear, that we have to devote our attention particularly to the capillary which connects the reservoir (at low temperature) with the manometer (at the ordinary temperature).

As regards (1), the uncertainty regarding the distribution of temperature along the capillary makes itself principally felt in the lowest, coldest part of the capillary, where the density of the gas is highest; the narrower this part in proportion to the rest, the smaller the uncertainty will be.

It would of course be advisable, if possible, to avoid the calculation of the correction for that part of the dead-space which is dependent on the capillary by placing an auxiliary capillary according to CHAPPUIS beside the capillary of the thermometer.[1] In our case we were unable to utilize this device owing to want of space in the cryostat. It was all the more important, therefore, to take the lower part of the capillary as narrow as possible, from which it follows in view of (2), that the capillary must be taken wider higher up.

At the lowest temperatures the question becomes of importance, whether helium still follows the gaseous laws. On the one hand the term $\frac{B}{v}$ in the equation of state $pv = A + \frac{B}{v}$ has to be considered, where B for a reduced temperature say of 0.2 acquires a fairly high value, so that the correction to be made on account of B may obtain an important influence. As long as the equation of state for helium is no better known than is at present the case and the calculation has to be made with the "mean" equation of state according to the law of corresponding states, great uncertainty exists with regard to this correction. On the other hand it might be a question, whether A may still be taken directly proportional to T or whether

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[1] We are dealing here exclusively with the constant-volume thermometer. A subsequent Communication will deal with the use of thermometers at constant pressure.

an absolute zero-point pressure according to the theory of quanta ought not to be introduced.

In both respects the difficulty might be sufficiently avoided by simply taking the melting-point pressure of the thermometer sufficiently small, but in that case, as already pointed out, the thermal molecular pressure begins to give difficulties which ultimately exceed all the others. In fact this pressure depends upon the ratio $\frac{2R}{\lambda}$, where R is the radius of the capillary and λ the mean free path.

Whereas we know the condition of the pressure-equilibrium between the bulb of the thermometer and the manometer, when the temperatures of both are given for the two extreme cases $\frac{2R}{\lambda} = \frac{1}{\infty}$ and $\frac{2R}{\lambda} = \infty$, this is no longer the case for intermediate values of this fraction. In ordinary gas-thermometers with a melting-point pressure of about the normal atmospheric pressure, the condition $\frac{2R}{\lambda} = \infty$ is very nearly satisfied and the pressures p_1 at the top and p_2 at the bottom of the capillary, where the temperatures are T_1 (normal) and T_2 (to be measured) respectively, may be taken as equal. As we shall see, this is by no means allowed when temperatures are to be measured at which the vapour-pressure of helium is no more than a few millimeters. In thermometers which are adapted to this object considerable corrections have to be dealt with, as will appear in the measurements to be discussed in this paper, indeed the question naturally arises, whether in this case it is not preferable in the temperature-measurement to start from the condition of equilibrium for $\frac{2R}{\lambda} = \frac{1}{\infty}$ viz. $\frac{\sqrt{T_1}}{\sqrt{T_2}} = \frac{p_1}{p_2}$.

3. *Description of the two thermometers.*

The thermometer with mercury-manometer (fig. 1) was the improved form of that in Comm. 119 as described in Comm. 124*b*. The bulb Th_1 had about three times greater capacity, 23.95 cc., and the capillary consisted of three parts, the first starting from below C_a—C_b 15.3 cms. of 0.0362 cm. radius, the next C_b—C_c 9.80 cms. of 0.0783 cm., the third C_c—C_d 22.59 cms. of 0.0947 cm. (the upper 5,25 cm. having 0,090 cm, radius). To the top of the glass capillary (being another part of 5,55 cm. of 0,090 cm. radius) was soldered (entering over this same length) a copper capillary of 1.2 mm. diameter, which was connected to the mercury manometer, first described in Comm. 119 Pl. I and more recently in Comm. 124*b* Pl. I fig. 3 and specially designed for thermometric work. After the improvement of Comm. 124*b* this manometer had only undergone a slight modification: in addition to the glass-tap in the glass capillary leading to the copper one, a side-tap has been added whose object is to connect the thermometer with the mercury-airpump if required.

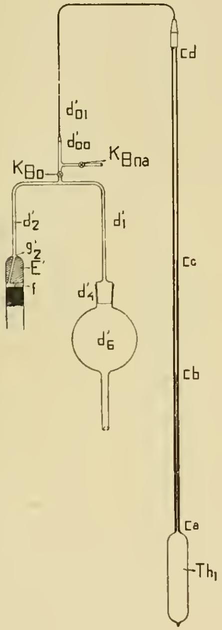

Fig. 1.

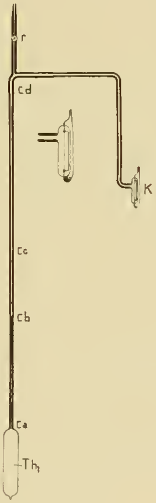

Fig. 2.

The part of the dead space of the thermometer which during the measurements remains at room-temperature had a volume of 4 87 cc.

The second thermometer (fig. 3) was provided with a very small heated-wire manometer[1]) *k*, designed to measure small pressures with sufficient accuracy. The bulb of the thermometer had the same volume as that of the first thermometer 23.956 cc. and the capillary was constructed in exactly the same way as with the latter. The part of the dead space which in this thermometer did not assume the low temperature was 2.67 cc.; the heated-wire manometer stood

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[1]) H. KAMERLINGH ONNES and SOPHUS WEBER, Comm N^o. 137*b*.

in ice. Previously this instrument had been carefully calibrated with the aid of a set of pipettes with pure helium. We are glad to offer Mr. P. G. Cath our thanks for his assistance in this work.

4. *Results.* The thermometers were mounted side by side in the helium-cryostat, which was vigorously stirred by means of a pump-stirrer. The bulbs were surrounded by brass tubes in order to protect them from radiation through the liquid helium. The vapour pressures of helium were corrected for the aerostatic difference of pressure between the helium liquid surface and the vapour-pressure manometer.

Two series of observations were made. In the first Mr. Chappuis did us the honour to take part in the measurements. In this series

Vapour-pressures and thermometer-readings with helium. 1st series.

Vapour-pressure helium-bath in mms	Thermometer with mercury-manometer $p_{0^\circ C.} = 25.738$ cms			Thermometer with heated-wire manometer $p_{0^\circ C.} = 5.240$ cms		
	Uncorrected T	Number of obs.	Mutual deviations of obs.	Uncorrected T	Number of obs.	Mutual deviations of obs.
756.6	4°.205 K.	3	0.5%	4°.468 K.	2	0.2%
564.5				4.155	2	0.2
363.3				3.800	2	0.2
359.5	3.535	3	0.25			
4.4	1.478	2	2.5	1.774	2	0.2

Vapour-pressures and thermometer-readings with helium. 2nd series.

Vapour-pressure helium bath in mms	Thermometer with mercury manometer $p_{0^\circ C.} = 25.358$ cms			Thermometer with heated-wire manometer $p_{0^\circ C.} = 1.2509$ cms		
	Uncorrected T	Number of obs.	Mutual deviations of obs.	Uncorrected T	Number of obs.	Mutual deviations of obs.
757.5	4°.215 K.	2	0.1%			
757.4				5°.472 K.	2	0.1%
4.15	1.509	2	1.0	2.558	2	0.1
756.5	4.219	2	0.1			
756.4				5.470	2	0.1

the melting-point pressure of the helium-thermometer with mercury-manometer was 25.738 cms. mercury, that of the helium-thermometer with heated wire manometer 5.240 cms. In the second series these pressures were 25.358 cms. and 1.2059 cm. mercury respectively. The vapour-pressure measurements were conducted in the same manner as before (comm. 119 and 124*b*). The results were as follows (uncorrected T stands for T not corrected for B and for thermal molecular pressure[1]):

The first column gives the vapour-pressure of helium at the corresponding temperature, the second the temperature as calculated with the aid of the ordinary gas-laws (with $B=0$). The great difference between the temperatures found in this way with the two thermometers is very striking, especially in the last series of measurements in which the melting-point pressure of the second thermometer was very low. The influence of the thermal molecular pressure causes a temperature of 5°.5 to be found instead of 4°.2.

5. *Correction for the thermal molecular pressure.* Expressions for the thermal molecular pressure which are valid for the ranges $0 \leq \frac{2R}{\lambda} \leq 1$ or $10 < \frac{2R}{\lambda} < \infty$ have been developed by KNUDSEN. It is clear, that the choice of the two limits 1 and 10 has been somewhat arbitrary, but we may assume, that, when these limits are attended to, the uncertainty of the results of calculation by means of these formulae, supposing the constants which occur in them to be known, is on the average smaller than 1°/₀. KNUDSEN's formulae do not hold for the intermediate range of $1 < \frac{2R}{\lambda} \leq 10$.

The condition of pressure-equilibrium in a tube with a gradient of temperature is in KNUDSEN's notation

$$2\pi R(M+B)+\pi R^2\frac{dp}{dl}=0.$$

$\frac{dp}{dl}$ is here the pressure-gradient, R the radius, M the tangential force per cm². exerted by the gas on the wall in consequence of

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[1] In controlling the calculations it was found that small errors and uncertainties remain about the data for calculating the gas contained in the capillary, which can change the numbers for the uncorrected T by some thousandths of a degree. The necessary corrections are inside the limits of the experimental errors. So we have left them mixed up with the latter. As soon as we shall have an opportunity to compare the present determinations with more accurate ones, we can perhaps return to this point. (Added in the English translation).

the temperature-slope and B the tangential force which the gas owing to its flow back along the axis of the tube exerts on the wall. M and B according to KNUDSEN [1]) are thus given by:

$$M = k_1 \frac{3\pi}{128} N m \Omega \lambda \frac{d\Omega}{dl} = -k_1 \frac{3\pi\eta}{128.0{,}30967} \frac{d\Omega}{dl}$$

and

$$B = \frac{3}{32} k_2 \Omega \frac{ap}{R^2} \frac{dp}{dl} \text{ where } a = \frac{\pi}{8} \varrho_1 \frac{R^4}{\eta},$$

N the number of molecules per cc., m the mass of a molecule, η the viscosity and λ the mean free path.

If λ is not small as compared to R, we may not assume, as is done in the derivation of the formulae, that a molecule in a collision with a second molecule possesses the velocity corresponding to the temperature at a point at a distance λ; in that case the collisions with the wall have also to be taken into account. The paths described by the molecules since the last collision are then found as follows:

In a disk of unit length cut out from the tube there are $\pi R^2 N$ molecules and therefore $\pi R N \frac{\Omega}{\lambda}$ mutual collisions occur per second and $2\pi R \frac{1}{4} N\Omega$ collisions with the wall; the joint number of collisions is thus

$$2\pi R \tfrac{1}{4} N\Omega + \pi R^2 N \frac{\Omega}{\lambda} \text{ per second,}$$

and each molecule collides $\left(\frac{1}{2R} + \frac{1}{\lambda}\right) \Omega$ times, while describing a path Ω. The path described without collision is therefore on the average

$$\lambda_1 = \frac{1}{\frac{1}{\lambda} + \frac{1}{2R}} = \frac{\lambda}{1 + \frac{\lambda}{2R}} \quad ^{2})$$

This leads to the following condition of equilibrium

$$2\pi R\left(-\frac{3\pi}{128} k_1 N m \Omega \frac{\lambda}{1+\frac{\lambda}{2R}} \frac{d\Omega}{dl} + \frac{3\pi k_2}{256.0{,}30967} \cdot \frac{R^2}{\lambda} \frac{dp}{dl}\right) + \pi R^2 \frac{dp}{dl} = 0$$

as $\eta = 0{,}30967\, N m\, \Omega\lambda$ or

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[1]) M. KNUDSEN, Ann. d. Phys. 33, p. 1435, 1910. 31, p. 633, 1910 and 31, p. 205, 1910 and SOPHUS WEBER, Leiden, Comm. 137c.

[2]) The temperature change of the coefficient of accommodation for collisions with the wall is disregarded on account of its smallness.

$$\frac{dp}{p} = \frac{3}{4} k_1 \frac{d\Omega}{\Omega} \frac{1}{\left(1 + \frac{2R}{\lambda}\right)\left(1 + \frac{3\pi k_2}{0,30967.256} \frac{2R}{\lambda}\right)} \quad . \; . \; . \quad (1)$$

As for $\frac{2R}{\lambda} = 0$ we have $\frac{dp}{p} = \frac{d\Omega}{\Omega}$ or $\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$, it follows, that $k_1 = \frac{4}{3}$ for $\frac{2R}{\lambda} = 0$.

In the case, that $\frac{2R}{\lambda}$ becomes large, we obtain

$$\frac{dp}{p} = \frac{k_1}{k_2} \cdot \frac{8}{\pi} \cdot 0,30967 \frac{\lambda^2}{R^2} \frac{dT}{T}$$

or introducing

$$\lambda^2 = \frac{\pi}{8} \frac{1}{0,30967^2} \frac{\eta^2}{p^2 \varrho_0} \frac{T}{273}$$

where ϱ_0 is the density of the gas at 0° and 1 dyne per c.m.^{2}, we get the formula

$$p dp = \frac{1}{0,30967.273^2} \frac{\eta_0^2}{\varrho_0 R^2} \cdot \frac{k_1}{k_2} \left(\frac{1 + \frac{c}{273}}{1 + \frac{c}{T}} \right) T \, dT$$

calculating, like Knudsen, with Sutherland's formula (which however is no longer applicable at temperatures below those of liquid air) and calling the viscosity at 0° C. η_0.

Knudsen has determined the value of k_1 and k_2 for hydrogen and oxygen and found $\frac{k_1}{k_2} = 2.3$ and $k_2 = 1$.

It is easily shown, that our formula (1) differs from Knudsen's formula only by the factor $\frac{1}{1 + \frac{\lambda}{2R}}$, which has no influence for high values of $\frac{2R}{\lambda}$.

It is therefore obvious, that the factor k_1 in (1), if this equation is to hold for all values of $\frac{2R}{\lambda}$, cannot be a constant, seeing that for all gases it approaches the value $\frac{4}{3}$ for $\frac{2R}{\lambda} = 0$ and that for high values of $\frac{2R}{\lambda}$ it becomes 2.3 for oxygen and hydrogen.

It is further to be remembered that in the theoretical deduction of the relation between heat-conduction and friction numerically correct results can only be arrived at by taking for the mean free path in the case of conduction a somewhat higher value than that which follows from internal friction. In other words the velocity of the molecules at a collision is not that which corresponds to the temperature at a distance λ, but at a distance $\alpha\lambda$, where α is 2.5 for monatomic gases and 1.7 for di-atomic gases. If we introduce this into the expression for M we obtain, as found by KNUDSEN, taking $k_2 = 1$, for di-atomic gases $k_1 = 1.7 \times \frac{4}{3}$ for high values of $\frac{2R}{\lambda}$ or $k_1 = 2.3$. For helium we shall have to take $k_1 = 2{,}5 \,.\, \frac{4}{3} = 3.33$: for this gas k_1 thus changes between the limits $^4/_3$ and 3.3. The question, as to how k_1 depends upon the mean free path will have to be decided by experiment. This problem is analogous to that concerning the relation between heat-conduction and friction, when there is also slipping along the wall. Keeping that in view we have ventured to make a simple assumption which does not clash with the available experimental data and explains the nature of the deviations between our thermometers with different melting-point pressures as well as possible. In how far this assumption may be correct, can only be settled by future experiments. In the mean time it may perhaps be considered as a rough representation of what will be found, when this problem, which is of great importance for the insight into the mechanism of heat-conduction and internal friction, will be specially taken up. The assumption in question is, that

$$k_1 = \frac{4}{3}\,\frac{1 + c_1 c_2 \dfrac{2R}{\lambda}}{1 + c_1 \dfrac{2R}{\lambda}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

In this formula c_1 and c_2 are two coefficients, c_1 having a special value for each gas and being 0.550 for helium and c_2 differing for monatomic and diatomic gases. For the former $c_2 = 2.5$ and for the latter $c_2 = 1.7$.

If we abandon the assumption, that $k_1 = \frac{4}{3} \times 2.5$ for large values of $\frac{2R}{\lambda}$, there is an additional constant c_1 available to adapt the formula to our observations. A very good agreement is in that case obtained with $c_1 = 2.865$ and $c_2 = 0.3101$ [1]). The corrections obtained by this method are indicated in the tables of § 6 below by ( ).

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[1]) It may be observed, that the ratio of this c_1 to the more theoretical value is the value of the power of T in the viscosity-law for helium.

Returning to our equation (1) we have for a monatomic gas

$$\frac{dp}{p} = {}^1/_2 \left(\frac{1 + c_1 c_2 \frac{2R}{\lambda}}{1 + c_1 \frac{2R}{\lambda}} \right) \frac{1}{\left(1 + \frac{2R}{\lambda}\right)\left(1 + c_3 \frac{2R}{\lambda}\right)} \frac{dT}{T}$$

where for helium $c_3 = 0.1190$ [1].

We have now to express T as a function of p and λ.

As the relation $\eta = \eta_0 \left(\frac{T}{273.1}\right)^{0.647}$ holds down to the boiling point of hydrogen (comp. Comm. N°. 134*b* March 1913) and as the thermometer-corrections are almost entirely due to that part of the capillary which is at a higher temperature than 20° K, we may apply this formula to the whole temperature-range in the form $\eta = \eta_0 \left(\frac{T}{273.1}\right)^{1/2 + n}$.

According to the expression for λ given above, we have:

$$dlgp = (1 + n)\, dlgT - dlg\lambda .$$

or also

$$dlgp = (1 + n)\, dlgT + dlgy$$

if

$$y = \frac{2R}{\lambda}.$$

With y as independent variable we may therefore write:

$$\int \frac{dp}{p} = -\tfrac{3}{8} \int \frac{k_1\, dy}{y\left[(1+y)(1+c_3 y)(1+n) - {}^3/_8 k_1\right]}.$$

The correction consists in our case in the sum of three corrections for the different parts of the capillary, each with a different R. For each of the three parts the integral might be easily found by mechanical quadrature, taking into account the changing value of k_1, as soon as the limits of the integration are known. We may also for the sake of simplicity divide each part into smaller parts such, that in the integration a mean value may be assumed for k_1. The limits are each time determined by the value of the viscosity

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[1] It follows from this expression, that there is a maximum value of $\frac{dp}{dT}$ (S. Weber Comm. N⁰. 137*c* Sept. 1913). In arranging the measurements in question care must be taken that at the place where this maximum occurs the distribution of temperature is known as accurately as possible.

The determination of this maximum may possibly be of importance in the investigation of the relation between k_1 and $\frac{2R}{\lambda}$.

of helium corresponding to the temperature and the density, as also by the value of the radius at the ends of the given portions of the tube[1]).

As the density depends on p as well as on T and as p varies along the tube, the limits at the ends of the various parts will depend upon the local values of p themselves: of these only that at the top of the capillary is immediately known, whereas at the bottom the density is approximately known, it is true, but neither p nor T. It is therefore necessary to proceed by successive approximation and starting at the top to calculate the diminution of pressure assuming as a first approximation $p =$ constant equal to the value at the top of that portion of the tube, and then, using the distribution of pressure which is found and the known distribution of temperature to improve the calculation, etc.

The uncertainty regarding the distribution of temperature along the capillary is of course a source of error, but as a rule the errors arising from this uncertainty are not of any importance, especially because usually, according as this uncertainty is greater for a given portion of the tube, its contribution to the total correction for the molecular pressure becomes smaller. Finally for that portion which reaches down to the range of temperatures which have to be determined by the thermometer itself the contribution to the correction can be entirely neglected. The most important contribution to the correction is due to the upper part of the capillary.

5. *Corrected temperatures.* Applying the corrections on the basis of the pressure-distribution along the capillary, as found by the above calculation, the following results are obtained: (see tabel II p. 505).

The values between brackets ( ) refer to the calculation with the more empirical values of c_1 and c_2, introduced solely with a view to the observations without taking into account the theoretical limiting values.

Calculating the correction of the helium-thermometer with mercury-manometer by means of the formulae tested in the above series of observations, we find (considering only the most reliable observations (see table III p. 505).

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[1]) If afterwards a changing value of n were found for helium at the lower temperatures, as in other gases, the same formula will be applicable, for each piece into which the tube is divided its own value of n being introduced.

TABLE II. Temperature-measurements in the helium-region with the heated wire helium-thermometer.

Vapour-pressure of the bath	Series I. $p_{0^\circ C.} = 5, 240$ cm.		Series II. $p_{0^\circ C.} = 1, 2059$ cm.	
	T uncorr.	*T* corr.	*T* uncorr.	*T* corr.
756.6 mm.	4°.468 K.	4°.260 K. (4°.230)		
757.4			5°.472 K.	4°.245 K. (4°.207)
564.5	4.155	3.937 (3.912)		
363.3	3.800	3.587 (3.568)		
4.4	1.774	1.495 (1.490)		
4.16			2.558	1.445 (1.461)
757.4			5.472	4.245 (4.207)

TABLE III.

Vapour-pressures of helium measured by the helium-thermometer with mercury-manometer and corrected for the thermal molecular pressure.

Vapour-pressure of helium in mms.	Accurate series 1913.		Series 1911.	
	T uncorr.	*T* corr.	*T* uncorr.	*T* corr.
760			4°.29 K.	4°.22 K. (4.21)
757.5	4°.215 K.	4°.204 K. (4.205)		
565			3.97	3.90 (3.89)
359.5	3.535	3.519 (3.516)		
197			3.26	3.18 (3.17)
51			2.34	2.25 (2.24)
4.15	1.509	1.480 (1.475)		
3			1.47	1.36 (1.35)

In the same manner the vapour-pressure above the boiling point is found as follows (Comm. N°. 124*b*, p. 16): (see tabel IV p. 506).

The corrections to be applied to the temperature-values as given in previous communications will be seen to be but small. Both the

TABLE IV.
Vapour-pressures measured by the helium-thermometer with mercury-manometer, corrected for thermal molecular pressure (above the boiling point).

p	T uncorr.	T corr.
767 mm.	$4^{\circ}.28$ K.	$4^{\circ}.22$ K. (4.21)
1329	4.97	4.91 (4.90)
1520	5.10	5.05 (5.04)
1569	5.15	5.10 (5.09)
1668	5.22	5.15 (5.16)
1718	5.25	5.20 (5.19) crit.

boiling point and the critical point go down a little, but the change is within the limits of accuracy as previously given. The conclusions formerly drawn from the temperature-measurements thus remain valid, especially the rapid change of the constant f in VAN DER WAALS's vapour-pressure law which we inferred at the time.

With the chosen pressures in the helium-thermometer with mercury-manometer the correction for B becomes of minor importance.

At the boiling point of helium it is too small to have any influence. According to Comm. N°. 119b § 5 in $pv = RT + \frac{B}{v}$ we found $B_{4^{\circ}.21\,\mathrm{K}} = -0.000047$ and we thus have with $p_{0^{\circ}\,\mathrm{C}} = 25.5$ cc. at $4^{\circ}.21$ K. $\frac{T_{\text{corrected for } B}}{T} = 1 + 0.000128$.

It is true, that at lower temperatures, as discussed in § 1, B becomes much larger. An extrapolation according to the "mean" equation of state, in itself certainly little justified, would give. $B_{1.5^{\circ}\,\mathrm{K.}} = 56.1\, B_{4.^{\circ}21\,\mathrm{K.}}$ Even on this supposition an error of only $2\,^{0}/_{0}$ or 0,03 degrees would have to be expected from B being neglected. This deviation is smaller than the uncertainty of the correction for the thermal molecular pressure.

When the melting-point pressure in the thermometer with heated-wire manometer is as low as it was taken in the above 2nd series, the uncertainty regarding the last-named correction becomes predominant. From this it appears, that a very accurate knowledge of

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1) W. H. KEESOM, Suppl. N^0. 30, p. 12.

the thermal molecular pressure will be needed, if values of B are to be derived from the comparison of thermometers with different initial pressure. The same is true with respect to possible corrections for deviations, as predicted by the theory of quanta.

7. *Approximate formula for the vapour-pressure of helium.* We did not succeed in representing our observations by NERNST's vapour-pressure formula, treated as interpolation-formula.

The BOSE-RANKINE form [1])

$$lg\, p_{\mathrm{cm.Hg}} = A + B\frac{1}{T} + C\frac{1}{T^2} + D\frac{1}{T^3}$$

gave with

$A = +3.7290$, $B = -7.9780$, $C = -0{,}13628$, $D = +4.3634$

the results shown in Table V

TABLE V. Vapour-pressure of helium.

T	$p_{\mathrm{obs.}}$	p_{calc}
1.475° K.	0.415 cm.	0.419 cm.
3.516	35.95	35 50
4.205	75.75	76.38
4.9	132.9	136.5
5.16	166.8	162.1

Even with this formula containing four constants the observations appear to agree only very imperfectly.

Physics. — *Methods and apparatus used in the cryogenic laboratory. XVI. The neon-cycle.* By H. KAMERLINGH ONNES. (Comm. 147*c* from the Physical Laboratory at Leiden).

(Communicated in the Meeting of June 26, 1915).

1. *Introduction.* In several accurate investigations on the law of dependence on the temperature of the properties of substances the difficulty is encountered, when going below 55° K., that not till 20° K. is reached liquid baths of the desired constancy are again available. The gap between 55° K. and 20° K. in a range which other-

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[1]) C. A. CROMMELIN, Comm. N°. 138*c*.

wise extends far in both directions without any break and in which the temperature is under complete control from 90° K. to 55° K. by means of liquid oxygen and from 20° K. to 14° K. of liquid hydrogen, — this gap is all the more to be regretted as in the absence of a liquid bath comparisons of auxiliary thermometers with the helium- or hydrogen-thermometer in this region of temperatures are completely wanting. It would be specially valuable, if this gap could be filled for the lower portions of the temperature-range in question by the addition of a portion above the boiling point of hydrogen joining on to the range of reduced temperatures which is governed by hydrogen between 20° K. and 14° K. As instances of investigations for which this extension would be greatly desired we can name (besides the equations of state of hydrogen and neon) that of paramagnetic susceptibility, that of specific heat, and that of galvanic resistance.

We have now succeeded in utilizing neon for this purpose. During the experiments which have led to this result some thermal quantities of neon were determined, which will be discussed in the next communication (147*d*, these Proceedings) by Dr. CROMMELIN and myself. Amongst other data the boiling point of neon was found at about 27° K. and the triple-point at about 24.5° K. By using neon exactly in the same way as hydrogen, the range of 14°—20° K. can, therefore, now practically be extended from 14° K. to 27° K. As we have also found, that there is no serious difficulty in constructing cryostats for pressures some atmospheres above the normal (e. g. with hydrogen it is possible to go from 20° to 25° K.), a pressure-cryostat with neon will probably allow us to ascend to a temperature of 34° K., by which it would become possible to study by the eye the critical phenomena of hydrogen in a bath of liquid neon. A future communication conjointly with Dr. CROMMELIN will, I hope, deal with an investigation of this question.

Further as regards the region from 34° to 55° K., we may mention even now, that one of the next communications will contain a description of an arrangement by which I have succeeded by a satisfactory method by means of hydrogen-vapour heated to the desired temperature in obtaining constant temperatures in this region. In a further communication to be given conjointly with Dr. CROMMELIN, which will follow soon afterwards we hope to give an experimental determination of the critical temperature of neon (compare our Comm. 147*d* below) made by means of this new arrangement. The same arrangement may also be utilized in the temperature-region from 20°—34° K. But for most experiments, particularly when phenomena have to be followed by the eye, the cryostat with liquid neon is very much to preferred.

It was gratefully mentioned before, when the attempts to arrange a neon-cryostat were discussed for the first time (Comm. 112 June 1909), that the gas was very kindly put at our disposal by Mr. G. Claude and the "Société d'Air Liquide" in Paris. This gas was rich in neon and from it the large quantity of pure neon which is now in circulation in the laboratory has been separated (Comp. Leiden Comm. Suppl. 21*b* p. 40—41). It is there described, how by a preliminary purification of the crude gas by means of freezing in liquid hydrogen, pumping off the helium and separation of the large quantity of nitrogen present, a gas was obtained almost totally free from hydrogen and helium and principally only containing some nitrogen. Continued fractionation further diminished the quantity of the admixtures and the ultimate purification was conducted by means of the neon cycle itself and the removal of the last traces of oxygen and nitrogen by the aid of carbon cooled in liquid air.

2. *The neon-liquefactor and neon-cryostat.* These are combined into one piece of apparatus (see fig. 1 below). The liquefactor somewhat resembles in its construction the apparatus for the purification of hydrogen (Comm. 109*b* March 1909). The cryostat is constructed exactly as the helium-cryostat in its most recent form (Comm. 123, June 1911). The connection between liquefactor and cryostat is essentially the same as that between the helium-liquefactor and the helium-cryostat of Leiden. Comm. Suppl. 21 fig. 5 (Oct. 1910). To facilitate a comparison with the helium-cryostat, the parts of the neon-liquefactor in fig. 1 are marked with the same letters as the corresponding parts of the helium-cryostat in the Plate of Comm. 123. For parts of modified construction, but of analogous purpose accented letters have been used.

The principle of the apparatus (comp. fig. 1) consists in this, that in the liquefactor the neon is made to condense on a spiral $a_1\, a_2\, a_3$ (comp. $a_1\, a_2\, a_3$ in Plate of Comm. 109*b*), which is cooled below the boiling point of neon by means of liquid hydrogen. From the coils of this spiral the liquefied neon flows down into the cryostat. If locally the temperature of the cooling-spiral descends below the melting-point of neon, the substance will there be deposited as a solid crust on the spiral. The external surface of the spiral, where this happens, and the remaining free passages between the spiral and the vessel, inside which the spiral is suspended are so large, that a considerable quantity of solid neon can be deposited in this

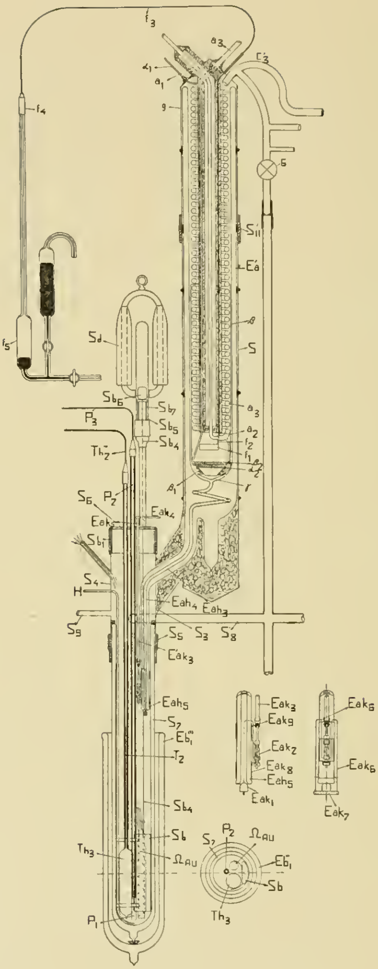

Fig. 1.

manner, without the apparatus becoming plugged. As soon as the lower part of the spiral returns to a temperature above the melting-point, the neon melts, drips down and flows into the cryostat.

In applying this principle of liquefying the neon by cooling with liquid hydrogen the difficulty lies in the circumstance, that the boiling-point and melting-point of neon are only a few degrees apart. The construction of our apparatus is specially designed to meet the difficulty arising from the almost unavoidable freezing of the neon. If we had applied LINDE's principle of liquefaction on neon, cooled only in liquid air, and had thus liquefied neon in the same manner as DEWAR first showed, how to liquefy hydrogen, this difficulty of the neon freezing would not be encountered. But in that case the other difficulty would make itself felt, that only a part of the available gas appears as liquid in the bath. As long as neon is still so difficult to obtain as at present, this objection weighs very much more than that inherent in the principle of our apparatus. Moreover as we have the excellent hydrogen-cycle ready at our disposal, it would be much more complicated constructing a separate neon-cycle with liquid-air cooling only, than following the method adopted. In future, when neon will be equally easily obtained as at present hydrogen and there will thus be no necessity for anxiously guarding against the smallest loss and such a loss will be considered in the same light as a loss of hydrogen is now, it will become more profitable to prepare the liquid hydrogen itself by means of a neon-cycle. For that case a purifying-apparatus of neon by means of liquid neon, similar to that of hydrogen described in Comm. 109, will be practically a necessity. If the neon is not completely deprived beforehand of the less volatile admixtures, such as nitrogen, the narrow tubes of the regenerator-spiral, through which the gas is made to flow during its expansion, would be apt to get plugged. In the method chosen by us it is of no account, whether the neon still contains a few percentages of the less volatile constituents, like nitrogen. Without obstructing the passages they are deposited on the less cooled upper parts of the spiral, while the neon is liquefied or solidified on the lower coils. If the temperature of the cooling spiral is so regulated that the vapour-pressure of neon at that temperature is above one atmosphere, while the solid nitrogen and oxygen have still only a negligible vapour-pressure, all the liquid and solid neon which might be present will evaporate and the less volatile admixtures of the neon can all be retained in the apparatus and so removed from it. This procedure may be utilized for the purification of the neon (see § 3). We will however at present adhere to the supposition, made in the beginning of our description, that the neon is already pure.

The liquid neon flowing down from the spiral is caught (fig. 1) in the silvered vacuum-vessel with silvered draw-off-tube E_{ak3} and then flows through the small stop-cock E_{ak1} into the vacuum-vessel S_7 of the cryostat; for the description of the cryostat and its pump-stirrer we may refer to Comm. 123*b*, where the lettering is identical. The difference between the valve used at present (for details see separate drawing in fig. 1) and that of Comm. 123*b* is of minor importance and consists in the valve not having a turning movement, but moving vertically up and down, being guided by the two rods E_{ak6} and carried by the german-silver strip E_{ak7}. The small stop-cock is connected to the orifice E_{ak5} by means of two german-silver rings E_{ak8} and E_{ak9}.

Fig. 1 represents the condition, in which the cryostat contains a helium-thermometer Th_3''' with capillary Th_2''' (as in the Plate of Comm. 123*b*, this time however the thermometer used in Comm. 147), a resistance ΩAu, as in the same Plate, and moreover a piece of apparatus for the measurement of the vapour-pressure of hydrogen above its boiling point (vessel P_1, which contains the liquid hydrogen, besides tube and capillary P_2, P_3, P_4 for connection with the further apparatus): the measurements with this arrangement will be dealt with in a communication to be made conjointly with Mr. P. G. CATH.

Two tubes are attached to the cover of the cryostat, S'_8 (comp. figure of Plate in Comm. 24, where however the corresponding letter is wanting) and S'_9 leading to a manometer and the apparatus (comp. § 3) for regulating the temperature in the cryostat.

The temperature in the cooling-spiral $a_1 a_2$ in the liquefactor, a, being protected from supply of heat by a covering of wool, may be regulated by the aid of the thermometer $f_1 f_2 f_3 f_4 f_5$, exactly as in the apparatus for the purification of hydrogen, for the description of which we may again refer to Comm. 109.

Care has to be taken, that only liquid neon can enter the draw-off tube. For this purpose a small vessel β is contrived, which fits in the vacuum-vessel with a thin layer of flannel; it is open at the bottom and just above the opening β_2 carries a filter β_1, which can be warmed by means of hydrogen of ordinary temperature which can be blown through the tube α_1 and the small spiral α_2; by which means the temperature of the draw-off tube can be permanently kept above that of the melting-point of neon. Solid and less volatile substance, say nitrogen, which might fall down, is retained on the filter and if the nitrogen which has collected there happened to melt by the temperature rising it flows on the small tray γ, where it remains while only liquid neon can flow down [1]).

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[1]) In order to make the arrangement completely adequate — solid nitrogen is lighter than liquid neon — this tray should be provided with a standing-up rim of gauze, which was not yet the case.

3. *The neon-cycle.* This cycle is very similar to that of helium (Comm. 108 July 1908). The neon is stocked under compression in one or more receivers R_1 (fig. 2). From R_1 the gas is made to flow into the gasometers G_1, G_2, floating in oil and arranged exactly as in the hydrogen-cycle (Comm. 94*f*, June 1906), the oil being here also freed from air and moisture.

If necessary, the neon, before it is brought into circulation, can

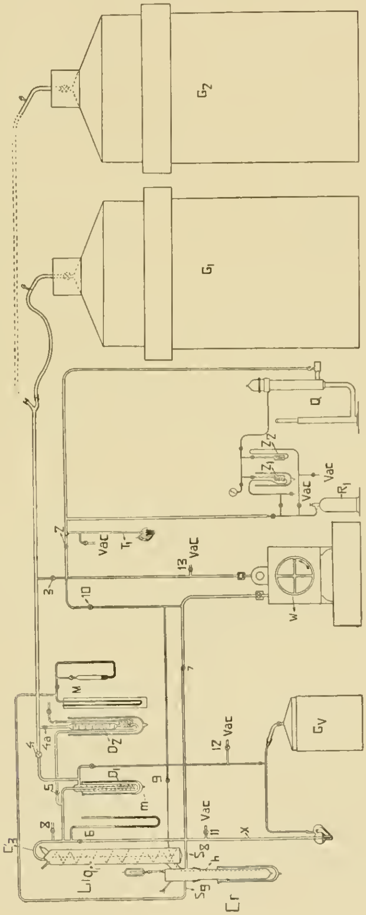

Fig 2.

be drawn under pressure through carbon, cooled with liquid air, by means of the compressor with mercury-piston Q (compare Comm. 54 Jan. 1900) and returned to R_1 or to the gasometer in purified condition. The carbon is contained in Z_1 (which is cooled) and Z_2 (a reserve tube), copper hardsoldered receivers which may be exhausted by the mercury-airpump (*vac* in the figure) at red heat. The remaining gas is transferred by the air-pump to a gasholder for impure neon. The way of using the cocks and the object of the safety-tube T, which in case of need takes back the gas to the gasholder for impure neon, as also of stop-cock 2 will be clear without special elucidation.

The cryostat is filled with the pure neon from the gasometer by stop-cock 4 through a drying-tube D_1 immersed in liquid air; from here it flows with stop-cock 6 open by c'_2 (comp. fig 1) into the liquefactor, from which as explained in § 2 the liquefied neon flows down into the cryostat. The vaporized neon escapes through S'_8 to the gasometers G_1 and G_2. When the cryostat is filled the small cock E_{ak_1} and stop-cock 6 are closed. The neon which might then evaporate in the liquefactor may escape through stop-cock 8 into the gasholder for impure neon.

As usual the cryostat has attached to it a safety-tube X; the gas which might escape through it is caught in the small safety-gasometer Gv. When the small cock E_{ak_1} is closed, the temperature of the bath may be regulated in the usual manner according to the indication of manometer M and with the aid of the differential-manometer shown beside it (comp. Comm. 83, Dec. 1902) by opening 7 more or less.

The apparatus itself and the connections may be evacuated by manipulating stop-cocks 10 and 11. The exhaustion is performed before the experiment to make sure of a proper operation of the cryostat and again after the completion of the experiment to transfer the gas contained in the apparatus back to the gasholder for impure neon. Before proceeding to the latter operation the liquid neon is transferred to the gasometers G_1 and G_2, either by allowing the liquid to evaporate with the cryostat connected to the gasometers, or by flowing the liquid to the gasometers by pressure through the syphontube h, allowing the liquid neon to evaporate in the passages on its way to the gasometers, or finally by pumping the liquid out and forcing it into the gasometers with the Siemens-pump W. The gas which is left in the Siemens-pump is transferred by the mercury-pump to the gasholder for impure neon with all the other gas remaining in the whole apparatus and connections at the end of the experiment as already mentioned.

To prevent too rapid an evaporation of the bath the cryostat-vessel S_7 (fig. 1) is protected by a tube with liquid air.

If the available neon is not quite pure and if it is still desired to start the work with it without the previous purification by means of the circulation under pressure over carbon cooled in liquid air, it will be possible instead of the drying tube D_1 to insert between 4 and 5 a carbon-tube D_2 arranged for purification under ordinary air-pressure, immersed in liquid-air with a drying-apparatus preceding it.

In the experiments the liquid gas in the bath was always obtained in a perfectly transparent condition. Only the first quantity of liquid neon which flows into the cryostat-vessel and evaporates there very rapidly, left behind a little of a white substance (solid nitrogen or solid air?) which dissolved again in the liquid gas which flows in afterwards. A slight ring-shaped deposit was also noticed above the liquid surface in the evaporation of the bath. The gas had thus not been quite pure; as a matter of fact this can hardly be expected, as long as it is allowed to come into contact with the oil of the gasometers. The use of the latter, however, simplifies the operations considerably, and the very slight impurity does not give the least trouble.

It was found that the quantity of liquid in the bath could be made as much as 400 cc.

I am glad to thank Mr. G. J. Flim, chief instrumentmaker in the cryogenic laboratory, once again for his help in the construction of the apparatus described in this paper.

Physics. — "*Isothermals of monatomic gases and of their binary mixtures XVII. Isothermals of neon and preliminary determinations concerning the liquid condition of neon.*" By Prof. H. Kamerlingh Onnes and C. A. Crommelin. (Communication 147*d* from the Physical Laboratory at Leiden).

(Communicated in the meeting of June 26, 1915).

1. *Isothermals of neon.* This section contains a first instalment of the isothermal-determinations, by which we hope to obtain the equation of state of neon at low temperatures. The isothermals of 0° C. and 20° C. have been investigated from 20—93 and from 20—84 atmospheres respectively; they give sufficient data for the connections which are required for the reduction of the observations concerning the isothermals of lower temperatures. Parts of isothermals for —182°.6 C., —200°.1 C., —208.°1 C., —213°.1 C. and —217°.5 C. are also given, which may serve as a first survey and even now

allow a preliminary application of the law of corresponding states to be made.

In Table I and II the symbols θ, p, d_A, and v_A, have the usual meaning.

TABLE I. Isothermals of neon.

Series	No.	θ	p	d_A	pv_A (obs.)	pv_A (calc.)	calc. – obs.	calc.– obs. in %
VI	1	+ 20°.00	22.804	21.046	1.0835	1.0843	−0.0008	−0.06
VI	2		25.015	23.052	852	854	— 2	−0.02
VI	3		26.575	24.464	863	862	+ 1	+0.01
VI	4		29.090	26.757	872	875	— 3	−0.03
VI	5		32.572	29.891	897	892	+ 5	+0.04
VIII	1		34.887	32.002	902	904	— 2	−0.02
VI	6		35.423	32.447	917	907	+ 10	+0.09
VI	7		37.812	34.601	928	919	+ 9	+0.08
VIII	2		39.168	35.843	928	926	+ 2	+0.02
VIII	3		44.762	40.862	955	956	— 1	−0.01
VIII	5		54.149	49.213	1003	1005	— 2	−0.02
VIII	6		59.717	54.161	026	035	— 9	−0.08
VIII	7		65.021	58.797	059	063	— 4	−0.04
VIII	9		77.360	69.338	131	128	+ 3	+0.03
VIII	10		82.545	73.967	160	158	+ 2	+0.02
VIII	11		88.239	78.886	186	189	— 3	−0.03
VIII	12		93.298	83.154	220	217	+ 3	+0.03
VII	1	0°	22.064	21.869	1.0089	1.0095	−0.0006	−0.06
VII	2		23.555	23.314	103	101	+ 2	+0.02
VII	3		25.867	25.558	121	112	+ 9	+0.09
VII	4		28.468	28.089	135	124	+ 11	+0.11
VII	5		30.790	30.345	147	135	+ 12	+0.12
IX	1		39.753	39.098	168	178	— 10	−0.10
IX	2		44.892	44.030	196	203	— 7	−0.07
IX	5		59.777	58.234	265	279	— 14	−0.14
IX	6		66.104	64.135	307	311	— 4	−0.04
IX	7		74.059	71.495	359	353	+ 6	+0.06
IX	8		79.108	76.127	392	380	+ 12	+0.12
IX	9		84.662	81.347	408	411	— 3	−0.03

TABLE II. Isothermals of neon.

Series	N⁰.	θ	p	d_A	pv_A (obs.)
V	1	—182°.6	[67.468	211.34	0.31924]
V	2		[74.232	234.61	31641]
V	3		[79.168	251.84	31436]
III	1	—200°.1	61.657	263.77	0.23375
III	2		67.456	291.10	23172
III	3		73.850	320.85	23017
III	4		79.923	348.59	22928
IV	1	—208°.1	58.472	308.32	0.18965
IV	2		64.451	345.22	18670
IV	3		69.692	377.89	18443
IV	4		74.532	409.18	18215
IV	5		79.228	439.12	18043
II	1	—213°.1	53.896	334.59	0.16108
II	2		59.769	382.03	15645
II	3		66.271	435.46	15218
II	4		22.858	484.75	15030
II	5		79.698	534.62	14908
I	1	—217°.5	49.930	358.51	0.13927
I	2		53.528	395.62	13530
I	3		59.618	458.40	13006
I	4		64.975	511.85	12694
I	5		71.649	571.69	12533
I	6		79.417	632.23	12561

2. *Virial-coefficients.* So far virial-coefficients have been calculated for the temperatures of 20° C. and 0° C. only, in both cases using least squares. The following values were found:

TABLE III. Virial-coefficients of neon.

θ	A_A	$B_A \times 10^3$	$C_A \times 10^6$
20° C.	+ 1.0731	+ 0.51578	+ 0.82778
0°	+ 0.99986	+ 0.41334	+ 1.1538

The differences between the observed values of pv_A and those calculated with the above coefficients are found in Table I in the last two columns. As the table shows, the isothermal of 20° C. seems to be slightly more accurate than that of 0° C., a circumstance which may be connected with the fact of its being more difficult to keep a vessel at a constant temperature of 0° C. than at one of 20° C., when an efficient thermostat is being used.

The communication of the value of the virial-coefficients for low temperatures, as also the calculation of the Boyle-point ($B_A = 0$) we defer to a subsequent paper.

3. *Boiling point, vapour-pressures, liquid densities, triplepoint.*

The vapour-pressures were directly determined as the pressures of a bath of liquid neon, in which a helium-thermometer was placed, the same as served for the measurements by Kamerlingh Onnes and Weber.[1]

The value found for the pressure at the triple-point differs but

TABLE IV.
Vapour-pressures and liquid densities of neon.

$\theta = T - 273°.09$ K.	vapour-pressure in cm. mercury	liquid density
— 245.68 C.	81.62	
— 245.88	76.71	1.204
— 245.92[2]	76.00 boiling point	
246.66	60.52	
247.49	45.16	
— 248.51	32.50	1.248
— 248.67	32.35 triple point	

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[1] H. Kamerlingh Onnes and S. Weber, These Proceedings supra. Comm. N° 147*b*.

[2] Calculated by interpolation.

little from that given Comm. 112, June 1909. Our results (yet of a preliminary kind) were (see table IV p. 518).

The density of the liquid was measured by a small hydrometer for densities of 1,20 to 1.30, floating in the bath, which after a preliminary trial was specially made for this purpose.

4. *Preliminary investigation of the behaviour of neon with respect to the law of corresponding states.*

The pieces of isothermals of low temperatures given in § 2 are too short and have therefore too few characteristic features, to be able to yield the critical constants of neon by the method of drawing them in a logarithmic diagram and making this fit the logarithmic diagram of another substance of known critical data, by parallel motions in two directions.

They are still insufficient for this purpose, if the improved method is used of taking as one of the coordinates in the diagram in which the isothermals are drawn the expression $\frac{pv}{T}$, which has the same value for all substances in corresponding states, so that now only a motion in one direction is required. Definite results are to be obtained, however, if in addition the value of the critical pressure (Comm. 112 June 1909) is utilized, although it is only a preliminary value. Following this plan we have placed the net of isothermals of neon in a $\frac{pv}{T} - \log p$-diagram on top of that of hydrogen, oxygen and argon and by ascertaining what temperatures the isothermals which coincide belong to for each of the substances, we have arrived at a few estimates of the critical temperature.

The results were as follows:

1. *Hydrogen.* (Kamerlingh Onnes and Braak).

a. The isothermals $-200.^\circ 1_{Ne}$ and $-217.^\circ 41_{H_2}$ coincide and cover each other completely over a long distance. Taking for the critical temperature of hydrogen the value found experimentally by Bulle $\theta_{kH_2} = -241.^\circ 14$ C., we get

$$\theta_{k.Ne} = -231.^\circ 2 \text{ C.}, \quad T_{k.Ne} = 41.^\circ 9 \text{ K.}$$

b. The isothermals $-182.^\circ 6_{Ne}$—$200.^\circ 6_{H_2}$ coincide. This gives:

$$\theta_{k.Ne} = -233^\circ.2 \text{ C.}, \quad T_{k.Ne} = 39.^\circ 9 \text{ K.}$$

In this case we used also $\theta_{k.H_2} = -241.^\circ 14$ C., but, as this value belongs to monatomic hydrogen and hydrogen at —200° C. is certainly not yet completely monatomic, whereas at the higher temperatures much higher critical reduction-temperatures have undoubtedly to be used, no weight can be attributed to the latter determination.

2. *Oxygen* (Amagat).

The isothermals $-198^\circ.4_{Ne}$ and $0^\circ_{O_2}$ coincide, so that, with $\theta_{k\,O_2} = -118^\circ.84$ C. (according to Kamerlingh Onnes, Dorsman and Holst),

$$\theta_{k.Ne} = -230.^\circ 9 \text{ C.}, \quad T_{k.Ne} = 42.^\circ 2 \text{ K.}$$

3. *Argon* (Kamerlingh Onnes and Crommelin).

a. The isothermals $-217^\circ.5_{Ne}$ and $-87^\circ.05_{Ar}$ coincide. With $\theta_{k\,Ar} = -122\,.44$ C., according to Crommelin this leads to:

$$\theta_{k.Ne} = -228.^\circ 2 \text{ C.}, \quad T_{k.Ne} = 44^\circ 9 \text{ K.}$$

b. The isothermals $-200.^\circ 1_{Ne}$ and -28°_{Ar} coincide; hence

$$\theta_{k.Ne} = -228.^\circ 2 \text{ C.}, \quad T_{k.Ne} = 44.^\circ 9 \text{ K.}$$

c. The isothermals -191°_{Ne} and 0°_{Ar} coincide; which yields:

$$\theta_{k.Ne} = -227.^\circ 9 \text{ C., and } T_{k.Ne} = 45.^\circ 2 \text{ K.}$$

It will be seen that on the one hand the two values obtained from hydrogen and oxygen and on the other the three values from argon agree closely, the mutual agreement between these two groups of values being much less perfect.

If, using the critical temperature as obtained by the comparison with argon, the data of Table IV are plotted in the diagram of reduced vapour-pressure curves ($\mathfrak{p}$ as function of $\mathfrak{t}$, where $\mathfrak{t}$ is the reduced temperature for the several substances) and in that of the reduced liquid- (and vapour-) densities (Comm. 131*a* fig. 3 Oct. 1912) respectively, the curves for neon range themselves very well between those of the other substances in their proper order.

Neon thus appears to correspond closely with argon and to deviate from it in the direction indicated by its lower critical temperature. We hope to be able soon to be in a position to communicate fuller data regarding the equation of state of neon, especially to replace the preliminary measurement of the critical pressure by a more accurate one and to give a direct determination of the critical temperature.

We are glad to record our thanks to Mr. P. G. Cath for his assistance in the investigation of the liquid state of neon.

Botany. — "*Sloanea javanica (Miquel) Sszyszylowicz, a remarkable tree growing wild in the jungle of Depok, which is maintained as a nature reserve*". *Contribution to the Flora of Java, part VIII.*[1]) By Dr. S. H. KOORDERS. (Communicated by Prof. M. W. BEIJERINCK).

(Communicated in the meeting of June 26, 1915).

Original habitat. Between Batavia and Buitenzorg the jungle of Depok has been constituted a permanent reserve since 1913 by the Nederlandsch-Indische Vereeniging tot behoud van Natuurmonumenten (Dutch-Eastindian Society for the Protection of Natural Monuments), and here I found on March 15th last fruits, which I immediately recognized as those of Sloanea javanica (Miquel) Sszyszylowicz. The fruits were borne by two trees, which I had "numbered" in 1914 (provided for botanical examination with a number board and registered, as 23*n* and 39*n*). This observation was especially interesting, since the original habitat of Sloanea javanica has remained quite unknown to botanical literature and to myself, although this javanese forest tree had already been carefully described and figured half a century ago by Miquel in the Annales Musei botanici I 1865—1866 p. 68, table 3.

This fact, remarkable in itself, namely that an original habitat of Sloanea javanica should remain unknown for almost half a century, becomes all the more remarkable when considered in connection with the following facts:

Firstly, that the original habitat discovered by me namely the forest of Depok, is in the neighbourhood of a scientific centre like Buitenzorg.

Secondly, that especially in the last thirty years numerous persons, including myself, have botanized in the above jungle.

Thirdly, that this forest tree, which had escaped notice for so long, is found to be one of the largest trees of the wood.

Fourthly, that a herbarium specimen, collected by me in the forest of Depok on August 27 1898 and provided with the correct native name, has remained in the Buitenzorg Herbarium for 17 years, without having its scientific name affixed to it, although the specimen in question was within the immediate reach of anyone working in the Buitenzorg Herbarium during these years.

The material collected by me in 1898, consisting of a few dry sterile leaf twigs (Kds. n. 31118 β), remained quite undetermined

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[1]) Compare Verslagen Kon. Acad. v. Wetenschappen, Amsterdam, Sept. 25 1909, p. 300 and Nov. 27 1909, p. 488.

for thirteen years (until 1911) among the "Indeterminata", no one having even recognized the natural order. Then, in 1911, when revising my herbarium collections for the Systematisches Verzeichnis of Mrs. KOORDERS—SCHUMACHER, the twigs came again under my eyes, and misled by an external resemblance to some species of the genus Litsea, and in the absence of flowers and fruits, I labelled them doubtfully as an undeterminable species of Litsea. Under this preliminary determination, namely as Litsea? spec. div. the above material (Kds. n. 31118 β) was first published in the Systematisches Verzeichnis (I Abteil § 1 Fam. 102, p. 34), with mention of the station and time of collection.

Recently, on March 25th, when re-examining this 17 year old herbarium material (Kds. n. 31118 β) I found that, without the least doubt, it was identical with the fruiting twigs collected by me on March 15th at the same spot, and then at once recognized as Sloanea javanica; these twigs (Kds. n. 42813 β and 42807 β) were derived from two of my "numbered" trees (namely [1]) tree 23n and tree 39n). The old herbarium material was also identical with a specimen consisting only of leafy twigs (Kds. n. 42814 β), which bore especially large leaves and had also been collected by me in the jungle of Depok on March 15th, from a very young unnumbered tree.

Geographical distribution. Whereas Sloanea Sigur may be counted among the commonest forest trees of Western and Central Java, as well as of Eastern Java, growing chiefly at an altitude of 600—1200 metres, and also occurs far outside Java, e.g. in India, Sloanea javanica, which is sharply differentiated from the former species by its not prickly fruits and entire petals, is so far not known outside Java, and has not been found wild in Java outside the forest of Depok.

Sloanea javanica is the only species of the subgenus Phoenicospermum (Miq.) Schumann, in Engler and Prantl's Natürliche Pflanzenfamilien III 6, (1890) 5. This subgenus was formerly (1865—1866) erroneously published by Miquel as a new genus, under the name Phoenicosperma.

Oecological conditions. In the very heterogeneous, shady nature-reserve of Depok, lying at an altitude of about 100 metres above sea-level, and consisting principally of evergreen trees with many

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[1]) The letter n does not signify here number, but indicates the series to which the trees numbered 23 and 39 belong.

climbing plants and a fairly rich under-growth, Sloanea javanica only grows very sparsely, but is by no means rare, at least not in young specimens. Adult trees, however, are only found in very small numbers. The soil in the forest of Depok is fertile, and like the climate, it is rather moist throughout almost the entire year. With regard to rain-fall and location of this station (Depok) the following data are taken from "Regenwaarnemingen in Ned. Indië" II (1913) p. 66, published by the Royal magnetic and metereological observatory of Batavia.

Depok is situated at an altitude of 93 metres above sea-level; 33 kilometres from the coast. Annual rainfall 3156 millimetres. Monthly rainfall maxima 487 millimetres in November and 678 millimetres in April. Monthly minima of rainfall 95 millimetres in June and 61 millimetres in August.

Means of distribution. The well developed, brilliantly coloured arillus of the fairly large seeds, and the brilliant colour of the fruits would already indicate that the distribution is effected by fructivorous animals. Since the arillus has, however, an extraordinarily bitter taste, many animals will probably soon drop the seeds they have taken. The very scattered occurrence and the relatively small number of specimens of this tree in the Depok forest may perhaps be thus explained to some extent. I myself have not yet observed any transport of the seeds by animals. I did indeed observe on March 31 that the numerous fruits lying below tree 39*n* had all, without exception, been gnawed by animals before dehiscence. The mature seeds, although damaged in some cases, were still within the fruit. As far as I have been able to ascertain, this damage to fallen fruits and also to fruits still on the tree, was probably all due to monkeys (Semnopithecus) occurring near Depok in large numbers. As a rule the strong woody pericarp was completely gnawed away at or near the apex of the fruit, down to the arillus of the seeds. The large embryo, which has a particularly pleasant taste, had only been eaten up in a few cases. Apparently the intensely bitter arillus, which surrounds the greater part of the seed, had protected it in most cases against the monkeys.

So it seems that Sloanea javanica depends for its means of distribution on exozoic seed-distribution by small mammals and large birds, which, having been attracted by the brilliant colour of the pericarp and arillus, take seeds from fruits which have opened, but soon drop them again on account of the intensely bitter taste of the arillus.

Season of flowering and fruiting. The two numbered trees (23*n* and 39*n*) fruited in March, the older specimen (39*n*) very abundantly. The flowering season is for Depok in the first half of the wet monsoon (October—December).

Economic use. According to my native guides the wood is not durable and is therefore only used as fire-wood, in spite of its large dimensions. Formerly the disc-shaped wheels of pedatis (buffalo-carts), were sometimes made from the thick plank-buttresses, found on the roots of these, as of other trees. The older of the two trees mentioned (39*n*) now within the wire fence of the nature reserve, still bears clear traces of this custom, now obsolete for many years, for evidently a wheel of a buffalo-cart has been cut out of one of the plank-buttresses. Formerly the natives of Depok also prepared an oil from the interior of the seeds (from the embryo). No other economic application of Sloanea javanica is known.

Culture. On account of its size and fine arboreal habit, and of the brilliant colour of its large fruits and seeds, this species deserves to be cultivated as ornamental tree, at least in the lower districts of Java. So far, however, Sloanea jevanica has not been planted outside the Buitenzorg Gardens.

Description of tho species. In 1894 Koorders and Valeton, in their "Bijdragen tot de kennis der Boomsoorten van Java", p. 240, under "Aanmerkingen", included a note on Sloanea javanica, of which the following is a translation: "The description of the leaves from a living specimen in the Buitenzorg Gardens (VI. C. 94); the rest according to Miquel l.c.". "The actual habitat is not known, and the tree is only known from the above gardens, so that it perhaps originates from one of the outer islands, and not from Java".

"This species is still wanting in "Herb. Kds". (Thus in Bijdragen Booms. Java I).

I further wrote in 1912 in vol. II. (p. 571) of my "Exkursionsflora von Java" the following:

"Java? Angeblich (nach Miquel l.c.) wild in Java, jedoch vermutlich dort nich ausserhalb des botanischen Gartens von Buitenzorg vorkommend. Jedenfalls sah ich noch keine einwandfreie javanische Spezimina".

The finds and observations made in 1898 and in March 1915 in the nature reserve of Depok have filled up in a gratifying manner the lacuna in our knowledge of the habitat of this rare tree.

The examination of the specimens of Sloanea javanica found in the forest of Depok, have shown me that the specific description and figure, published by Miquel, is in the main, correct, but requires amplification and, with regard to a few points, also correction.

I confine myself here entirely to my observations on the material from Depok (Herb. Kds. n. 42807 β, 42814 β, 42778 β, etc.):

Tree attaining a height up to 25 metres. Trunk up to ¾ metre in diameter, fairly straight and sometimes columnar, with large plank-buttresses formed by the roots, branching irregularly and only high above the ground. Crown high, dense, irregular. Bark externally dark grey, with watery sap (no latex and no resin). Leaves with dark green upper surface, lower surface bluish green; smooth and shiny on both sides. The leaves of very young plants, only 2 metres high, may attain a length of 40 centimetres, but those of the fertile branches of a very old tree, 25 metres high, are only 10—20 centimetres long. Young twigs pale green; older branches dark grey (not brown).

Fruits (ripe, but not yet dehisced): externally a beautiful orange (not brick red). Mesocarp thick, woody, dry, grey, almost tasteless and odourless. Endocarp thin, of a beautiful purple colour. Seeds (ripe) almost completely enveloped by a fine orange yellow or orange (not red), glistening, almost odourless and very bitter arillus. Testa externally shiny black, crustaceous (not osseous). Endosperm small, opal-white, fleshy. Embryo large, pure white, odourless, of pleasant taste.

Literature:

Sloanea javanica (Miquel) Sszyszylowicz in Engler's Botanische Jahrb. VI. (1885) 454; Schumann in Engler und Prantl, Natürl. Pflanzenfam. III. 6. (1890) 5; Koorders en Valeton, Bijdragen Booms. Java I. (1894) 239; Koorders und Valeton, Atlas Baumarten Java II. (1914) Fig. 433; Koorders, Exkursionsflora von Java. II. (1912) 571. (Here read line 17 from foot of p. 571 Miquel instead of: (Miq.) Sszysz.); Phoenicosperma javanica Miquel in Annales Mus. bot. Lugd. Bat. II. (1865—1866) 68. t. 3; Echinocarpus tetragonus Teijsm. et Binn., Catal. Hort. Bog. (1866) 184 (sine descript.).

Trees grown in the Buitenzorg Gardens. Of Sloanea javanica I already saw in last March correctly labelled Buitenzorg garden-herbarium specimens of two trees, cultivated in the Hortus Bogoriensis under numbers 92 and 94 in division VI. C. The latter of these two numbered trees from the Gardens (namely 94 VI. C.), was already published by us in 1894 in KOORDERS en VALETON, Bijdragen Booms. Java I, p. 240, under the correct name Sloanea javanica (Miquel) Sszyszylowicz.

An old garden collection-label of a sterile herbarium specimen of tree 92 (VI. C.) indicates, that its numbered Hortus-tree was formerly cultivated under the incorrect, and as far as I know unpublished garden name of *Elaeocarpus stipularis Bl. var. latifolia.*

Habit. In the fruiting season this forest giant with a trunk, more than 1¾ metres in diameter, is very striking. The dark green crown is then adorned by numerous fruits, almost as large as fists, externally orange, internally a beautiful purple and opening by four valves. These generally contain 1—2, rarely 3—4 glistening jet black, oblong, fairly large seeds, for the most part enveloped by an arillus of a fine orange yellow colour. Except on account of the large dimensions of the trunk, with the large plank-buttresses formed by the roots, this tree is not very conspicuous outside the fruiting season. Young trees easily escape the attention of the field botanist, because this species, even in the sole original habitat so far known, i.e. in the forest of Depok, only occurs very scattered and does not produce flowers and fruits until it has attained an advanced age; a further reason why young specimens are inconspicuous, is that their leaves show such a close resemblance to those of some other Javanese trees, as regards shape, size and innervation, that they are only distinguished after close scrutinizig. The latter reasons explain the fact that the original habitat of Sloanea javanica could have remained unknown for nearly half a century, in spite of its situation near a scientific centre like Buitenzorg, in the forest of Depok, often visited by many botanists.

Buitenzorg, April 9th 1915.

Botany. — "*On the influence of external conditions on the flowering of Dendrobium crumenatum Lindl.*" By Prof. F. A. F. C. WENT and A. A. L. RUTGERS.

Dendrobium crumenatum is a small epiphytic Orchid, occurring pretty frequently in the Dutch East Indies, and especially common in Western Java, e.g. at Buitenzorg; it has often attracted the attention of naturalists by peculiarities of its flowering[1]). These

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[1]) F. A. F. C. WENT. Die Periodicität des Blühens von *Dendrobium crumenatum* Lindl. Ann. d. Jard. bot. de Buitenzorg, Supplément II, Leyde, 1898, p. 73—77.

peculiarities are so striking, that the plant has even received a Dutch name and is known in Java as "duifjes", in Singapore as "pigeon orchid". This name refers to the white flowers of a size of about 3 centimetres, which appear simultaneously on many plants and are all the more noticeable, because they remain open only for a single day. Everywhere hundreds of these small, white flowers are seen, which are, moreover, delicately scented. Next day the phenomenon is over and only after several weeks, or even months, the "pigeon orchids" again suddenly appear in full bloom; next day only faded flowers can be found.

We have now studied the phenomenon in question with plants in their native habitat and with others, sent to Utrecht, which were finally cultivated there in two different glass houses. A few results, obtained by us in this manner, are briefly communicated here; for further details we refer to a fuller paper, which will soon be published elsewhere. We wish to emphasize, that we have not succeeded in solving the problem completely, but nevertheless our observations appear sufficient to deprive the phenomenon of its air of mystery.

In the first place we found that the interval between two successive flowering periods is subject to considerable variation; at Buitenzorg minima of 4 and 10 days, and a maximum of 94 days were observed, but in Utrecht the intervals were generally much longer, while in winter flowering cannot be observed at all.

Furthermore it became very evident, that external conditions influence the outset of the flowering. Accordingly the time varies in the East Indies from place to place, and only coincides occasionally for neighbouring places, such as Meester Cornelis, Weltevreden and Menes (March 14th 1913) or Maos, Klampok and Bandjarnegara (March 26th 1913). Likewise the time of flowering often differed at Utrecht in the two glass houses, in which temperature and humidity were not kept equal; on the other hand the flowering period in spring was once found to synchronize in glass houses at Utrecht, Bonn and Hamburg.

When plants, previously grown at a spot A, and hence having definite flowering days, are transferred to a spot B, they acquire another flowering time, which is identical with that of plants grown at B from the beginning. This was found on transporting plants from various parts of Java and from Deli to Buitenzorg and conversely on moving plants from Buitenzorg to Medan. The same change was observed in plants sent from the tropics to the hothouses of European botanic gardens.

With respect to the question, what external factors play a part in determining the flowering period, it should be noted that the two above mentioned planthouses in Utrecht supply an indication, for here the differences could at most extend to the amount of light, the temperature and the degree of humidity of the air. Observations at Buitenzorg (and also earlier ones at Tegal) have shown that the light may here be dismissed from consideration, for the flowering time is the same for plants growing in the shade as for those in sunny places, although the *number* of the flowers is evidently determined to some extent by the amount of light. Temperature and degree of humidity on the other hand, probably both influence the flowering time, or sometimes the one and sometimes the other of these factors. At Buitenzorg it was occasionally noticed that heavy rains, following a period of drought, soon induced an abundant flowering of *Dendrobium crumenatum*. On the other hand the coincidence of the spring flowering in planthouses at Bonn, Hamburg and Utrecht can only be attributed to the temperature. During winter the temperature of such houses is kept very constant; when in spring the sun becomes more powerful, their temperature rises considerably. It was indeed remarkable, that the above mentioned coincidence was preceded by a period of bright, sunny weather over the whole of Western Europe.

In what way can we now imagine the external conditions to bring about the simultaneous flowering of very different individuals of the same species? The explanation may be as follows: The buds of this *Dendrobium* develop up to a certain stage, but cannot pass it, unless certain favourable conditions are found in the environment, e.g. of temperature or of humidity, or of both; then these conditions, acting for a sufficient time, give an impulse, which carries the buds to their last stage of development; it is further necessary that these last stages should be gone through in a very short time.

What is observed in a state of nature is in complete agreement with this explanation Not only are many flowers found at one time, and few, or even a single one at another time, but different plants do not behave in the same manner. We do not mean by this so much that some plants always flower abundantly and others sparingly (for this is more likely the result of internal disposition, of which we know as yet very little) but rather, that on one and the same plant sometimes many flowers unfold, sometimes only a few. The favourable circumstances were present, but there were not always the same number of buds in the sensitive stage, sometimes not even a single one, so that there are flowering days when a given plant unfolds no flower, other days, when the number of open flowers is fairly large. Not only do different plants behave very unequally, but the same is noticed on comparison of the various inflorescences of the same plant.

Without careful inspection one gets the impression that the flowers of this *Dendrobium* are solitary in the axils of the leaves; closer observation, however, shows that these axils do not contain a solitary flower, but an inflorescence, of which the axis remains extremely short and generally only a single flower opens at a given time. Sometimes, however, two open flowers are found together in the inflorescence, very rarely even three. Now when careful notes are made as to which inflorescences of a plant produce open flowers at a given flowering period and subsequent flowering data are compared with these, it is found, that in some cases a flower opens in the inflorescence at each time of flowering and that at other times it is left out one or more times. Nor is any order discernible in the combination of inflorescences, which bear open flowers at successive flowering periods. All this was of course to be expected on the assumption that the unfolding of the flowers depends on the presence of buds in a definite developmental stage at the moment that favourable external conditions occur.

The question arises, whether a closer examination of the buds gives any indication as to the nature of this stage of development. The inflorescence is found to arise in the axil of a sheathing leaf without lamina. The young bud is completely surrounded by the sheath and the breaking through of this sheath is evidently difficult. Each bud consists of a number of bud scales and the rudiments proper of the flower. These bud scales completely surround the interior of the bud and present themselves as closed sheaths, which are hard and little permeable — so little, that a bud which has lain in alcohol for some days, does not show internally a trace of this liquid. When the interior of the bud has once broken through these sheathing scales, the latter become fibrous and resemble straw, since hardly anything remains beyond the vascular bundles. Every floral bud is generally cut off from the outside world by two of these scales; these must be broken through before the flower can open. As long as the bud is not longer than 4—5 m.m. it remains between these sheaths; at this stage all the floral parts are easily recognized, although their dimensions are small; only the spur is not yet visible. When the scales are broken through a sudden extension of all the floral parts takes place and after a few days the flowers have opened. Hence just before the flowering a number of buds are found, having a length of 4—5 m.m., while immediately afterwards this number is much smaller. An investigation at Utrecht on the size of the adult floral buds, just before flowering, showed some diversity, probably connected with the fact that not all buds opened on the same day, and that the flowering extended over two days. This was repeatedly the case at Utrecht, but also at Buitenzorg stragglers are sometimes found, which only open on the day after the general flowering, although it is not so common there as at Utrecht. Probably this is due to a more rapid development under the favourable conditions of the tropics. Careful observation indeed shows, that the opening of the flowers is not absolutely synchronous and that it takes place at different hours; nor is the end of the flowering reached simultaneously, for it may vary by some hours or even by half a day. Moreover the interval between opening and fading is not identical for different flowers.

Attempts to induce flowering experimentally, by a choice of external conditions, have not yet furnished any result. Such attempts are rendered all the more difficult by the necessity of having plants bearing buds at the desired stage of development.

The phenomena shown by *Dendrobium crumenatum* do not indeed, differ fundamentally from those observed in other Orchids. In these also the simultaneous flowering of different plants is often seen, but it is less striking, because the flowering generally extends over days, or sometimes even over weeks and hence one flower may open several days before the other.

Still more generally the flowering of the "pigeon orchids" may even be regarded as the extreme case of what is observed with respect to the flowering of plants in our own climate. Here also, for instance in spring-flowering plants, the floral buds reach an advanced stage of development, which is not passed, until external conditions are favourable and then simultaneous flowering of numerous individuals occurs; the simultaneity is only less striking because the last stages of development are gone through more slowly. Of late these phenomena have been repeatedly investigated, e.g. by KLEBS; a plant like *Dendrobium crumenatum* would perhaps be a suitable experimental object for a further investigation of these cases.

Utrecht, August 1915.

Chemistry. — "*In-, mono- and divariant equilibria*" *II*. By Prof. F. A. H. SCHREINEMAKERS.

5. *Ternary systems.* [1])

In an invariant point of a ternary system five phases occur, which we will call 1, 2, 3, 4 and 5; consequently this point is a quintuplepoint. Five curves, therefore, start from this point, which we shall call (1), (2), (3), (4) and (5) according to our former notation. Further we find $\frac{1}{2}(n+2)(n+1)=10$ regions, viz. 123, 124, 134, 234, 125, 135, 235, 145, 245 and 345.

We call the three components of which the ternary system is composed: A, B and C; the five phases then can be represented by five points of the plane $A\,B\,C$. These five points may be situated with respect to one another in three ways, as has been indicated in figs. 1, 3 and 5. In fig. 1 they form the anglepoints of a quintangle; in fig. 3 they form the quadrangle 1 2 5 3, within which the point 4 is situated; in fig. 5 they form the triangle 1 2 5, within which the points 3 and 4 are situated.

We can however consider figs. 3 and 5 also as quintangles; in each of them the sides have been drawn and the diagonals have been dotted. We call fig. 3 a monoconcave and fig. 5 a biconcave quintangle.

We are able to make of fig. 3 a monoconcave quintangle in different ways; we do this, however, in the following way. We draw in the quadrangle, within which the point 4 is situated, the diagonals 15 and 23. These divide the quadrangle into four triangles; the point 4 is situated within one of these triangles. Now we unite the anglepoints 1 and 2 of this triangle with the point 4 and we consider the lines 14 and 24 as sides of the quintangle, so that a monoconcave quintangle is formed.

In order to change fig. 5 into a quintangle we draw a straight line through the points 3 and 4; this intersects two sides of the triangle, in our case the sides 12 and 15. We now replace the side 12 by the two lines 14 and 24, the side 15 by the lines 13 and 35, so that a biconcave quintangle arises.

In the figs. 1, 3 and 5 the anglepoints are numbered in the following way. We take any anglepoint and we call this the point 1; two diagonals start from this point. Now we go along one of

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[1]) For another treatment confer F. A. H. SCHREINEMAKERS. Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM III[1]. 218.

these diagonals towards another anglepoint and we call this 2, from this point we go again along a diagonal towards another anglepoint, which we shall call 3; in the same way we go from point 3 towards point 4 and from this point towards point 5. (See the figs. 1, 3 and 5). We call this order of succession "the diagonal succession". It will appear from our further considerations for what reason this definite order of succession has been chosen.

Type I. Now we shall deduce the *P*, *T*-diagram when the five phases form, as in fig. 1, the anglepoints of a convex quintangle.

As the lines 23 and 45 intersect one another, it follows for the phases of curve (1):

$$\left.\begin{array}{c} 2 + 3 \rightleftarrows 4 + 5 \\ (2)(3) \mid (1) \mid (4)(5) \end{array}\right\} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We find for the phases of curve (2):

$$\left.\begin{array}{c} 3 + 4 \rightleftarrows 1 + 5 \\ (3)(4) \mid (2) \mid (1)(5) \end{array}\right\} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now we draw in a *P*, *T*-diagram (fig. 2) arbitrarily the curves (1) and (2); for fixing the ideas we take (2) at the left of (1). With regard to this the above mentioned reactions have been written at once in such a way that also herein curve (2) is situated at the left of (1). [For the distinction of "at the right" and "at the left" of a curve we have previously assumed that we find ourselves in the invariant point on this curve facing the stable part].

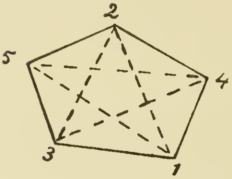

Fig. 1

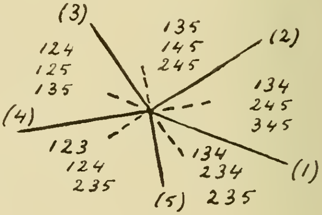

Fig. 2.

Now we shall determine the position of curve (3). It is apparent from the first reaction that the curves (2) and (3) are situated at the same side of curve (1); as (2) is situated at the left of (1), (3) must consequently be situated also at the left of (1).

It is apparent from the second reaction that (3) and (1) are situated on different sides of (2); as, according to our assumption curve (1) is situated at the right of (2), (3) must consequently be situated at the left of (2).

Consequently we find: curve (3) is situated, at the left of (1) and of (2); curve (3) is situated therefore, as is also drawn in fig. 2, between the stable part of curve (2) and the metastable part of curve (1).

Now we determine the position of curve (4). It follows from the first reaction that (4) is situated at the right of (1); it is apparent from the second reaction that (4) is situated at the left of (2). Curve (4), therefore, as is also drawn in fig. 2, must be situated between the metastable parts of the curves (1) and (2).

At last we have still to determine the position of curve (5). It is apparent from the reactions above that curve (5) is situated at the right of (1) and of (2). Consequently curve (5) is situated within the angle, formed by the stable part of curve (1) and the metastable part of curve (2). Within this angle we also find however the metastable part of curve (3); consequently we now still have to examine in what way curve (5) is situated with respect to curve (3). We take for this the reaction between the phases of curve (3); we find from fig. 1:

$$\left.\begin{array}{c} 4+5 \rightleftarrows 1+2 \\ (4)\,(5) \mid (3) \mid (1)\,(2) \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As we know already that (1) and (2) are situated at the right of (3), we have written this reaction immediately in this way that also herein (1) and (2) are situated at the right of (3). From this is at once apparent that (5) must be situated at the left of (3). According to the previous it is apparent, therefore, that curve (5) must be situated between the metastable parts of the curves (2) and (3).

Besides the reactions 1, 2, and 3 we may still deduce two other reactions from fig. 1; those reactions refer to the phases of the curves (4) and (5). Although those reactions are no more wanted, they may however be used as confirmation. We find:

$$\begin{array}{c} 1+5 \rightleftarrows 2+3 \\ (1)\,(5) \mid (4) \mid (2)\,(3) \end{array} \quad \text{and} \quad \begin{array}{c} 1+2 \rightleftarrows 3+4 \\ (1)\,(2) \mid (5) \mid (3)\,(4) \end{array}$$

The partition of the curves, which follows from this is also in accordance with fig. 2.

Now we have still to deduce the partition of the regions. Between the curves (1) and (2) the region (12) = 345 extends itself, between (1) and (3) the region (13) = 245, between (1) and (4) the region (14) = 235 and between (1) and (5) the region (15) = 234. When drawing those regions we have to bear in mind that a region-angle is always smaller than 180°. When we determine in a similar way the position of the other regions, we find a partition as in fig. 2.

The following is apparent from fig. 2. When we move, starting from a point of the curve (1), around the quintuplepoint, the succession of the curves is: (1), (2), (3), (4), (5) or the reverse order (1), (5), (4), (3), (2); we shall express this in the following way:

"The curves follow one another in diagonal order".

Further it is apparent that the partition of the curves is symmetrical in that respect, that we find between every two curves the metastable part of another curve. Also we see that the regions are divided symmetrically with respect to the different curves.

This symmetrical position of curves and regions with respect to one another is based of course on fig. 1; this is viz. also symmetrical in so far that each phase is situated outside the quadrangle, which is formed by the four other phases.

Further we see in fig. 2 again the confirmation of the rule that each region which extends over the metastable or stable part of a curve (F_p) contains the phase F_p. Let us take e. g. curve (1); the region 134 extends over the stable part of this curve, the regions 124, 125 and 135 extend over the metastable part; each of these regions contains the phase 1.

Type II. Now we consider the case that the five phases form the anglepoints of a monoconcave quintangle (fig. 3). In order to determine the position of the curves (1)—(5) we take the five reactions:

$$\left.\begin{array}{cc}
4+5 \rightleftarrows 2+3 & 1+5 \rightleftarrows 3+4 \\
(4)(5) \mid (1) \mid (2)(3) & (1)(5) \mid (2) \mid (3)(4) \\
1+2+5 \rightleftarrows 4 & 2+3 \rightleftarrows 1+5 \\
(1)(2)(5) \mid (3) \mid (4) & (2)(3) \mid (4) \mid (1)(5) \\
\multicolumn{2}{c}{4 \rightleftarrows 1+2+3} \\
\multicolumn{2}{c}{(4) \mid (5) \mid (1)(2)(3)}
\end{array}\right\} \quad . \quad . \quad (4)$$

Now we draw in a P, T-diagram (fig. 4) the curves (1) and (2); for fixing the ideas we take (2) at the right of (1). According to this the above-mentioned reactions, which refer to the phases of the curves (1) and (2) have been written at once in such a way that herein curve (2) is situated at the right of (1).

It follows at once from the first and the second of the reactions above, that curve (3) is situated at the right of (1) and (2). Consequently curve (3) is situated, as is also drawn in (fig. 4) within the angle, which is formed by the stable part of curve (2) and the metastable part of curve (1).

It also follows immediately from the first and the second of the reactions above, that curve (4) is situated at the left of (1) and at the right of (2). Curve (4) is consequently situated between the metastable parts of the curves (1) and (2), and reversally the metastable part of curve (4) is situated between the stable parts of the curves (1) and (2). This is therefore drawn in fig. 4.

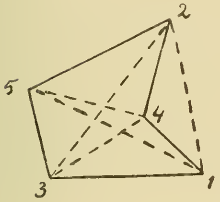

Fig. 3.

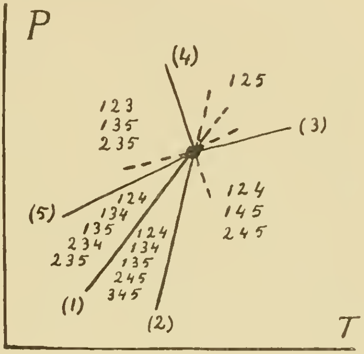

Fig 4.

It follows also from the first two reactions that curve (5) is situated at the left of (1) and (2). Consequently curve (5) is situated within the angle, which is formed by the stable part of curve (1) and the metastable part of curve (2). [Confer fig. 4]. This angle, however, is divided into two parts by the metastable part of curve (3), so that we have still to know the position of (5) and (3) with respect to one another. We can do this with the aid of the third of the reactions mentioned above; from this it appears viz. that the curves (1), (2), and (5) are situated on the same side of curve (3); curve (5) is consequently situated on the left side of (3), therefore, within the angle, which is formed by the stable part of curve (1) and the metastable part of curve (3). [Confer fig. 4].

We have used for the determination of the mutual position of the five curves, the three first reactions only; we see that the division with respect to the curves (4) and (5), which follows from the last two reactions, is also in accordance with fig. 4.

When we determine, in the way treated above, the partition of the regions, we find this as is indicated in fig. 4.

It is apparent from fig. 4 that again also in this case the curves follow one another in diagonal succession. The partition of the curves is no more symmetrical, however; between the curves (1) and (5) and between (2) and (3) no metastable curve is found; between (1) and (2) we find the metastable part of one curve [viz. of curve (4)]; between (3) and (4) and also between (4) and (5) we find two metastable curves. This is also in accordance with fig. 3; herein phase 4 has a particular position with respect to the phases 1 and 2; this is also the case in fig. 4 with curve (4) with respect to the curves (1) and (2). In fig. 3 phase 4 has also a particular position with respect to the phases 3 and 5; this is moreover the case in fig. 4 with curve (4) with respect to the curves (3) and (5).

We see also in fig. 4 the confirmation of the rule, that each region, which extends over the metastable or stable part of a curve (F_p), contains the phase F_p. When we take e. g. curve (1); the regions 124 and 134 extend themselves over the stable part of this curve; the regions 125 and 135 extend themselves over the metastable part; each of these regions contains the phase 1.

The regions 125 and 135 extend themselves over the metastable parts of the curves (1) and (5); both the regions contain the phases 1 and 5. The region 124 extends itself over the curves (1) and (2); it contains therefore the phases 1 and 2.

Type III. Now we shall yet consider the case that the five phases form the anglepoints of a biconvex quintangle (fig. 5). In order to determine the position of the five curves with respect to one another, we take the reactions:

$$\left.\begin{array}{cc}
2+3 \rightleftarrows 4+5 & 3 \rightleftarrows 1+4+5 \\
(2)\,(3)\mid(1)\mid(4)\,(5) & (3)\mid(2)\mid(1)\,(4)\,(5) \\
4 \rightleftarrows 1+2+5 & 1+2+5 \rightleftarrows 3 \\
(4)\mid(3)\mid(1)\,(2)\,(5) & (1)\,(2)\,(5)\mid(4)\mid(3) \\
\multicolumn{2}{c}{1+2+3 \rightleftarrows 4} \\
\multicolumn{2}{c}{(1)\,(2)\,(3)\mid(5)\mid(4)}
\end{array}\right\} \quad . \quad . \quad (5)$$

We now draw in a P,T-diagram (fig. 6) the curves (1) and (2); we take curve (2) at the left side of (1). In connection with this we have written both the first reactions immediately in such a way that also herein (2) is situated at the left of (1).

The position of curve (3) follows also at once from both the first reactions, viz. at the left of (1) and of (2), consequently we have to draw in fig. 6 curve (3) within the angle, which is formed by the stable part of curve (2) and the metastable part of curve (1).

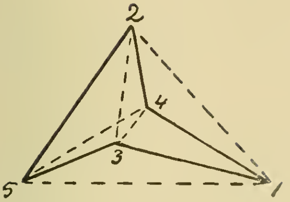

Fig. 5.

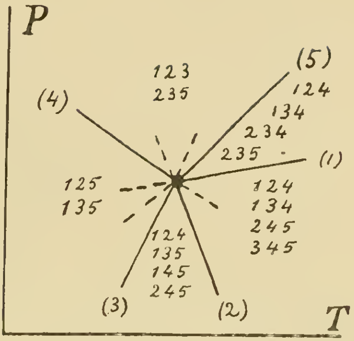

Fig. 6.

It follows also from both the first reactions that curve (4) is situated on the righthand side of (1) and of (2); consequently it is situated in fig. 6 within the angle, which is formed by the stable part of curve (1) and the metastable part of (2). Within this angle, however, also the metastable part of the curve (3) which has already been determined, is situated; consequently we have yet to examine the position of curve (4) with respect to curve (3). This follows from the third reaction; we know viz. already from the previous that (1) and (2) are situated on the righthand side of (3) [in connection with this the third reaction is written in such a way that herein (1) and (2) are situated at the righthand side of (3)], so that (4) must be situated at the left of (3). Hence it follows that (4) is situated within the angle, formed by the metastable parts of curves (2) and (3).

It follows still also from both the first reactions that curve (5) is situated at the right of (1) and of (2); consequently curve (5) must be situated within the angle which is formed by the stable part of (1) and the metastable part of (2). This angle is divided into three parts by the stable part of curve (4) and the metastable part of curve (3), so that we have still to examine within which of these parts the curve (5) is situated. This appears immediately from the third reaction, from which it is apparent that curve (5) is situated at the righthand side of (3). Consequently curve (5) must be situated within the angle, which is formed by the metastable part of curve (3) and the stable part of curve (1).

We have only used the first three reactions for the determination of the mutual position of the five curves. The partition of the curves, which follows from both the last reactions, is also in accordance with fig. 6.

When we determine, as has been indicated formerly, the partition of the regions, then we find this as is indicated in fig. 6.

It is apparent from fig. 6 that also again in this case the curves follow one another in diagonal succession. The partition of the curves is not symmetrical. The phases 2 and 5 (fig. 5) are situated in the same way with respect to 1, 3 and 4, the phases 3 and 4 with respect to 1, 2 and 5, while phase 1 has a particular position with respect to the others. This shows itself therefore in the position of the curves in fig. 6.

Also we see again in fig. 6 the confirmation of the rule, that each region which extends itself over the metastable or stable part of a curve (Fp), contains the phase Fp. The region 125 extends itself over the metastable part of curve (1), the regions 124, 134 and 135 extend themselves over the stable part; each of these regions contains the phase 1.

The metastable parts of the curves (1), (2) and (5) are situated in the region, which is limited by the curves (3) and (4); this region contains therefore the phases 1, 2 and 5.

When we combine the results, obtained above, then the following is apparent.

1. Three types of P, T-diagrams exist

a) as in fig. 2, when the five phases form the anglepoints of a convex quintangle (fig. 1);

b) as in fig. 4, when the five phases form the anglepoints of a monoconcave quintangle (fig. 3);

c) as in fig. 6, when the five phases form the anglepoints of a biconcave quintangle.

2. The three types differ from one another by the position of the metastable parts of the curves and by the partition of the regions; they are in accordance with one another in so far that the curves follow one another in diagonal succession.

In order to formulate the obtained results in another way, we shall call "a bundle" a group of curves, which follow one another, without metastable parts of curves occurring between them. Consequently in fig. 6 (5), (1) and (2) form a "bundle", which we shall call a "threecurvical" bundle, as it consists of three curves; curve (3) forms a "onecurvical" bundle, the same applies to curve (4).

In fig. 4 (1) and (5) form a "twocurvical" bundle; the same applies to (2) and (3); curve (4) forms a "onecurvical" bundle.

In fig. 2 each of the curves forms a "onecurvical" bundle. We may express the results combined sub 1°, in the following way. There exist three types of P, T-diagrams; the five phases form the anglepoints of:

a) a convex quintangle (fig. 1); then in the P, T-diagram the five curves form five "onecurvical" bundles (fig. 2).

b) a monoconcave quintangle (fig. 3); then in the P, T-diagram the five curves form two "twocurvical" and one "onecurvical" bundle (fig. 4).

c) a biconcave quintangle (fig. 5); then in the P,T-diagram the five curves form one "threecurvical" and two "onecurvical" bundles. We can apply the obtained results also in the following way.

When we know the position of the five curves of a P,T-diagram, then we can easily determine to which of the types 2, 4 or 6 this diagram belongs. Hence follows at once the position of the five phases with respect to one another, viz. whether they form the anglepoints of a convex, monoconcave or biconcave quintangle.

We shall discuss now an example of the partition of the curves, starting from a quintuplepoint as is found experimentally in the system: water, $CuCl_2$ and KCl. In this system occur as solid phases: KCl, $CuCl_2.2H_2O$ and the doublesalts: $CuCl_2.2KCl.2H_2O$ and $CuCl_2.KCl$. We use the following abbreviations: $CuCl_2.2H_2O = Cu_2$; $CuCl_2.2KCl.2H_2O = D_{1.2.2}$ and $CuCl_2.KCl = D_{1.1}$. We represent by G the vapour, which consists in this system of water only.

In fig. 7 the equilibria, experimentally defined, are represented; for the sake of clearness this figure is strongly schematized, otherwise it would have to be much larger e.g. the point Cu_2 is situated far too close to the point $CuCl_2$, the point $D_{1.2.2}$ far too close to the side $CuCl_2$—KCl, etc. Yet we have taken into consideration that the different points which we have to consider, form together in fig. 7 the same quintangles as this is really the case.

At the temperature $T' = 56.1°$ occurs the equilibrium:

$$Cu_2 + D_{1.2.2} + D_{1.1} + L_f + G$$

at $T_b = 93.3°$ occurs the equilibrium:

$$KCl + D_{1.2.2} + D_{1.1} + L_b + G$$

As the vapour G consists of water only, in fig. 7 the points W and G coincide.

Of course five curves start from the point f, they are:

$$\begin{aligned}
(Cu_2)_f &= D_{1.2.2} + D_{1.1} + L + G \\
(D_{1.2.2})_f &= Cu_2 + D_{1.1} + L + G \\
(D_{1.1})_f &= Cu_2 + D_{1.2.2} + L + G \\
(L)_f &= Cu_2 + D_{1.2.2} + D_{1.1} + G \\
(G)_f &= Cu_2 + D_{1.2.2} + D_{1.1} + L
\end{aligned}$$

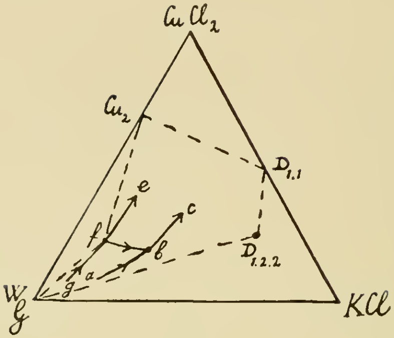

Fig. 7.

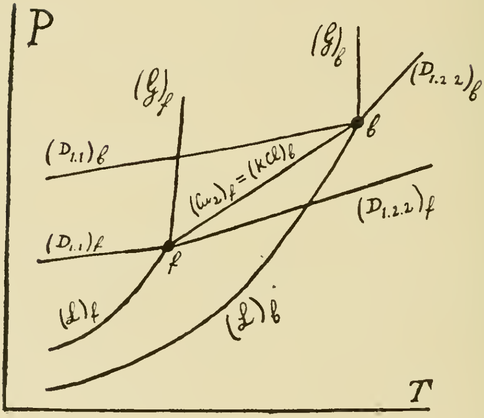

Fig. 8.

In order to indicate that these curves start from the point *f*, outside the parentheses the letter *f* is written. In fig. 7 *gf* represents the solutions of the equilibrium $(D_{1.1})_f$, *fe* those of the equilibrium $(D_{1.2.2})_f$ and *fb* those of the equilibrium $(Cu_2)_f$. The small arrows indicate the direction in which the temperature increases.

Also from the point *b* five curves start; they are:

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[1] W. MEYERHOFFER. [Zeitschr. f. phys. Chem. **3**, 336 (1889); **5**, 97 (1890)] defined the compositions of the solutions of the quadruplecurves.

J G. C. VRIENS. [Zeitschr. f. phys. Chem. **7**, 194 (1891)] has measured the vapour-tensions of several points of these curves.

$$\begin{aligned} KCl)_b &= D_{1.2.2} + D_{1.1} + L + G \\ (D_{1.2.2})_b &= KCl + D_{1.1} + L + G \\ (D_{1.1})_b &= KCl + D_{1.2.2} + L + G \\ (L)_b &= KCl + D_{1.2.2} + D_{1.1} + G \\ (G)_b &= KCl + D_{1.2.2} + D_{1.1} + L \end{aligned}$$

The equilibria $(Cu_2)_f$ and $(KCl)_b$ are the same, as is apparent from the occurring phases. In fig. 7 fb represents the solutions of the equilibrium $(KCl)_b$, bc represents the solutions of the equilibrium $(D_{1.2.2})_b$, and ab those of the equilibrium $(D_{1.1})_b$.

Fig. 8 gives a figure of the P,T-diagram, which is experimentally defined 1). This is somewhat schematized for the sake of clearness. The point f represents the quintuplepoint with the phases:

$$Cu_2,\ D_{1.2.2},\ D_{1.1},\ L_f \text{ and } G$$

the temperature is 56.1°, the pressure is ± 73 mm. of mercury. The curves $(Cu_2)_f$, $(D_{1.2.2})_f$, $(L)_f$ and $(D_{1.1})_f$ starting from this point, have been defined experimentally. Curve $(G)_f$ has not been defined; it is apparent, however, that it must proceed in fig. 8 steeply onwards, a little to the right or to the left.

The five phases of the quintuplepoint form a monoconcave quintangle in fig. 7, its sides Gf, fCu_2, $Cu_2\ D_{1.1}$, $D_{1.1}\ D_{1.2.2}$ and $D_{1.2.2}\ G$ are dotted in fig. 7. [The point f therefore, corresponds with the point 4, the points G and Cu_2 with the points 1 and 2 of fig. 3]. When we take a diagonal succession of the phases, then we have, starting from G:

$$G,\ Cu_2,\ D_{1.2.2},\ L_f \text{ and } D_{1.1}.$$

In the P,T-diagram consequently the succession

$$(G)_f,\ (Cu_2)_f,\ (D_{1.2.2})_f,\ (L)_f,\ (D_{1.1})_f$$

must occur, which is also found experimentally, as is apparent from fig. 8. The metastable continuations of the curves are not drawn in fig. 8; we find them by the same discussion, which has led us to fig. 4. So far as some of these metastable conditions have been realized, they are in accordance herewith.

The point b represents the quintuplepoint with the phases:

$$KCl,\ D_{1.2.2},\ D_{1.1},\ L_b \text{ and } G$$

the temperature is 93.3°, the pressure ± 340 m.m. Hg. The curves, starting from this point have been defined experimentally, except curve $(G)_b$; it is apparent, however, that this must proceed in fig. 8 steeply onwards and a little to the right or to the left.

The five phases form a biconcave quintangle, the sides of which are: $W.b$, $b.D_{1.1}$, $D_{1.1} . D_{1.2.2}$, $D_{1.2.2} . KCl$ and $KCl . G$ [The

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1) J. G C. Vriens, l.c. fig. 6, p. 208.

point $D_{1.1}$, therefore, corresponds with the point 1, the points b and $D_{1.2.2}$ with the points 3 and 4 of fig. 5]. When we take a diagonal succession of the phases, then we have, starting from point G: G, $D_{1.2.2}$, L_b, KCl and $D_{1.1}$. In the P,T-diagram the succession of the curves must be, therefore:

$$(G)_b,\quad (D_{1.2.2})_b\quad (L)_b,\quad (KCl)_b,\quad (D_{1.1})_b\quad .$$

As is apparent from fig. 8, this succession has been found also experimentally. We find the metastable parts of these curves (not drawn in fig. 8) by a similar discussion, as has led us to fig. 6.

(To be continued).

Crystallography. — "*On the Symmetry of the* RÖNTGEN-*patterns of Trigonal and Hexagonal Crystals, and on Normal and Abnormal Diffraction-Images of birefringent Crystals in general.*"

By Prof. H. HAGA and Prof. F. M. JAEGER.

§ 1. In connection with the peculiar phenomena observed some time ago with respect to a number of RÖNTGEN-patterns of birefringent, and more especially of rhombic crystals[1]), we thought it necessary to investigate in a rigorously systematical way, what kind of symmetry would be found in the diffraction-patterns of uniaxial crystals, if radiated through in directions perpendicular to the optical axis. For if the supposition were right, that the suppression of the symmetry-planes expected by theory in the RÖNTGEN-patterns of rhombic crystals were connected in any way with the double refraction, — as was thought at that time by one of us, — then we might expect something of the kind also in the case of the patterns obtained by means of planeparallel sections of uniaxial crystals, if cut parallel to the optical axis, and radiated through in a direction perpendicular to that axis.

To obtain the closest analogy in the orientation with that present in the case of the rhombic crystals, which were always cut parallel to the three pinacoïdal faces $\{100\}$, $\{010\}$ and $\{001\}$, we investigated in the case of tetragonal crystals those sections, which were parallel to the first and the second prisms $\{100\}$ and $\{110\}$; in the case of trigonal and hexagonal crystals we used in the same way the sections parallel to the prism-faces $\{10\bar{1}0\}$ and $\{\bar{1}2\bar{1}0\}$. In the last mentioned crystals thus the sections parallel to $\{10\bar{1}0\}$ will be analogous to those parallel to $\{100\}$ in the case of rhombic crystals, the sections parallel to $\{\bar{1}2\bar{1}0\}$ corresponding in the same way to those parallel to $\{010\}$ in the mentioned biaxial crystals.

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[1]) These Proceedings, **17**, 1204, (1915),

To deduce the symmetry of the RÖNTGEN-patterns of these crystal-sections, as it may be expected after the theory of the phenomenon, it must be kept in mind, that this symmetry will be the same, as in the case of the corresponding sections of a fictive crystal, whose symmetry would be that of the investigated crystal after addition of the symmetry-centre there-to. Indeed, for the phenomenon of the RÖNTGEN-radiation the symmetry-centre would play the rôle of "additive" symmetry-element; and inversely this supposition may be judged satisfactorily proved, if the experiments will show on the other hand a complete concordance between the facts and the theoretical deduction.

In the accompanying table therefore the theoretically expected symmetry of the RÖNTGEN-patterns, as deduced from the now adopted theory, is summerized for all the optically uniaxial crystals from the classes 9 to 27. From this table the expected symmetry of the diffraction-image for all uniaxial crystals can immediately be seen.

§ 2. In the following pages we publish the results obtained in

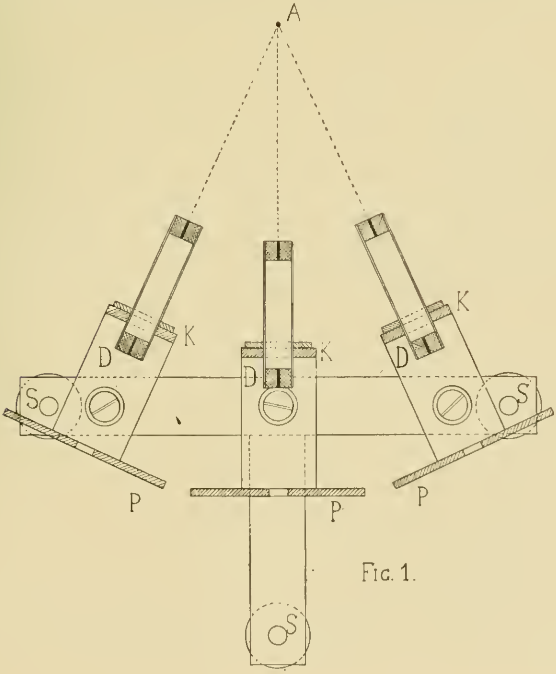

FIG. 1.

the study of trigonal and hexagonal crystals; the data relating to the investigations made with tetragonal crystals will be published by us later-on in a separate communication.

Most of these researches were executed by means of Röntgen-tubes with platinum-anticathode, some of them, however, by the aid of the Coolidge-tube with wolframium-anticathode and separate heating-coil. In most of these experiments we used an apparatus, which enabled us to make *three* Röntgenograms (in the case of rhombic crystals, by radiation along the three principal crystallographical axes, or perpendicular to the first and second prism) *at the same time.* This apparatus was arranged in the following way (vid. the horizontal projection in fig. 1 p. 543).

On a T-shaped brass support, provided with three levellingscrews S, (dimensions: 3 c.m. broad, 1 c.m. thick, longer beam: 28 c.m., shorter beam: 12,5 c.m.), three similar "crystal- and plate-holders" D (vid. also fig. 2) were fixed in the right position by means of strong screws. Every one of these bearers (fig. 2) consists of a brass bar D of 1 c.m. thickness, whose limiting faces are turned on the lathe perfectly rectangularly and parallel to each other. At the one end is fixed the likewise rectangularly turned-off plate-holder P, — whose dimensions are 9,5 c.m. broad, 12 c.m. high and 3 m.m. thick; at the other end, however, the special crystal-support K (high: 9 c.m., broad: 4 c.m. and thick: 5 m.m.) was immovably fixed by good screws. In a hole in K a brass tube of 8 c.m. length is fixed, which is closed at both ends by two lead-cylinders e of 1 c.m. length, these being pierced along their axes by a straight canal of 1 m.m. diameter. An accurately fitting cover A (fig. 2) can be pushed on that end of the brass tube, which is next to P; its front face consists of a small brass plate with a central hole of 2 m.m. diameter.

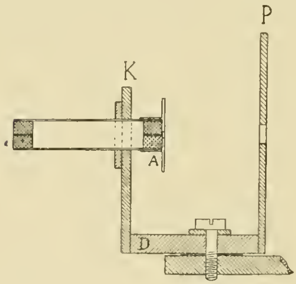

Fig. 2.

The crystals were smoothly pressed against this brass plate, and then held in position by means of sticking-wax.

As a result of the careful finishing of this apparatus, one could be sure, that the Röntgen-rays, after having passed the small canals in the lead cylinders, progress in a thin pencil, which is perpendicular as well to the crystal-plate, as to the photographic plate.

The dimensions are chosen in such a way, that the distance from the front face of the cover to the sensitive film in *P* is precisely 50 m.m.; of course the thickness of the fluorescent screen and of the two black paper covers, with which the plate and screen are protected, are taken into account here.

The photographic plate, with the fluorescent "Eresco"-screen pressed against the sensitive film, was wrapped in two covers of black paper and then firmly pressed against *P*; it had an opening measuring 8 × 8 cm., and the whole apparatus thus was held together much in the same way as in the case of a photographic copying-press.

The three plate-bearers *D* could be adjusted into the right position with sufficient accuracy by means of three straight, thin knitting-needles, which after being pushed through the canals in the lead cylinders, must meet in the same point *A*. For the purpose of making the anti-cathode coincide with this point *A*, the wooden bearer of the Röntgen-tube was fixed on a heavy brass support, which had smoothly running sliding-motions in three perpendicular directions; thus it was made possible, to fix the Röntgen-tube exactly in such position that the three pencils of Röntgen-rays generated three equally strongly luminous little spots on a fluorescent screen, which was placed behind *P*. In the plates *P* three central holes of 1 cm. diameter were bored to enable us to see these luminous spots. To protect the photographic plate against undesired attack by direct or secondary Röntgen-rays, some larger lead screens were interposed between the Röntgen-tube and the plate-holders with a total thickness of 2 c.m.; in the same way the three crystal-, and plate-holders themselves were surrounded by a lead cover, which could be closely fitted to the large lead screens. In the backside face of the lead cover three holes were bored, big enough to let the undiffracted Röntgen-rays freely pass.

An inconvenience, met with in our former experiments when using the fluorescent screen, was the abnormal sizeof the central spot on the photos, which spot would even seem still larger in the reproductions from the negatives ¹). The extension of this spot must be caused by the action of the secondary Röntgen-rays, which were produced by the passing of the undiffracted pencil through the glass and the sensitive film; these secondary rays will provoke a rather strong fluorescence of the vicinal parts of the screen and thus an intense

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¹) The diameter of the image of the undiffracted rays was about 2 m.m., as can also be calculated from the used dimensions of our apparatus: by photographic irradiation or by the mentioned secondary rays however, the central spot on the photos appeared to be about 8 m.m. in some cases.

action on that place of the photographic plate. We were able to eliminate this obstacle for the greater part, by cutting from the centre of the screen a small disc of about 1 c.m. diameter, and to cover the inner rim of the hole with a layer of black ink. On the photo however a very small halo was still visible in some cases; but this could be easily removed by covering the central part of the negative during the reproduction with a small disc of black paper. In this way the disturbance of the image by the above mentioned causes was finally completely prevented.

§ 3. From the representative of each crystal-class, necessary for our purpose, not all could be obtained in a sufficiently excellent quality, or they could not be used from some other cause in our experiments. So for instance the *sodium-periodate*-crystals were unsuitable, because of their very rapidly occurring efflorescence and loss of their water of crystallisation; the crystals of *benzil* on the other hand appeared to show optical anomalies and peculiar phenomena to be described in a later communication. Notwithstanding much trouble it was impossible to obtain larger crystals of *cinnabar*, which were not at the same time twins or appeared to be too inhomogeneous. From *zincite* we could have only badly disturbed and lamellar crystals; in the case of *nephelite* the obtained crystals still appeared finally to be polysynthetic twins, notwithstanding the choice of very small, clear-looking individuals.

Completely reliable results we obtained finally in the case of the following minerals: *phenakite*, *dolomite*, *quartz*, *turmaline*, *calcite*, *apatite* and *beryl*, while also our experience with some *nephelite*-preparations, and with *cinnabar* cut perpendicularly to the *c*-axis, can be judged as to be in agreement with the theoretical deduction.

§ 4. *Description of the examined substances.*

a. Turmaline. For our observations we used a beautiful, dark green turmaline-crystal of Brazil. The image obtained by radiation through the direction of the optical axis, was already formerly reproduced[1]; it possesses the expected symmetry, namely: one ternary principal axis and three vertical symmetry-planes (vid. the stereographical projection in fig. 1, Plate VI).

The first crystal-plate parallel to $\{10\bar{1}0\}$ had a thickness of 3,05 m.m.; a second one however only of 1,15 m.m. Both images (vid. Plate I, fig. 1 and 2, and Plate VI fig. 2.) show only one

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[1] Vid. these Proceedings, **17**. 1204. (1915); Plate I, fig. 4; Plate IV, fig. 4.

single plane of symmetry, perpendicular to the prism-face. The spots in the image of the thick crystal-plate are very heavy and *not* oval-shaped, but *rectangular*. We have already drawn attention to this phenomenon on a previous occasion, in the cases of *sodiumchlorate*, of *sylvine*[1]), etc.

It now becomes clear that it is principally connected with the *thickness* of the crystal-plate: the formerly described patterns of sodiumchlorate and sylvine are indeed also obtained by means of *very thick* plates.

This peculiarity was also stated by us in many other cases, if thicker plates of not very strongly absorbing substances were used in the experiments; often the spots appear to be double ones in such cases, which by joining finally give the impression of a more or less rounded rectangular shape. We think that an explanation can be given in this way: that in the case of not powerfully absorbing substances so great a number of successive molecular layers contribute to the intensity of the spot on the photographic plate, that the images of the outer layers of the whole pile will appear in a discernible distance from each other on the film, because of the different distance of these outer layers from the sensitive plate. If the spots thus properly produced will coalesce with each other, the rounded rectangular shape of the resulting image is easily explained.

The fourth turmaline-plate was cut parallel to $\{\bar{1}2\bar{1}0\}$; the RÖNTGEN-pattern shows as a single symmetry-element, a binary axis coinciding with the plate-normal. (Plate I, fig. 3). The results of the experiments are therefore in this case in complete accordance with those of the theoretical deductions.

b. Phenakite. We had at our disposition very beautiful, colourless and lustrous *phenakite*-crystals from *San Miguël, Minas Geraës,* in *Brazil.*

The crystal plate cut perpendicularly to the *c*-axis, showed in convergent polarized light, a uniaxial interference-image of positive character; it manifested however a small abnormality in the form of a feebly biaxial image with extremely small axial angle. However this abnormality did not appear to have any influence on the diffraction-pattern. The plate had a thickness of 1,1 mm.; the photographic image was not very beautiful, and the most important spots appeared to be covered by the strong irradiation of the central spot. Later-on we obtained by means of our newer apparatus described previously, a feeble but completely symmetrical image, which was used in the

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[1]) Ibid. 1207, note 1.

construction of the stereographical projection in Plate VI, fig. 3. Evidently there is only one ternary axis present, but no planes of symmetry in the pattern.

The plate parallel to $\{10\bar{1}0\}$ was 1,20 m.m., that parallel to $\{\bar{1}2\bar{1}0$ was 1,15 m.m. thick; we obtained with them two very beautiful photos, reproduced in Plate I, fig. 4 and Plate II, fig. 5; in these photograms the direction of the *c*-axis is vertical. The diffraction-patterns are wholly unsymmetrical; the results are therefore exactly what could be expected from the theory.

c. In the same symmetry-group also *Dolomite* must be placed. From a splendid, perfectly translucid crystal of *Binnenthal* in *Switzerland*, three faultless plates parallel to $\{0001\}$, $\{10\bar{1}0\}$ and $\{\bar{1}2\bar{1}0\}$ were carefully cut. The plate perpendicular to the *c*-axis had a thickness of 0,92 m.m.; the beautiful interference-image of negative character appeared to be exactly centrical. The plate parallel to $\{10\bar{1}0\}$ was 1.14 m.m. thick; that parallel to $\{\bar{1}2\bar{1}0\}$ was 1,11 mm.

The very beautiful diffraction-patterns obtained are reproduced in fig. 6, 7 and 8 on Plate II, and in stereographical projection on Plate VI, in fig. 4 to 6. The image perpendicular to the *c*-axis possesses only a ternary axis; both the other images are completely unsymmetrical, just as in the case of *phenakite*. Also in this case therefore experience and theoretical deduction are in full agreement with each other.

d. Calcite. From a lustrous calcite-crystal from *Iceland* two plates were cut: the plate parallel to $\{10\bar{1}0\}$, as well that parallel to $\{\bar{1}2\bar{1}0\}$ were 1,15 m.m. thick. Both images were too feeble to allow good reproduction; they are however reproduced as stereographical projections in fig. 7 and 8 on Plate VI. The Röntgen-pattern for a plate perpendicular to the *c*-axis was published some time ago by Bragg [1]): the image exhibits a ternary axis and three vertical planes of symmetry. The symmetry of all these patterns is the same, as was found in the case of the *turmaline*, — just as could be expected from the theory. It must be remarked that the image parallel to $\{10\bar{1}0\}$, although possessing only a single (vertical) plane of symmetry, shows, however, a very strong approximation to a case, where two perpendicular symmetry-planes were present.

e. Beryl. We had very beautiful plates at our disposition, cut from a splendid, colourless, translucid crystal from the *Aduntschilon*-mountains in the *Transbaical*. The plate parallel to $\{0001\}$ had a

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[1]) W. L. Bragg Vid. Zeits. f. Anorg. Chem. **90**. 206. (1914); Proc. Royal Soc. A. **89** 248. (1913).

thickness of 1.10 mm., that parallel to $\{10\bar{1}0\}$ 1.17 mm., and that parallel to $\{\bar{1}2\bar{1}0\}$ 1.16 mm.

The diffraction-image parallel to $\{0001\}$ (vid. Plate IIII, fig. 9), shows a senary axis and six vertical planes of symmetry. Thus it is again proved, that the *beryl* is really *di*hexagonal, and that the arguments against this supposition, formerly brought to the fore by VIOLA[1]), can hardly be considered as valuable any more.

The two remaining images (Vid. Plate III, fig. 10 and Plate IV, fig. 11) are, quite in concordance with the theory, symmetrical after two perpendicular planes of symmetry. They are reproduced as stereographical projections in fig. 9—11, on Plate VI. The image of the plate parallel to $\{10\bar{1}0\}$ appears to be somewhat sloping, evidently caused by not wholly perfect orientation of the crystal-section.

f. Apatite. From a beautiful crystal from *Zillerthal*, in *Tyrol*, two plates were cut. The image of the plate parallel to $\{0001\}$ was reproduced already previously[2]). The second plate was parallel to $\{10\bar{1}0\}$; its thickness was 1,30 mm. The beautiful diffraction-pattern is reproduced in fig. 12 on Plate IV, and both images as stereographical projections on Plate VI, fig. 12 and 13. The pattern parallel to $\{10\bar{1}0\}$ exhibits only one horizontal plane of symmetry, quite in agreement with the theoretical expectations.

g. Quartz. From a translucid crystal from the *St. Gothard* four plates were cut. The image of a plate perpendicular to the *c*-axis was too feeble to make reproduction by any means possible. A schematical drawing of the most important, — and always *double*, — spots, is given in fig. 14, Plate VII. The pattern shows a ternary axis and three vertical planes of symmetry.

Two different plates, each of which was parallel to $\{\bar{1}2\bar{1}0\}$, and having a thickness of 1,12, resp. 1,05 m.m., gave particularly remarkable patterns. For although both plates were very accurately orientated, and did not manifest, with the microscope, any differences, nor any inhomogeneity discernible by optical means, — the image obtained with the first mentioned plate appeared to be *symmetrical after two perpendicular planes*; the other image however, notwithstanding its being composed of precisely the same spots, showed quite another distribution of their intensities, in such a way, that the pattern was *only symmetrical after a single binary axis.* On repeating the experiment with the first mentioned quartz-plate, which

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[1]) VIOLA. Z. f. Kryst. **34**. 381. (1901).

[2]) loco cit. **17**. Plate I.

now was radiated through in another place, its abnormal symmetry was found once more.

Here now we could, for the first time, observe in the case of a uniaxial crystal a very particular abnormality: indeed it appears, that properly a plane of symmetry perpendicular to the trigonal axis seems to be added to the crystal, which involves at the same time the addition of three new vertical planes of symmetry passing through the *c*-axis, making this axis necessarily a *senary* one. In the original negatives this different symmetry in both cases is very evident, somewhat less, however, in the reproductions (Plate IV, fig. 13 and 14); but the differences between the normal and the abnormal pattern are clearly expressed in the stereographical projections, which here are given together in fig. 3 and 4.

The same abnormality, i.e. the addition of a horizontal plane of symmetry perpendicular to the ternary axis, seems to be also present in the Röntgen-ogram, obtained with a crystal-plate parallel to $\{10\bar{1}0\}$; this plate had a thickness of 1,10 m.m. Although this plate was parallel to the *c*-axis, it appeared to be not completely parallel to the prismface; the pattern, which therefore very probably did not show a true *vertical* symmetry-plane, is here not reproduced. The stereographical projection of the normal patterns are given in fig. 14, 15 and 16, Plate VII.

A careful microscopical examination of both the plates parallel to $\{\bar{1}2\bar{1}0\}$, did however *not* reveal any optical differences.

One might be inclined to suppose, that the plate parallel to $(\bar{1}2\bar{1}0)$ which had given the abnormal pattern, were really a twin-formation after the brasilian rule; i.e. with a plane of $(\bar{1}2\bar{1}0)$ being the twinning-plane. Because perpendicularly to $(\bar{1}2\bar{1}0)$ there is a binary axis present, the Röntgen-ogram therefore should indeed show a symmetry with respect to two planes, perpendicular to each other. But by this supposition it could never be made evident, that the diffraction-pattern obtained with a plate cut from *the same* crystal parallel to $(10\bar{1}0)$, shows very probably *also a horizontal plane of symmetry.* Thus the said explanation can hardly be considered a final one already for the peculiar Röntgen-patterns which were obtained parallel to $(12\bar{1}0)$ *and* to $(\bar{1}0\bar{1}0)$. The observed abnormality therefore cannot be said to be explained fully, and we intend to make further experiments on this phenomenon in future.

h. Nephelite. From a small, clear crystal from the *Vesuvius*, three crystal-plates were investigated. The plate perpendicular to the optical axis showed a well-centred, uniaxial interference-image, possessing only a slightly abnormal character. The plate had a

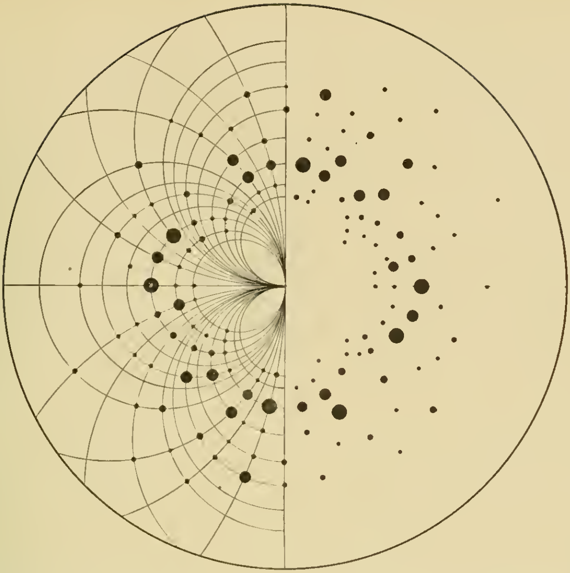

Plate 3. Stereograpcical Projection of the Röntgen-pattern of dextrogyratory Quartz. Plate parallel to $(1\bar{2}10)$. (Normal Image).

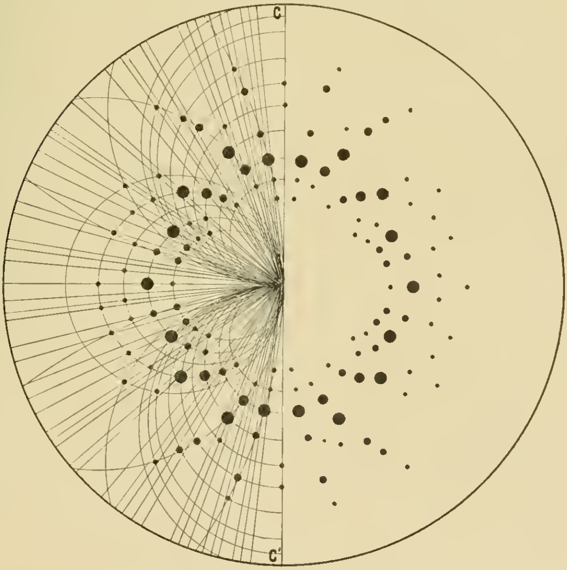

Fig. 4. Stereographical Projection of the Röntgen-pattern of dextrogyratory Quartz. Plate parallel to (1 2 1 0). (Abnormal Image).

thickness of 0.70 m.m. The obtained diffraction-image was extremely feeble: the spots, which, — as in the case of the quartz, — were all *double*-ones, — were situated very far from the centre and were so feeble, as to make any reproduction impossible. It was however possible to see, that the pattern possessed a senary axis (schematical projection in fig. 17, Plate VII); *no* vertical planes of symmetry were present.

The plate parallel to $\{10\bar{1}0\}$ was 0,78 m.m. thick, and gave a rather good image, which as a stereographical projection is reproduced on Plate VII, fig. 18. All spots here were also doubled, and the axes of the oval impressions were inclined to each other, giving to each pair of spots the shape of an arrow-point; this seems to indicate a twin-formation of the used mineral. The pattern was merely symmetrical after a horizontal plane. The third plate was too disturbed and inhomogeneous, to give any suitable image.

i. That *cinnabar*, if radiated through in the direction of the *c*-axis, will give a Röntgen-pattern, whose symmetry is in full concordance with the theory, was already formerly recorded [1]). The stereographical projection of the Röntgen-ogram is reproduced here once more in fig. 19, Plate VII. Finally in fig. 15, Plate V, the very beautiful photo of *pennine* is reproduced; although this mineral is only *mimetic* and clearly shows optical abnormalities, the structure of the lamellae is evidently here a so regular and perfect one, that the whole pile cannot be distinguished from a real trigonal crystal. Attention must be drawn to the remarkable fact, just as formely stated in the case of *sylvine*, that the central spot seems to irradiate in about eighteen directions; it seems, that this irradiation is connected in some way with the presence of certain gliding-planes in the crystal. The thickness of the dark green, positively birefringent, and clearly optically anomalous crystal-plate, was 0,81 m.m.

§ 4. If we now review all the results hitherto obtained in these researches, it becomes clear, that, — with the exception of the phenomena observed in the case of the two quartz-plates, which phenomena undoubtedly are to be considered as true "abnormalities",— *the symmetry of the* Röntgen-*patterns is always in agreement with that predicted by the now adopted theory of the diffraction-phenomenon.* On the other hand the correctness of the supposed *centrical symmetry* of the said phenomenon is thus sufficiently proved in this way. Our experience can be considered evidently as a strong argumenta-

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[1]) These Proceed. **17**. p. 1204: vid. Plate IV, fig. 5.

tion *against* the supposition, that the particular fact of the disappearance of certain symmetry-planes in the RÖNTGEN-patterns of birefringent crystals would have anything to do with their optical anisotropy. For if this were true, it would be hardly possible to understand, why not one of the numerous patterns of uniaxial crystals, which were radiated through in the direction of their optical axis, and thus likewise are birefringent plates, exhibited the formerly described phenomenon. On the other hand the case of the quartz-images makes prudence necessary: for evidently the symmetry of the patterns can by yet partially unknown *secondary* causes, appear *otherwise* than may be expected from the theory of the diffraction phenomena, — as well of *higher* symmetry (quartz) as of *lower* symmetry (rhombic crystals).

§ 5. In connection with these considerations, we have recommenced our studies with some optically biaxial (rhombic) crystals, and have begun with a renewed investigation of *the same*, translucid and very beautiful plate of *hambergite* parallel to {010}, which formerly[1]) had given a so strongly abnormal image. After having radiated through in another place, we now repeatedly obtained a perfectly normal diffraction-image, quite symmetrical after two perpendicular planes. The normal pattern is reproduced in fig. 16, Plate V, as a photo, and both images by the side of each other as stereographical projections, in fig. 5 and 6. Using the normal image as standard, it may be called very remarkable, that the abnormal image appears in comparison to it as a "distorted" normal pattern, as if the crystal-plate were rotated round the vertical principal direction at a certain angle. Very striking indeed is the completely different intensity-distribution of the spots, and also their altered position in both cases. Microscopically *no* differences could be found in the one place of the plate and the other: with a very strong enlargement the crystals showed certainly very small and long-shaped inclusions, but these were in precisely the same way and arrangement present also in both the other *hambergite*-plates, cut parallel to {100} and {001}, which plates however in striking contrast to the one mentioned, *always gave completely normal* patterns. From this it must follow, that these inclusions cannot be the cause of the phenomenon observed.

On repeating our experiments with *the same* plates of *sodium-ammoniumtartrate*, as we used formerly, we obtained with the, — now superficially somewhat rougher, — plate parallel to {100}, *the same abnormal* pattern as previously: only a few of the spots

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[1]) These Proceed. **17**, 1204, Plate II, fig. 8; Plate IV, fig. 11.

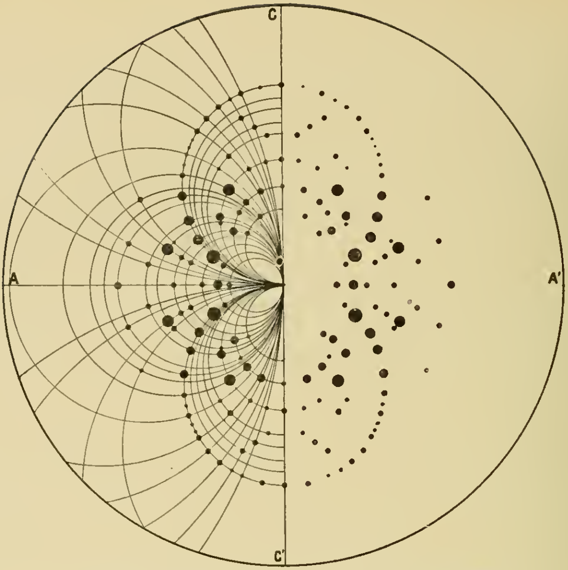

Fig. 5. Stereographical Projection of the Röntgen-pattern of Hambergite. Plate parallel to 010). (Normal Image).

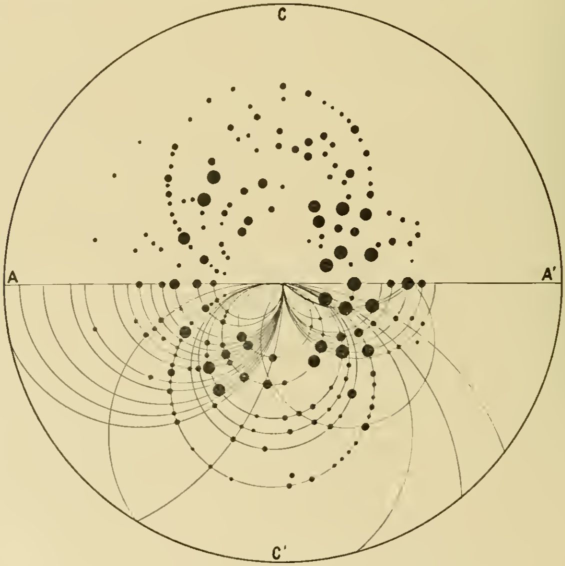

Fig. 6. Stereographical Projection of the Röntgen-pattern of Hambergite. Plate parallel to (010). (Abnormal Image).

H. HAGA AND F. M. JAEGER. ON THE SYMMETRY OF THE RÖNTGEN-PATTERNS OF TRIGONAL AND HEXAGONAL CRYSTALS, AND ON NORMAL AND ABNORMAL DIFFRACTION-IMAGES OF BIREFRINGENT CRYSTALS IN GENERAL.

PLATE I

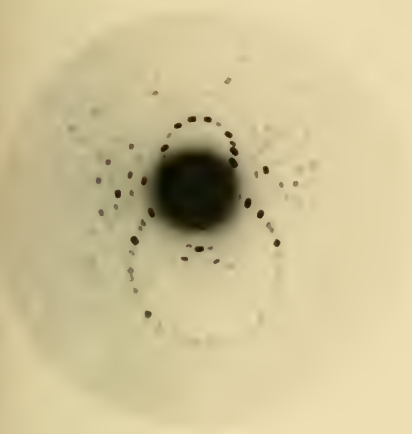

Fig. *1*.
Turmaline. Plate parallel to $(01\bar{1}0)$.

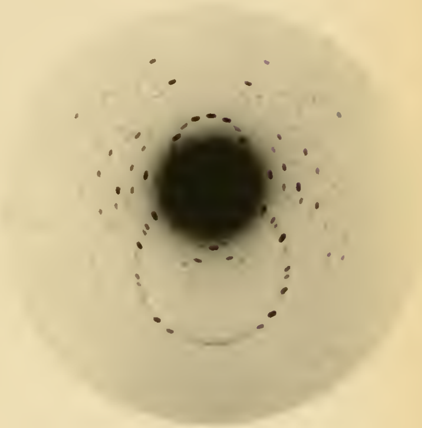

Fig. *2*.
Turmaline. Plate parallel to $(01\bar{1}0)$.

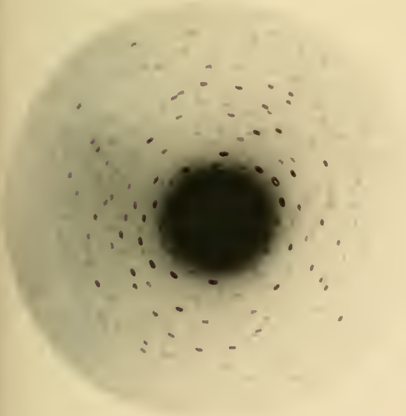

Fig. *3*.
Turmaline Plate parallel to $(\bar{1}2\bar{1}0)$.

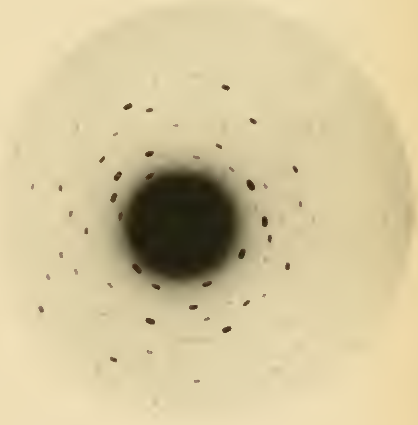

Fig. *4*.
Phenakite. Plate parallel to $(01\bar{1}0)$.

HELIOTYPE, VAN LEER AMSTERDAM

H. HAGA AND F. M. JAEGER. ON THE SYMMETRY OF THE RÖNTGEN-PATTERNS OF TRIGONAL AND HEXAGONAL CRYSTALS, AND ON NORMAL AND ABNORMAL DIFFRACTION-IMAGES OF BIREFRINGENT CRYSTALS IN GENERAL.

PLATE II.

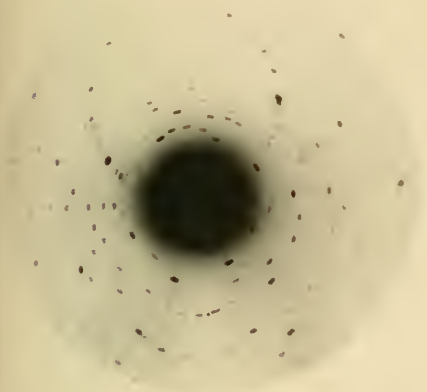

Fig. *5*.
Phenakite. Plate parallel to $(\bar{1}2\bar{1}0)$.

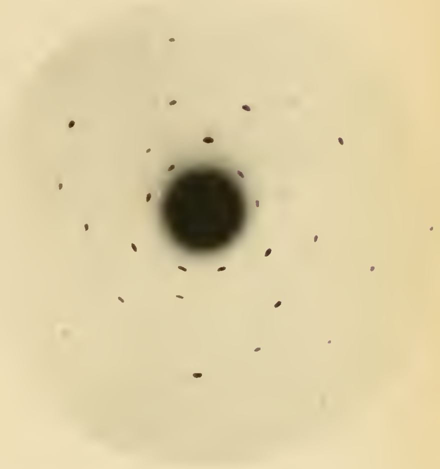

Fig. *6*.
Dolomite. Plate parallel to (0001).

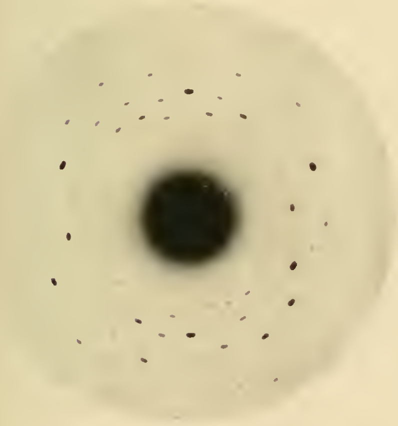

Fig. *7*.
Dolomite. Plate parallel to $(01\bar{1}0)$.

Fig. *8*.
Dolomite. Plate parallel to $(\bar{1}2\bar{1}0)$.

HELIOTYPE VAN LEER, AMSTERDAM

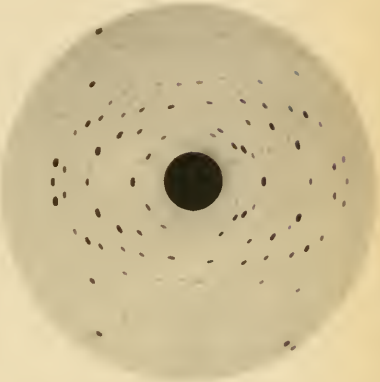

Fig. *10.*
Beryl. Plate parallel to $(10\bar{1}0)$.

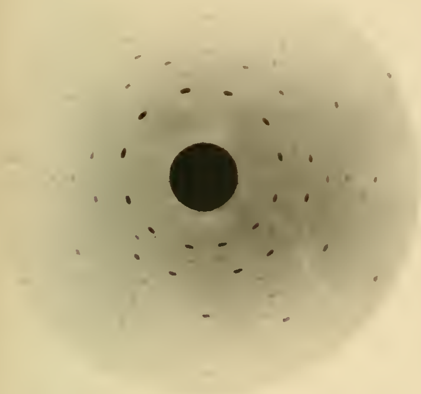

Fig. *9.*
Beryl. Plate parallel to (0001).

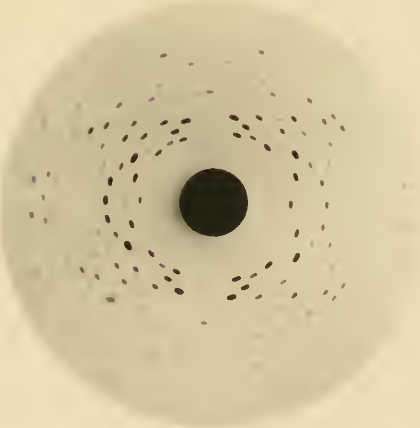

Fig. *11.*
Beryl. Plate parallel to $(\bar{1}2\bar{1}0)$.

HELIOTYPE, VAN LEER AM ERDAM

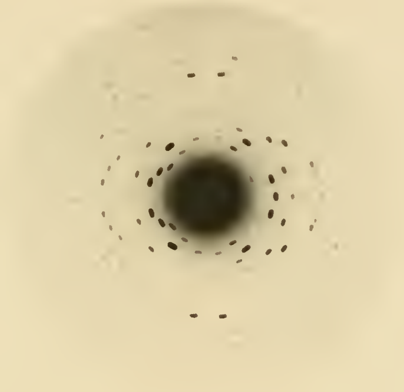

Fig. *12.*
Apatite. Plate parallel to $(10\bar{1}0)$.

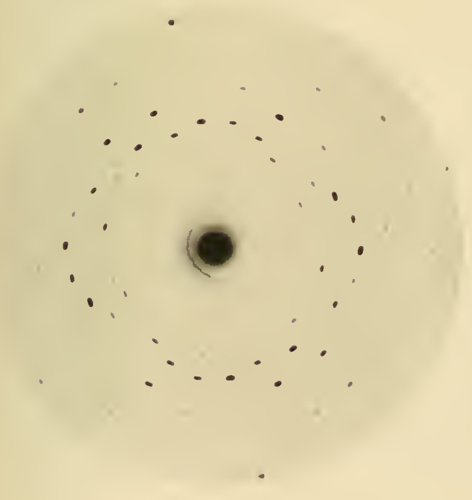

Fig. *13.*
Quarz. Plate parallel to $(\bar{1}2\bar{1}0)$.
(Normal Pattern).

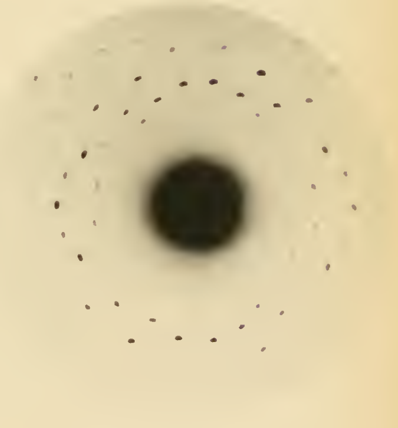

Fig. *14.*
Quarz. Plate parallel to $(\bar{1}2\bar{1}0)$.
(Abnormal Pattern).

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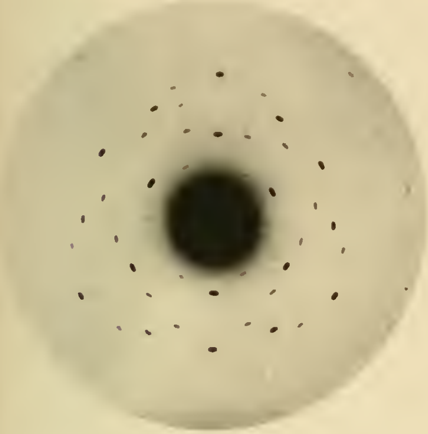

Fig. *15*
Pennine. Plate parallel to (0001).

Fig. *16*.
Hambergite. Plate parallel to (010).
(Normal Pattern).

Fig. *17*.
Zinc-Sulphate Cleavage-lamella, exactly parallel to (010).
(The *b*-axis is 1st bissectrix).

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PLATE VI.

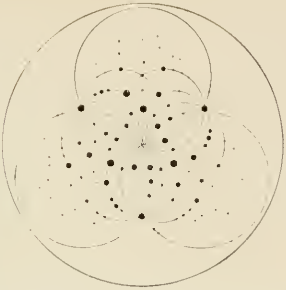


Fig. 4. Stereographical Projection of the Röntgenogram of Dolomite. Plate parallel to $(0\,0\,0\,1)$.

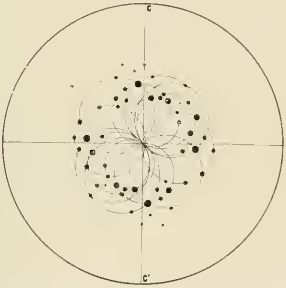
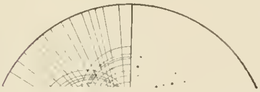


Fig. 8. Stereographical Projection of the Röntgenogram of Calcite. Plate parallel to $(\bar{1}\,2\,\bar{1}\,0)$.



Prof. Dr. H. HAGA and Prof. Dr. F. M. JAEGER. "On the Symmetry of the Rontgen-patterns of Trigonal and Hexagonal Crystals," etc.

PLATE VI.

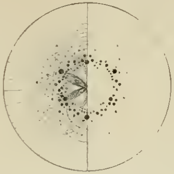


Fig. 1. Stereographical Projection of the Rontgenogram of Turmaline. Plate parallel to (0001).

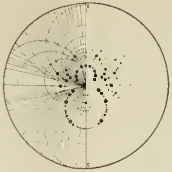


Fig. 2. Stereographical Projection of the Rontgenogram of Turmaline. Plate parallel to $(01\bar{1}0)$.

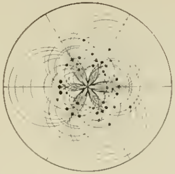


Fig. 3. Stereographical Projection of the Rontgenogram of Phenakite. Plate parallel to (0001).

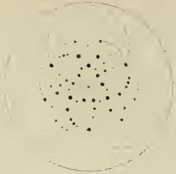


Fig. 4. Stereographical Projection of the Rontgenogram of Dolomite. Plate parallel to (0001).

Fig. 5. Stereographical Projection of the Rontgenogram of Dolomite. Plate parallel to $(01\bar{1}0)$.

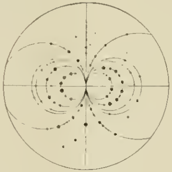


Fig. 6. Stereographical Projection of the Rontgenogram of Dolomite. Plate parallel to $(\bar{1}2\bar{1}0)$.

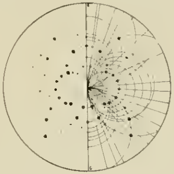


Fig. 7. Stereographical Projection of the Rontgenogram of Calcite. Plate parallel to $(10\bar{1}0)$.

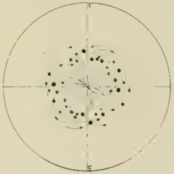


Fig. 8. Stereographical Projection of the Rontgenogram of Calcite. Plate parallel to $(\bar{1}2\bar{1}0)$.

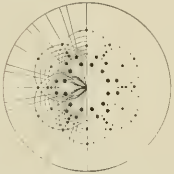


Fig. 9. Stereographical Projection of the Rontgenogram of Beryl. Plate parallel to (0001).

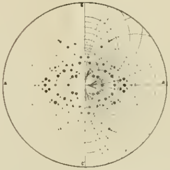


Fig. 10. Stereographical Projection of the Rontgenogram of Beryl. Plate parallel to $(10\bar{1}0)$.

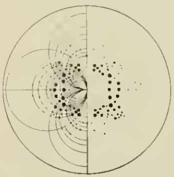


Fig. 11. Stereographical Projection of the Rontgenogram of Beryl. Plate parallel to $(12\bar{1}0)$.

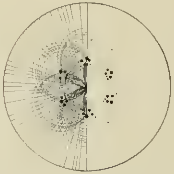


Fig. 12. Stereographical Projection of the Rontgenogram of Apatite. Plate parallel to (0001).

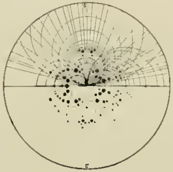


Fig. 13. Stereographical Projection of the Rontgenogram of Apatite. Plate parallel to $(10\bar{1}0)$.

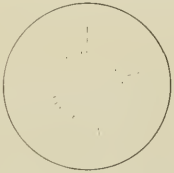


Fig. 14. Stereographical Projection of the Rontgenogram of dextrogyratory Quarz. Plate parallel to (0001).

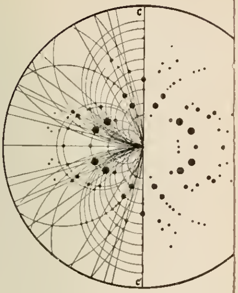
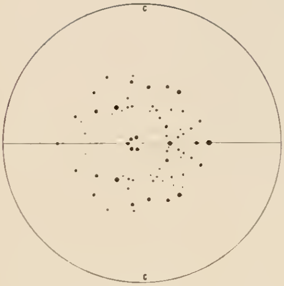


Fig. 15. Stereographical Projection of the
of dextrogyratory Quarz. Plate parallel



18. Stereographical Projection of the Röntgenogram of Nepheline. Plate parallel to ($\bar{1}2\bar{1}0$).

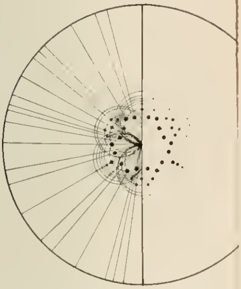
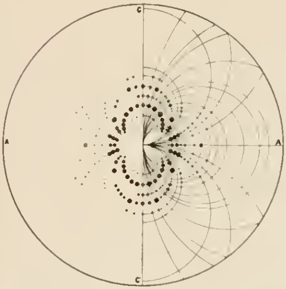


Fig. 19. Stereographical Projection of the
of dextrogyratory Cinnabar. Plate paralle



22. Stereographical Projection of the Röntgenogram of dextrogyratory Sodium-Ammonium-Tartrate. Plate parallel to (0 1 0). (Normal Image).

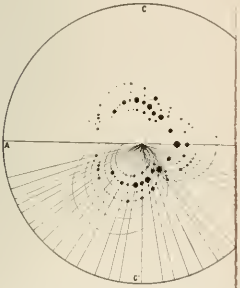
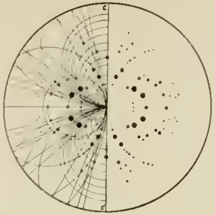


Fig. 23. Stereographical Projection of the
of dextrogyratory Sodium-Ammonium
Plate parallel to (0 1 0). (Abnorma

26. Stereographical Projection (schematical) of the
tgenogram of Zinc-sulphate. Plate parallel to (0 1 0).
ormal Image, obtained with a perfectly clear lamella,
pared by cleavage, and exactly perpendicular to
the first bissectrix.

Prof. Dr. H. HAGA and Prof. Dr. F. M. JAEGER. "On the Symmetry of the Röntgenpatterns of Trigonal and Hexagonal Crystals," etc. PLATE VII.



1 Stereographical Projection of the Rontgenogram of dextrogyratory Quarz. Plate parallel to $(1\,0\,\bar{1}\,0)$.

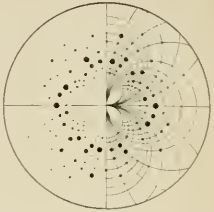


Fig. 16. Stereographical Projection of the Rontgenogram of dextrogyratory Quarz. Plate parallel to $(\bar{1}\,2\,1\,0)$. (Normal Image).

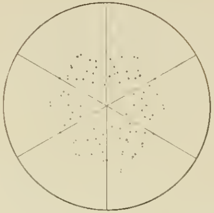


Fig. 17. Stereographical Projection of the Rontgenogram of Nepheline. Plate parallel to $(0\,0\,0\,1)$. (Schematical).

Fig. 18. Stereographical Projection of the Rontgenogram of Nepheline. Plate parallel to $(1\,2\,\bar{1}\,0)$.

19. Stereographical Projection of the Rontgenogram of dextrogyratory Cinnabar. Plate parallel to $(0\,0\,0\,1)$.

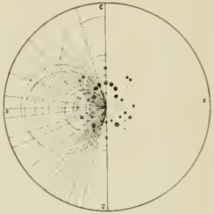


Fig. 20. Stereographical Projection of the Rontgenogram of dextrogyratory Sodium-Ammonium-Tartrate Plate parallel to $(1\,0\,0)$. (Abnormal Image).

Fig. 21 Stereographical Projection of the Rontgenogram of dextrogyratory Sodium-Ammonium-Tartrate. Plate parallel to $(1\,0\,0)$. (Normal Image).

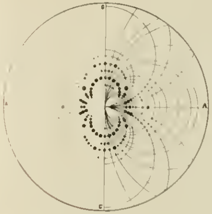


Fig. Stereographical Projection of the Röntgenogram of dextrogyratory Sodium-Ammonium-Tartrate. Plate parallel to $(0\,1\,0)$. (Normal Image).

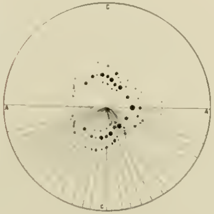


Fig. 23. Stereographical Projection of the Rontgenogram of dextrogyratory Sodium-Ammonium-Tartrate. Plate parallel to $(0\,1\,0)$. (Abnormal Image).

Fig. 24. Stereographical Projection of the Rontgenogram of dextrogyratory Sodium-Ammonium-Tartrate Plate parallel to $(0\,1\,0)$. Abnormal Image, perpendicular to the first one, with the same position of the plate.

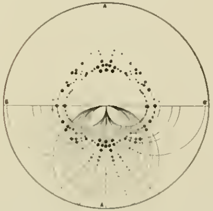


Fig. 25. Stereographical Projection of the Rontgenogram of dextrogyratory Sodium-Ammonium-Tartrate. Plate parallel to $(0\,0\,1)$.

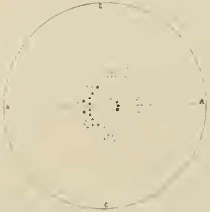


Fig. 26. Stereographical Projection (schematical) of the Rontgenogram of Zinc-sulphate. Plate parallel to $(0\,1\,0)$. Abnormal Image, obtained with a perfectly clear lamella, prepared by cleavage, and exactly perpendicular to the first bissectrix.

appeared to be absent on comparison with the former image. The also superficially somewhat rougher plate parallel to {010} however, gave now undoubtedly also an *abnormal* image, but as a very remarkable fact: *just the other (second) plane of symmetry as before was now manifested in the pattern, notwithstanding the same position of the crystalplate!* Formerly this plate had given an abnormal image, which was symmetrical after the plane {001}; now it showed a symmetry-plane parallel to {100}. As both plates of the *tartrate* were superficially a little altered by a feeble efflorescence, we prepared from a fresh, translucid crystal of the salt three new plates, which were examined in the same way.

With these plates we were now able to obtain RÖNTGEN-patterns, which were symmetrical after *two* planes; in this way it was possible at the same time to compare the partial symmetry of both the abnormal images parallel to {010} with the normal pattern. The three normal and the abnormal images are reproduced as stereographical projections in fig. 20 to 25 on Plate VII.

§ 6. We have convinced ourselves by especially arranged experiments of the fact that a deviation from the true plane-parallel shape of the *hambergite*-plate could *not* be the cause of the partial symmetry of its pattern formerly obtained. Moreover, in our numerous experiments with *cordierite*, with material from all localities, we *never* obtained other images than *abnormal* ones, which were only symmetrical after one single plane of symmetry. With this mineral the phenomenon thus seems to manifest itself *constantly*. In our way of experimenting, with the use of fixed, on the lathe rectangularly turned-off crystal-supports, a somewhat appreciable deviation from the true orientation is highly improbable. Moreover the same crystals, adjusted by the same apparatus, appeared formerly often to give quite normal patterns, if radiated through in one or two of the other principal directions, so that a *systematical* error of the whole arrangement can hardly be considered to be the cause of the phenomenon. If this were true, or if deviations in the right orientation of the prepared crystal-sections were the cause of the phenomenon observed, it could furthermore not be understood, why *never* a distortion of the normal pattern after *another* direction than only after the two principal ones of the plate, were till now observed. The fact, that the planes of symmetry of the rhombic crystals just play the preponderant rôle in this, proves sufficiently, that *no accidental* causes are responsible here, but that these are of such a nature, as to be connected intimately with the proper, internal molecular structure of the crystals.

But a further and persuasive illustration of this question is given also by the case of the rhombic *zinc-sulphate*. Here we used a splendid transparent crystal-plate, obtained by direct *cleavage* of the crystal along the plane of *perfect* cleavability {010}, whose perfectly right orientation could be controlled very rigorously by optical examination, the *b*-axis being at the same time the first bisectrix. Notwithstanding this, however, the corresponding diffraction-image appeared to be constantly *abnormal*, and to possess only one single plane of symmetry parallel to {001}, — i. e. parallel to the optical axial plane. (Vid. Plate V, fig. 17 and Plate VII, fig. 26).

The above mentioned observations undoubtedly must bring the conviction, that *the cause of the observed phenomenon must be ascribed to the crystal-plates themselves, — faultless as they may appear even on more detailed examination. Indeed further experiments* taught us, that also with other rhombic crystals than with *hambergite*, it is eventually possible to obtain *perfectly normal* patterns, with the aid of the same apparatus. In the following paper we will reproduce the photos and projections of the images, which we obtained with the plates of a number of biaxial minerals and artificial substances, cut parallel to the three pinacoidal faces. They will, besides some new cases of abnormal diffraction-patterns, also show many, which indeed must be judged to be quite "normal" ones; the fundamental exactness of the original theory thus being convincingly proved. As Prof. RINNE of *Leipzig*, who supposed already some time ago, that special secondary causes might be connected with the observed phenomena, wrote to one of us, — he obtained in the case of the *anhydrite* as well normal as abnormal diffraction-images, and with *calamine* parallel to {010} only abnormal ones. With respect to our own results with these minerals, we can refer here to the following paper.

§ 7. As a result of our completed experiences, we finally can make the statement, *that the now adopted theory of the diffraction-phenomena, really can describe sufficiently the general behaviour of crystals with respect to* RÖNTGEN-*rays*; *and that the peculiar partial symmetry of the* RÖNTGEN-*patterns, as observed till now in many cases and especially with rhombic crystals, must be caused by secondary circumstances, connected with a particular kind of disturbances of the internal molecular structure of the crystals, and which at the moment can be examined by no other physical means.*

Of course the question immediately arises; of what kind are these causes? On deviations in the right orientation of the crystal-plates, — (which are always present in a less or higher degree), — it is hardly necessary to expatiate: after a longer practice one learns to evaluate quite exactly the smaller and very typical distortions, arising from that source, and to pass over them as over the typographical errors in an ordinary text. But the anomalies here considered *are of a totally different order*; they must be caused by a breaking-up of the stratographic position of the molecular layers, by which certain parts of the parallel planes of the molecules will be locally rotated round one of the principal directions in the crystal, — in an analogous way, as on our earth the inversions and the folding of geological strata may be observed. But in every case these disturbances must be here *of molecular dimensions*; they can evidently not be studied or observed by other available means at the moment than by the Röntgen-radiation, because the crystal-medium, disturbed in its molecular relations, behaves in respect to all other known physical actions like a continuum, with exception just in respect to the extremely small wave-lengths of the Röntgen-rays.

If there are present in rhombic crystals some directions of higher or less perfect cleavability, which are parallel to the principal sections of the crystal, then it will be probable, that such "internal vicinal planes" of the molecular layers will appear to be turned exactly round these principal cleavage-directions as axes, — here round the one, and there round the second of them. It will then depend on the place, where the crystal will be radiated through, if the diffraction-image will show a symmetry after the one or after the perpendicular plane. It must be remarked here however, that exactly in the case of the *sodiumammoniumtartrate*, where the mentioned phenomenon was observed by us, *no* such directions of typical cleavability are present. It seems therefore, that the principal directions of the molecular structure can play this remarkable rôle also in the case, that they are *not* at the same time directions of distinct cleavability.

§ 8. We do not deny, that the explanation given here has some weak points, especially if it must be supposed, that *all* molecular layers, contained in the whole thickness of the crystal-plate, contribute their part to the final impression on the photographic film, while notwithstanding that, only for a certain number of these molecular layers the presence of such "internal vicinal planes" can be accepted, because otherwise they would manifest themselves at the surface of the crystal-plates in some typical way, e.g. as irregularities of that surface. In this connection it may be of interest to mention the fact, that really in some few cases we found such abnormal phenomena with crystalplates, cut parallel to some of such "striated" faces of the crystal.

Moreover the question may arise: why is this abnormal behaviour observed relatively so *often* in the case of *biaxial* crystals, while it occurs evidently hardly ever in the case of uniaxial crystals?

Finally we may yet draw attention to the following case. If a *pseudo-symmetrical* (mimetic) crystal is built-up by lower-symmetrical lamellae, it cannot à priori be understood, why such a combination, radiated through in the direction of the (new) optical axis, would in any way manifest its polysynthetic twin-structure. Indeed this conclusion appears to be verified here by our experience with the *pennine.* But if that lamellar structure can cause in any way the presence of such "internal vicinal planes", so that the molecular layers can be turned a little round these two, three, four of six directions of intergrowth, the possibility can then be foreseen, that these irregularities will be brought *accidentally* in one of these directions more strongly to the fore, than in the remaining ones: *that one direction will then appear in the diffraction-pattern as a single plane of symmetry of it,* and in this way the appearance of this can be considered to be an indirect proof for the lamellar structure of the investigated crystal. This was evidently the case with *apophyllite* [1]), *benitoite* [2]), and the *racemic triethylenediamine-cobalti-bromide* [3]); moreover we found it a short time ago also in the case of *benzil,* if cut perpendicular to the optical axis of the pseudo-trigonal complex. We expect to elucidate in every case these questions by systematical experiments, and especially to determine finally the true nature of these internal disturbances, evidently intimately connected with the normal molecular structure.

University-Laboratories for Physics and
Inorganical and Physical Chemistry.

Groningen, August 1915.

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[1]) These Proceed. **4.** 438.

[2]) Ibidem, **17.** 1204 (1915), Plate IV, fig. 14. (1915).

[3]) Ibidem, **18.** 50. (1915).

Crystallography. — "*On the Symmetry of the* RÖNTGEN *patterns of Rhombic Crystals*". **I.** By Prof. H. HAGA and Prof. F. M. JAEGER.

§ 1. With the purpose to test yet further by experiments the conclusions with respect to the special symmetry of the diffraction-patterns of RÖNTGEN-rays in crystals, as may be derived from the theory adopted till now, we have moreover made a series of experiments with optically biaxial crystals. In the following pages are recorded the results obtained in the investigations with *rhombic* crystals, and especially with representatives from each of the possible symmetry-classes of the rhombic system. As already formerly mentioned [1]), the RÖNTGEN-patterns of plates from rhombic crystals of *bisphenoidical, pyramidal,* or *bipyramidal* symmetry, must always show the symmetry which would be observed in the analogous crystal-sections of the rhombic-bipyramidal class. From this is deduced, that crystal-plates cut parallel to the three pinacoides {100}, {010} and {001}, in the case of crystals of each of the three possible classes of this system will give RÖNTGEN-patterns, which *will always appear symmetrical with respect to twoperpendicular planes of symmetry,* if they are radiated through in the direction of the plate-normal.

§ 2. The way, in which the true situation of the spots in the diffraction-pattern, or more correctly: in its stereographical projection, is related to the parameters $a : b : c$ of such rhombic crystals, can be elucidated more particularly as follows.

Let P in Fig. 1 be the plane of the photographic plate, and KC the distance of the crystal from that plate. This distance ($= A$) was in our experiments always 50 mm. [2]); the diameter of the sphere by means of which the stereographical projection on the plane P will take place, is therefore always 100 mm. The viewpoint of the projection is 0; the planes $XCY (= P)$, XCZ, and YCZ are supposed to coincide with (or to be parallel to) the three planes of symmetry of rhombic-bipyramidal crystals. Let the parameter-quotient in the directions CX, CY and CZ be: $a : b : c$, of which a and c are numbers, known by the measurements of the angular values, and b is taken arbitrarily $= 1$.

If, now, Kz represents a "possible" zône-axis of the crystal, the value of $\frac{Cz}{CK}$ must be: $n . \frac{1}{c}$, where $\frac{1}{c}$ is the parameter-relation in

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[1]) These Proceed. 17, 1204. (1915).

[2]) However attention must here be drawn to the remarks in § 4

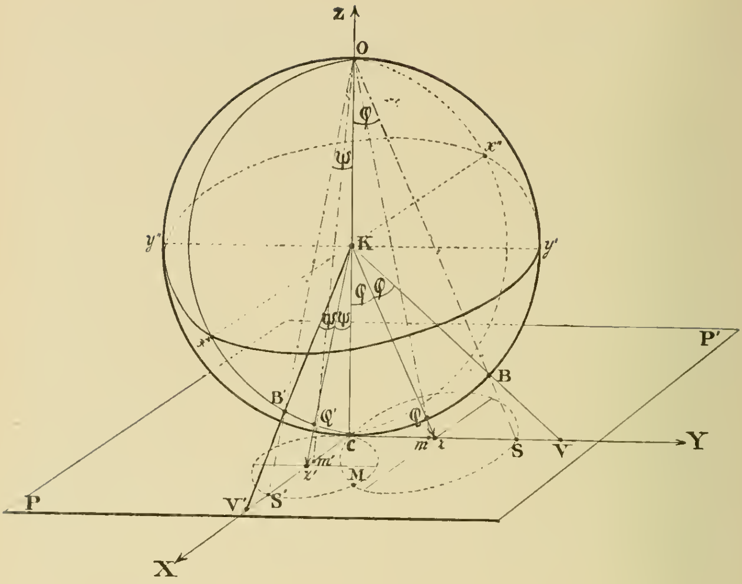

Fig. 1.

the directions CY and CZ, while n is some integer. If Kz' is equally such a zône-axis, then just in the same way $\frac{Cz'}{CK} = m \cdot \frac{a}{c}$, where m is also an integer. The projected spots S and S', corresponding with the reticular planes {101} and {011} of the crystal, are therefore in the directions CX and CY of the stereographical projection situated in distances from the central spot C, of: $2A\frac{a}{c}$ and $\frac{2A}{c}$, or in our case of: $\frac{100a}{c}$ and $\frac{100}{c}$ mm. In the same way for spots corresponding with the reticular planes of the symbols $\{ho1\}$ and $\{ok1\}$, these distances from C, become: $\frac{1}{h} \cdot \frac{100a}{c}$, resp. $\frac{1}{k} \cdot \frac{100}{c}$ m.m.

The point of intersection M of both zône-circles, corresponding with the zône-axes Kz, resp. Kz', possessing the symbols $[ho1]$ and $[ok1]$, represents the stereographical projection of a spot, corresponding with a plane of the structure with the symbol $\{hkl\}$; etc. In this way it is possible to determine the indices of every spot in the stereographical projection P by means of the existent zône-relations, and to investigate, which reticular planes will give the most intense impressions on the photographic film; or, what is the same: it will be possible to find out, in what way the spectral dissolving-power of the different molecular planes is connected with their reticular density.

We have chosen the case of a radiation perpendicular through a plate parallel to $\{001\}$. In the same way however it can be found, that:

On $\{100\}$ the spot corresponding with $\{101\}$, is situated in the direction of C-axis, at a distance of $\frac{100\,c}{a}$ m.m

On $\{100\}$ the spot corresponding with $\{110\}$, is situated in the direction of the B-axis, at a distance of $\frac{100}{a}$ m.m.

On $\{010\}$ the spot corresponding with $\{011\}$, is situated in the direction of C-axis, at a distance of $100\,c$ m.m.

On $\{010\}$ the spot corresponding with $\{110\}$, is situated in the direction of A-axis, at a distance of $100\,a$ m.m.

all distances reckoned from the image-centre C[1]).

§ 3. If in this way the indices of the molecular planes are determined, it is possible to construct a stereographical projection of them, and by means of this projection to execute the ordinary calculations, as usual in crystallography. However it is also possible to construct *directly* the stereographical projection of the reticular planes, with which the spots on the photo correspond, from the stereographical projection of the Röntgen-pattern itself. The way to do this, is as follows:

The part to the right of fig. 2 relates to the original stereographical projection of the Röntgen-pattern of *potassiumchloride*, obtained by Bragg, if the plate, cut parallel to a face of the cube, is radiated through in a direction perpendicular to that face. The part to the left of fig. 2 represents the stereographical projection of the molecular planes of the crystalline structure, corresponding with the spots in the part of fig. 2, situated to the right; the plane of projection is parallel to the same face of the cube. If now we again pay attention for a moment to fig. 1, we shall find that in this figure

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[1]) The relation between the situation of the spots on the photographical film, and that of the corresponding points in the stereographical projection on P, can also easily be seen from the fig. 1. For $CS = 2A.tg\,\varphi$ and $CV = A.tg\,2\varphi$, if V is the original spot. and S its stereographical projection on P. If CV $(= a)$ is measured on the photography, then $tg\,2\ \ = 0{,}02\,a$; from this and tg are calculated, and thus $CS = 100\,tg\,\varphi$ is found in m.m..

the point z is the centre of a zône-circle CMS, and thus also the point of intersection of the zône-axis KQ with the plane of the photographic plate P, this being in fig. 2 the plane of projection of the stereographical figure to the left.

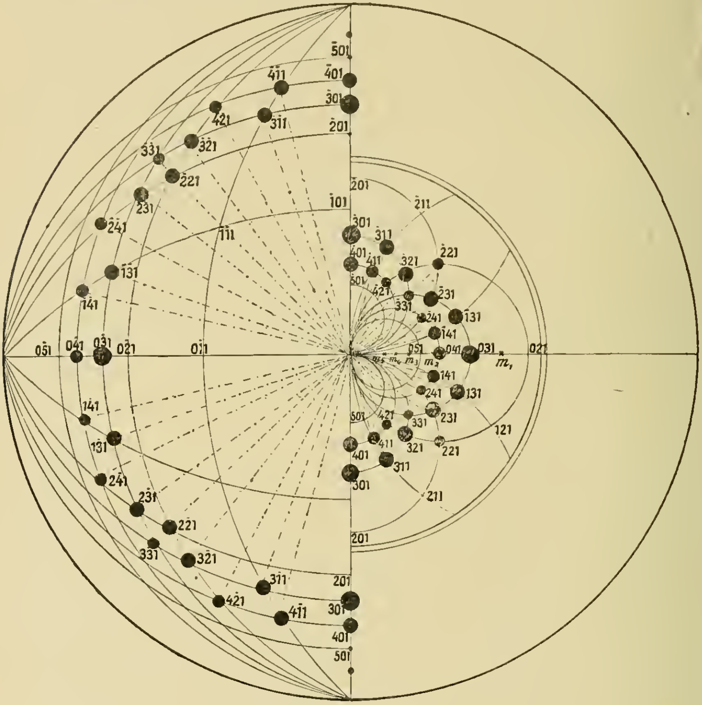

Fig. 2 Construction for the change of the Stereographical Projection of a RÖNTGEN-pattern (to the right: potassiumchloride after BRAGG), into the Stereographical Projection of the corresponding reticular planes of the Crystal-structure.

Let now m be the stereographical projection of the point Q, then, if the polar circle to m is drawn, this circle will contain all points, that are the projections of all tautozonal reticular planes, having KQ as their zone-axis. The azimuth of every spot in the plane P and the azimuth of the stereographical pole of each corresponding reticular plane in P always being equal, the place of every one of these stereographical poles on the polar circle just obtained, may be localised by joining the original spot, and to pass this straight line through, until it intersects the constructed polar circle in the left part of the figure.

This point of intersection is the stereographical projection of the molecular plane, which corresponds with the spot in the right part of fig. 2. The points m can be easily found from the points z by an additional construction, in which a circle with a radius of 50 m.m. is used; the contractions of the original distances to C, — which thus can be represented by mz, — are moreover for spots in the neighbourhood of C only so slight, that without considerable error, instead of m, the point z itself may be used; but at greater distances from C this of course is no longer allowable. The system of polar circles and poles of reticular planes obtained in this way, will give a direct review of the total zône-relation and of the indices of the molecular planes; while the calculation of the angles between the poles of those reticular planes and the plotting of graphical constructions etc., can be made in the way usual in crystallonomy. It is adviceable to keep the radius of the projection-circle in the left part of fig. 2 equal to $2A$ (100 m.m.); then it is possible to execute the different constructions by means of Wulff's stereographical projection plat with a diameter of 20 c.m. The indices of the poles of the reticular planes are the same as the original ones of the spots in the projection to the right of fig. 2.

Finally we can express the different intensities of the spots in the original figure, into the projection-figure of the corresponding molecular planes to the left of fig. 2; in this way a further discussion of the relations between the indices of the reticular planes and their spectral-resolving power can be made, in the way indicated for the first time by Bragg.

§ 4. As an application of the discussions given above, we will consider here more in detail the Röntgen-patterns of the *anhydrite*. The parameters of this mineral are: $a : b : c = 0.8932 : 1 : 1.0008$; from this it follows, that for a distance of 100 m.m. between the plane of projection P and the viewpoint O of the projection, the projected spots for the faces {101}, {011} and {110} will be situated at the distances:

For a plate parallel to {100}:

in the direction of the C-axis at 112.04 m.m. from C
,, ,, ,, ,, ,, B-axis ,, 111.95 ,, ,, ,,

For a plate parallel to {010}:

in the direction of the C-axis at 100.08 m.m. from C
,, ,, ,, ,, ,, A-axis ,, 89.32 ,, ,, ,,

For a plate parallel to {001}:

in the direction of the A-axis at 89.25 m.m. from C
,, ,, ,, ,, ,, B-axis ,, 99.92 ,, ,, ,,

If now we calculate from the *measured* distances of the spots on the photographic plate of *anhydrite*, using $A = 50$ m.m., the values of $tg\, 2\varphi$, then φ, and finally $100\ tg\, \varphi$, — we shall find that all these calculated values are *a little smaller* than the corresponding rational parts of the above mentioned fundamental distances in the directions of the resp. axes: moreover, these calculated values all appear to be diminished *in about the same ratio*.

In the case of the photo parallel to {100} e.g. we measured for some spots:

in the direction of the C-axis: 31.2 mm.; 24.1 mm. and 19.9 mm. from the centre;

in the direction of the B-axis: 27.4 mm.; and 21.8 mm.

For the same points the *calculated* distances are:

in the direction of the C-axis: 32 mm.; 24.8 mm.; and 22.4 mm.
in the direction of the B-axis: 28 mm.; and 22.4 mm.

But calculations and measurements now appear in much better agreement with each other, if we suppose A during the experiment to have had a *smaller* value, and to have been about 48,3 mm. Now the *thickness* d of the crystalplate was in our case precisely 1,64 mm.; and thus we must conclude, that in this case we must use in our calculations of the angles φ, for A *not* the value of the distance from the *front* face of the crystal-plate to the photographic film, but that from the *backward*-face of it to the photographic plate.

In other analogous cases we indeed now learned, that if A was supposed to be $= 50$ mm., during the experiment, the distances from the projected spots to the centre C appeared to be always too small, if in the final projection the distance OP is always kept $= 100$ mm.; but that ordinarily a sufficient agreement between calculation and experiment would result; if A during the experiment is supposed to be $(50 - \frac{1}{2}\, d)$, where d is the thickness of the crystal-plate used.

This influence of the plate-thickness becomes yet more evident, if of the same crystal RÖNTGEN-patterns are obtained with plates of very different thickness; for in that case the photos must manifest different distances from C for the same spots. We were able to observe something of the kind in the measurement of two analogous

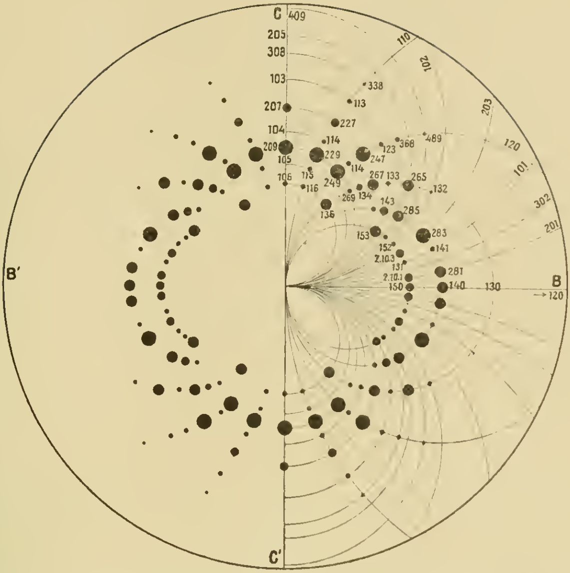

Fig. 3. Stereographical Projection of the Röntgenogram of *Anhydrite*. Plate parallel to (100).

photos of *arragonite*, obtained with crystalplates of different thickness.

Thus it seems undoubtedly necessary; to take into consideration the thickness of the crystal-plates in the calculations of the angles φ, and to diminish the distance of 50 m.m., if rather thick plates are used, with half the thickness of them [1]). The projections reproduced on Plate IV of this paper all relate to such stereographical projections, for which the distance OP is 75 m.m.: in such cases the diameter of the figure is also kept equal to 75 m.m.

In most of the drawings of Plate IV we have calculated the symbols $\{hko\}$, $\{okl\}$ and $\{hol\}$ of the zône-circles, (whose centres lie in the direction of the axes), in the way formerly described; the symbols of the most important spots in the figure can then be immediately seen from the indices of the zone-circles, after the method mentioned above.

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[1]) This is connected with the specific absorbing power for Röntgen-rays of the crystallised material. As this absorption is stronger, the distance of 50 m.m. will have to be diminished with a *smaller* part of the thickness d.

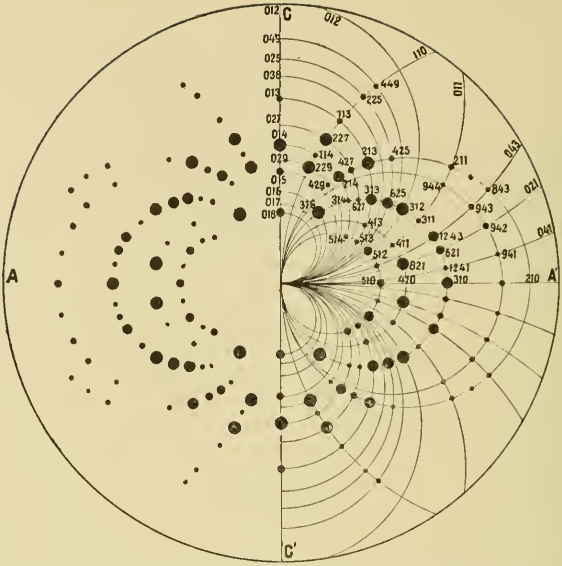

Fig. 4. Stereographical Projection of the Röntgenogram of *Anhydrite*. Plate parallel to (010).

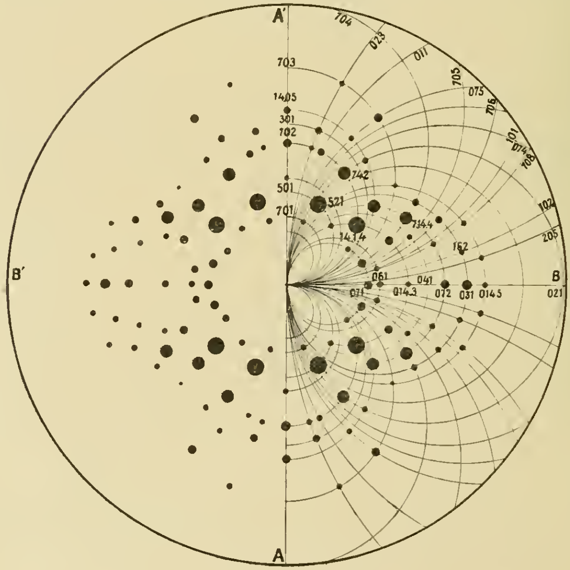

Fig. 5. Stereographical Projection of the Röntgenogram of *Anhydrite*. Plate parallel to (001).

In connection with the crystals investigated up to this moment, the corresponding principal distances in the direction of the axes, as in the case of *anhydrite*, may be recorded here [1]).

		Struvite	Topaz	Anhydrite	Arragonite	Hambergite	Zinc-sulphate	Asparagine	Sodium-ammonium-tartrate	Calamine	Cordierite
On {100}:	C-axis $\frac{100c}{a}$	160.9	180.5	112.0	115.8	91.0	57.4	175.8	51.0	61.0	95.2
	B-axis $\frac{100}{a}$	176.5	189.2	111.9	160.7	125.2	102.0	211.1	121.4	127.6	170.3
On {010}:	C-axis $100c$	91.2	95.4	100.1	72.1	72.7	56.3	83.3	42.0	47.8	55.8
	A-axis $100a$	56.7	52.8	89.3	62.2	79.9	98.0	47.4	82.3	78.3	58.7
On {001}:	A-axis $\frac{100a}{c}$	62.1	55.4	89.2	86.4	109.9	174.1	56.9	196.0	163.9	105.1
	B-axis $\frac{100}{c}$	109.6	104.8	99.9	138.8	137.6	177.6	120.1	238.1	209.3	179.1

§ 5. In previous papers we already discussed some crystals of rhombic symmetry, which will be reviewed again in connection with what is mentioned above. However we will principally discuss in this paper the results, to which our experiments till now have led us, with respect to the following crystals: *anhydrite*; *arragonite*; *zinc-sulphate*; *topaz*; *strurite*; *l-asparagine* and *calamine*. A following communication will then contain the results with other rhombic crystals, and at the same time we shall have then an opportunity to draw the attention to some problems, which are connected with the special choice of these crystals.

We will begin here with the crystals of the *rhombic-bipyramidal* class first [2]).

a. Anhydrite ($CaSO_4$). The used *anhydrite*-crystal was from STASSFURT. It was lustrous and translucid, and evidently quite homogeneous. Parallel to the three directions of cleavage: {100}, {010} and {001},

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[1]) Note that these numbers relate to a projection distance $OP = 100$ m.m.; our figures then have also a diameter of 100 m.m. But for the drawings on Plate IV, which are reduced to $^3/_4$ size, all these values need to be also multiplied with $^3/_4$.

[2]) The crystals discussed in this paper are supposed to have such a position, that their parameters become: *anhydrite*: $a : b : c = 0.8932 : 1 : 1.0008$; *arragonite*: $a : b : c = 0.6224 : 1 : 0.7206$; *zinc sulphate*: $a : b : c = 0.9804 : 1 : 0.5631$; *topaz*: $a : b : c = 0.5285 : 1 : 0.9539$; *strurite*: $a : b : c = 0.5667 : 1 : 0.9121$; *calamine*: $a : b : c = 0.7835 : 1 : 0.4778$; *l-asparagine*: $a : b : c = 0.4737 : 1 : 0.8327$; *sodium-ammonium-tartrate*: $a : b : c = 0.8233 : 1 : 0.4200$; *hambergite*: $a : b : c = 0.7988 : 1 : 0.7268$.

three rather thick crystal-plates were prepared, whose thickness was resp. 1.64 mm., 1,72 mm. and 2,09 mm. In this case and all others here we experimented again with the fluorescent screen "Eresco"; the time of exposition was ordinarily about 2,5 hours. In this case of the *anhydrite* we used more particularly a COOLIDGE-tube, with a *wolframium*-anticathode and separate heating-spiral.

The three photographs are reproduced in fig. 1—3 on Plate I; their stereographical projections already in fig. 3, 4 and 5 of the text. All three images appear to be quite normal, and every one has two perpendicular planes of symmetry; the normal to the plate (direction of radiation) is thus at the same time a binary axis of the RÖNTGEN-patterns.

b. Arragonite ($CaCO_3$). Our clear, lustrous crystals were from HORSCHENZ in *Bohemen*. The crystal-plate parallel to {100} had a thickness of 0,96 mm., that parallel to {010} 1,06 mm., and that parallel to {001} 1,10 mm. The photos are reproduced in fig. 4 on Plate I, and in fig. 5 and 6 on Plate II; their stereographical projections in fig. 1—3 on Plate IV. Also in this case the patterns appear to be symmetrical with respect to two planes of symmetry perpendicular to each other, just as might be predicted from theory. In the image parallel to {001} moreover the well-known pseudo-ditrigonal symmetry of the mineral is clearly recognisable.

c. Topaz. ($Al_2(F,OH)_2 SiO_4$). The *topaz*-crystal used by us was very homogeneous, vitreous and translucid; it possessed a yellowish hue, and originated from *Saxony*. The thickness of the three plates parallel to {100}, {010} and {001}, was from 1,20 mm. to 1,27 mm.; the time of exposition again two and a half hours. The plate parallel to {010} afterwards appeared to be a little inclined; therefore the corresponding photo was not reproduced here, but solely those of the other sections in fig. 7 and 8 on Plate II; their stereographical projections are to be found in fig. 4—6 on Plate IV.

Also in this case all three patterns appear to be symmetrical after two perpendicular planes, as might be expected from the theory.

To this same class belong furthermore the crystals of *cordierite* and of *hambergite*, already previously [1]) discussed.

d. In the case of *cordierite* the patterns of crystal-plates parallel to {100} and {010} appeared to be, till this moment, *always* abnormal, notwithstanding the fact that crystals of several localities were used in the experiments, and among these were present splendid, lustrous crystals. Only the pattern obtained with a crystal-plate parallel to {001}, appeared to exhibit the normal symmetry.

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[1]) These Proceed. **17**, 430, 1204. (1915).

e. About the *hambergite* and its normal and abnormal images we have said already something in the foregoing paper. In fig. 7—9 on Plate IV we reproduce here again the more exact stereographical projections of the normal Röntgen-patterns of this mineral, with indication of the corresponding indices of the reticular planes.

§ 6. Of the *rhombic-pyramidal* class, to which thus belong the hemimorphic crystals of the system, — we investigated here the *struvite* (= *magnesium-ammonium-ortho-phosphate*: $(NH_4)MgPO_4 + 6H_2O$)), and the *calamine*: $Zn_2(OH)_2SiO_3$.

f. From a big, brownish yellow and only little translucid crystal of *struvite* from Homburg, three plates were cut parallel to the three pinacoïdes {100}, {010} and {001}, whose thickness was from 1,20 to 1,26 mm. The time of exposition was two and a half hours.

The three very beautiful Röntgen-patterns are reproduced in the fig. 9, 10 and 11 on Plate III, and as stereographical projections in fig. 10—12 on Plate IV. Also in these images two planes of symmetry perpendicular to each other are evidently manifested; notwithstanding the polarity of the *c*-axis is very strongly revealed in the crystals themselves, the result is also in this case in full agreement with the theoretical prediction.

g. However in the case of *calamine* we obtained for crystal-plates parallel to {100} and {010}, cut from a very beautiful crystal¹), always *abnormal* patterns, from which one parallel to {010} is reproduced partially as a stereographical projection in fig. 13 of Plate IV; the image parallel to {100} was quite analogous to that parallel to {010}, but it was too bad to allow in any way a reproduction of it. Both patterns contained moreover such a great number of very small and feeble spots, that also in the projection of fig. 13 on Plate IV, only the most important spots could be reproduced.

The Röntgenogram of the *calamine* parallel to {001} however was very beautifully regular (fig. 14 on Plate IV) and (fig. 12 on Plate III); quite in concordance with the theory, it is symmetrical with respect to two planes perpendicular to each other. Why it is the images parallel to {100} and {010}, — (corresponding with those sections, that in the crystal itself do not possess the horizontal plane of symmetry), — where the plane of symmetry parallel to the *c*-axis is suppressed, can hardly be understood at this moment.

§ 7. Finally we used from the crystals of the *rhombic-bisphenodical*

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¹) For this very beautiful crystal we are much indebted to our colleague, Prof. Molengraaff at Delft, whom we render our best thanks here once more.

class, besides the already formerly discussed crystals of *d-sodium-ammonium-tartrate*, moreover: those of *l-asparagine*: ($C_4H_8O_3N_2+H_2O$), and of *zinc-sulphate*: $ZnSO_4 + 7H_2O$; of these compounds both the first named are optically active in solutions, while the *zinc-sulphate* does not change the plane of polarisation of the light, when passing through its solution.

h. Zinc-sulphate. From a beautiful crystal three rather thick plates were cut: that parallel to {100} had a thickness of 2.11 mm., that parallel to {010} of 3.30 mm., and that parallel to {001} of 3.10 mm. Even with a time of exposition of two and a half hours, the patterns parallel to {100} and {001} were too feeble, to allow of any reproduction; but in fig. 15 and 16 their stereographical projections are drawn.

These images are again symmetrical with respect to two perpendicular planes However the pattern obtained with a plate parallel to {010} appeared to be *always abnormal*; the respective photo is already reproduced in the foregoing paper on Plate V, while here in fig. 17 on Plate IV its stereographical projection is represented.

This last fact is indeed of high importance for our problem: for it may be supposed with good reason, that in cases, where such crystal-plates are prepared by *cleavage* along planes of *very perfect* cleavability, all chance to get a faulty orientation of the plate is altogether eliminated. Now in our case the very perfect orientation of this plate obtained by such cleavage, could moreover be very rigorously tested, because of the fact that the *b*-axis, being the direction through which radiation here takes place, is at the same time the first bisectrix of the crystal. Indeed the interference-image in convergent polarized light appeared after measuring with the microscope, to be accurately centred, so that *no* deviation between the *b*-axis and the normal on the plate could be found by any means. And while now the orientation of the perfectly clear and lustrous plate could hardly show any error exceeding a few minutes, the image was in two repeated experiments, absolutely abnormal in the way indicated here: evidently only the plane of symmetry parallel to the plane of the optical axes has remained.

This fact must convince us in a striking way, that the abnormalities occurring in the case of such crystals can*not* have their origin in a faulty orientation of the crystal-sections. Indeed, they must be caused by *internal* disturbances of the molecular structure, which evidently, as here with the *zinc-sulphate*, cannot even be discerned by the usual optical means. At the same time it appears furthermore by this fact, that the probability of such "internal vicinal

. M. JAEGER AND H. HAGA. ON THE SYMMETRY OF THE RÖNTGEN-PATTERNS OF RHOMBIC CRYSTALS. I.

Fig. 1.
Anhydrite. Plate parallel to (100).

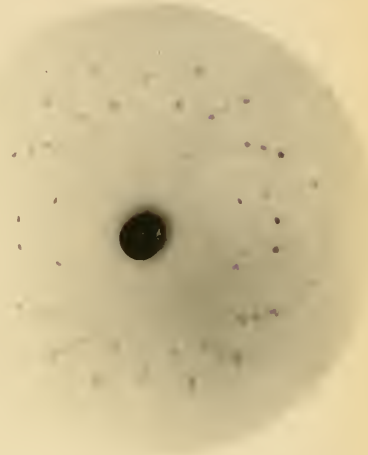

Fig. 2.
Anhydrite. Plate parallel to (010).

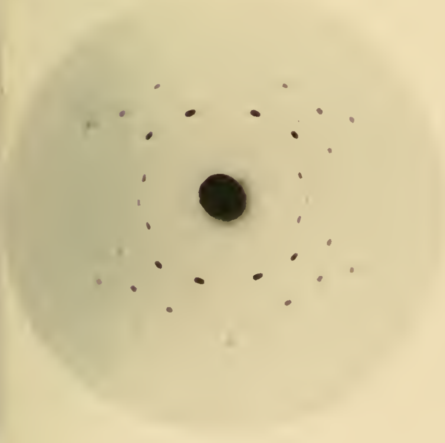

Fig. 3.
Anhydrite. Plate parallel to (001).

Fig. 4.
Arragonite. Plate parallel to (100).

HELIOTYPE, VAN LEER AMSTERDAM

Fig. 5.
Arragonite. Plate parallel to (010).

Fig. 6.
Arragonite. Plate parallel to (001).

Fig. 7.
Topaz. Plate parallel to (100).

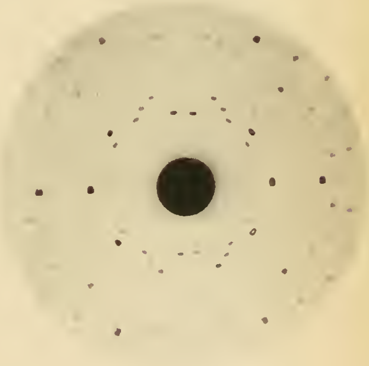

Fig. 8.
Topaz. Plate parallel to (001).

HELIOTYPE, VAN LEER AMSTERDAM

Fig. *9.*
Struvite. Plate parallel to (100).

Fig. *10.*
Struvite. Plate parallel to (010).

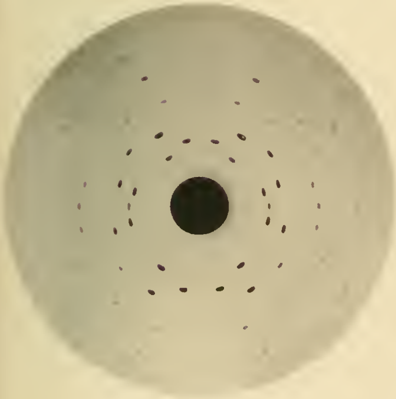

Fig. *11.*
Struvite. Plate parallel to (001).

Fig. *12.*
Calamine. Plate parallel to (001).

HELIOTYPE, VAN LEER, AMSTERDAM

Prof. H. HAGA and Prof. F. M. JAEGER: "On the Symmetry of the Röntgen-patterns of Rhombic Crystals," I.

Plate IV

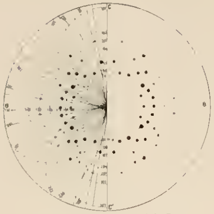
Fig 1. Stereographical Projection of the Röntgenogram of Arragonite. Plate parallel to (100).

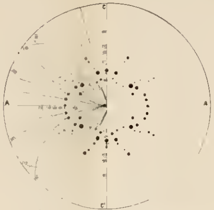
Fig. 2. Stereographical Projection of the Röntgenogram of Arragonite. Plate parallel to (010).

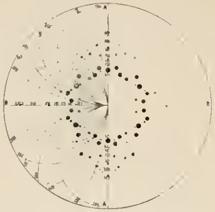
Fig 3. Stereographical Projection of the Röntgenogram of Arragonite. Plate parallel to (001).

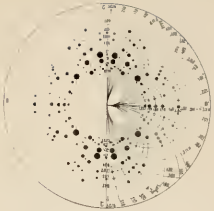
Fig 4. Stereographical Projection of the Röntgenogram of Topaz. Plate parallel to (100).

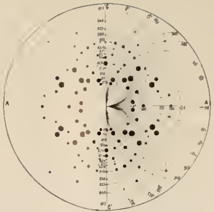
Fig 5. Stereographical Projection of the Röntgenogram of Topaz. Plate parallel to (010).

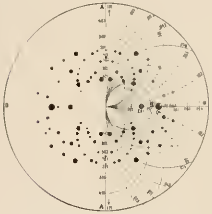
Fig. 6. Stereographical Projection of the Röntgenogram of Topaz. Plate parallel to (001).

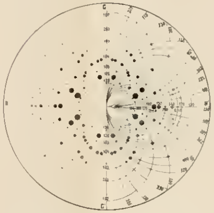
Fig. 7. Stereographical Projection of the Röntgenogram of Hambergite. Plate parallel to (100).

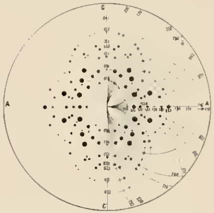
Fig 8. Stereographical Projection of the Röntgenogram of Hambergite. Plate parallel to (010).

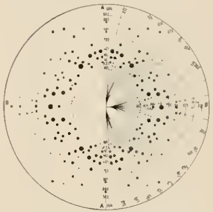
Fig 9. Stereographical Projection of the Röntgenogram of Hambergite. Plate parallel to (001).

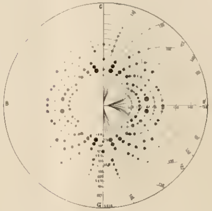
Fig 10. Stereographical Projection of the Röntgenogram of Struvite. Plate parallel to (100).

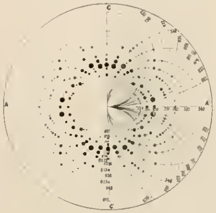
Fig 11. Stereographical Projection of the Röntgenogram of Struvite. Plate parallel to (010).

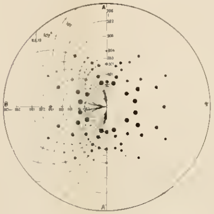
Fig. 12. Stereographical Projection of the Röntgenogram of Struvite. Plate parallel to (001).

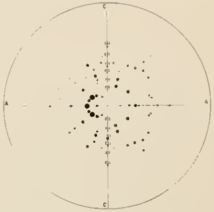
Fig. 13. Stereographical Projection of the Röntgenogram of Calamine. Plate parallel to (010). (Schematical).

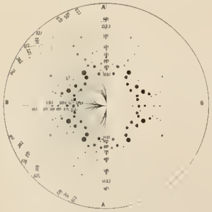
Fig. 14. Stereographical Projection of the Röntgenogram of Calamine. Plate parallel to (001).

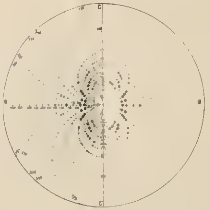
Fig 15. Stereographical Projection of the Röntgenogram of Zinc-sulphate. Plate parallel to (100).


Fig 16. Stereographical (schematical) Projection of the Röntgenogram of Zinc sulphate. Plate parallel to (010). Abnormal Pattern, obtained with a perfectly clear lamella prepared by cleavage, and exactly perpendicular to the first bissectrix.

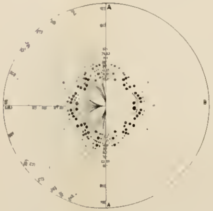
Fig 17. Stereographical Projection of the Röntgenogram of Zinc sulphate. Plate parallel to (001).

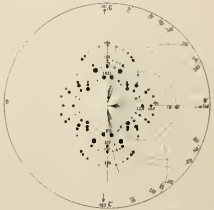
Fig 18. Stereographical Projection of the Röntgenogram of laevogyratory Asparagine. Plate parallel to (010).


Fig 19. Stereographical Projection of the Röntgenogram of laevogyratory Asparagine. Plate parallel to (001). (Schematical).

planes" is by no means diminished by the particular circumstance, that the considered molecular layers are just those, which play the role of directions of perfect cleavability in the crystals. (Thus being perpendicular to the direction of *minimal* cohesion[1]).

i. The Röntgen-patterns of *d-sodium-ammonium-tartrate*, as well the normal as the abnormal ones, and all particulars observed in that case, have been discussed already in detail in our last paper. We can here therefore refer to the resp. figures; only it may be remembered here once more, that the patterns parallel to all three pinacoidal faces, in the normal case appeared to be symmetrical with respect to two perpendicular planes.

k. From big, colourless and perfectly transparent crystals of laevogyratory *asparagine*, crystal-plates parallel to {100}, {010} and {001} were cut. The plate parallel to {100} had a thickness of 1,21 mm., that parallel to {010}, of 1,06 mm., and that parallel to {001}, of 1.22 mm.

The obtained Röntgen-patterns were all too feeble to make a direct reproduction possible. But in fig. 18 and 19 on Plate IV two of their stereographical projections are drawn. Also these images evidently are symmetrical with respect to two perpendicular planes. The third pattern was too disturbed to allow any valuable judgment about this question.

§ 8. From these researches, which will be still completed, it becomes clear even now, that in ordinary cases also with optically biaxial crystals, the theoretical predictions are in full concordance with experience.

The repeatedly observed suppression of one of the two expected planes of symmetry in the Röntgen-patterns, must be considered also in these cases as a peculiar "abnormality", which undoubtedly is caused by internal disturbances of molecular dimensions, whose true nature however at this moment cannot yet be more sharply defined.

University-Laboratories for Physics and for
Inorganic and Physical Chemistry.

Groningen, August 1915.

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[1] In this connection a remark made a short time ago by P. Ehrenfest (these Procced. **18.** 180. (1915) is of interest, considering the possibility of cleavage along planes, which are "vicinal" with respect to such directions of perfect cleavability.

Zoology. — "*The Physiology of the Air-bladder of Fishes.*" (From the Physiological Laboratory of the Amsterdam University.) By Dr. K. Kuiper Jr. (Communicated by Prof. Max Weber).

(Communicated in the meeting of May 29, 1915.)

III. *The Ductus pneumaticus of the Physostomi.*

Boyle (1670) already demonstrated experimentally that a tench when exposed to a lower pressure than the one under which it lives, can allow air-bubbles to escape from the air-bladder by means of the ductus pneumaticus. For a long time it was supposed that this channel also served to lead into the air-bladder gases which the fish had imbibed at the surface of the water. Evidently this would only be possible if the tension of the gas in the bladder is less than that of the atmosphere. The former being in a great majority of instances greater than the latter, this mode of filling the air-bladder is precluded. Besides a fish rising to the surface has to leave its "plan des moindres efforts", the plane where its S.G.=1. At the surface the tension is less, the air-bladder expands, the fish grows specifically lighter; it floats. To reach its static plane again it has to perform muscular labour in a direction opposite to the upward pressure. If it admitted air at the surface, which would lower its static plane in the water, the exertion in going down again would have to be greater still. This view of the function of the ductus has been relinquished by almost every one.

An annular muscle shuts off the entrance of the ductus into the esophagus. Structure and action of this muscle were first closely studied by Guyénot. He proved that this muscle has a tonic tension. When a physostomus is exposed to a decreased pressure, air-bubbles do not immediately escape from the mouth. Only when the decrease amounts to about 5 centimetres of mercury the gas leaves the bladder. At the death of the animal this tonus disappears. The resistance which the sphincter offers to the air in the bladder is reduced to about two fifths. The opening of the sphincter is brought about under the influence of the central nerve-system. The muscles get nerve-branches from the Ramus intestinalis Vagi. This appears distinctly from the microscopic preparations (microtomic sections) which I made of the sphincter and its surroundings. The gas-bubbles are not emitted continually but intermittently. This suggests the probability that the tonus of the sphincter is relaxed every now and then. A more accurate idea of the mechanism of this sphincter-orifice was the object of this part of my investigations.

At the outset it must be observed that the pressure-decrease to which a fish is submitted has to surpass a certain minimum before the animal lets an air-bubble escape. Already at a smaller difference in tension than that at which air-bubbles are sent forth, the fish shows by the restless motion of its fins that it responds to this difference. In the various species and also in the various individuals of the same species the difference between the pressure-decrease at which fin-reactions and at which air-bubbles appear is highly variable. Besides the minimum change at which fin-reactions are observed fluctuates strongly. Hence we shall have to experiment on as great a number of animals as possible in order to obtain reliable results.

If a fish adapts itself to a modified pressure, this does not take place at once. The relaxation of the sphincter seems to last but a short time and may repeat itself at intervals as long as the fish has not entirely adapted itself. The first air-bubble will be followed after a shorter or longer time by others. Generally speaking the interval between two air-bubbles will gradually become greater and this is quite natural for after each air-bubble the fish becomes more adapted to the new pressure. This lengthening of the intervals is, however, by no means regular.

If for instance a fish is exposed for a long time at a stretch, to a pressure-decrease which does not immediately cause air-bubbles to escape, then the long action of this weak stimulus has the same effect as the short action of the stronger one. It could not be demonstrated that the product of time and degree of stimulus was a constant one, but it was very evident that below a certain minimum of pressure-difference no bubbles were emitted, and that above it, at the increase of the pressure-difference, the periods before the emission of the first air-bubble grew smaller and smaller.

If a fish is narcotized then the sphincter-reflex, as was shown by Guyénot, is retarded. The opening of the sphincter is the result of the removal of the tonus in the muscle. It is an inhibitory reflex removed by narcosis. I can confirm the results of Guyénot's experiments. It is remarkable that this reflex-retardation remains a long time after the narcosis. First the respiratory rhythm grows normal, then the equilibrium is restored, afterwards defensive reflexes, caused by fright or decreased pressure manifest themselves. Only much later the tonus-reflex of the sphincter becomes active again. It seems that the centre whence the efferent part of this reflex proceeds remains disturbed for a longer time than the centres of respiration, motion, etc. The same retardation which is caused by narcosis also manifests itself if the fish is exposed to the action of an electric current.

We shall now try to investigate the course of the inhibitory sphincter reflex.

Guyénot states that in tench, carp, etc. a delay in the manifestation of the reflex could be observed if the connection between the forepart of the air-bladder and the perilymphatic space of the vestibulary apparatus, which is formed by the so-called bones of Weber, was interrupted. If this view is correct, the function or at least one of the functions of the bones of Weber must consist in communicating to the brain modifications in the gas-tension of the bladder. Air-bladder + organ of Weber must be looked upon, in accordance with the views of Hasse, Bridge and Haddon and others, as a hydrostatic organ. In this hydrostatic organ the ductus-sphincter acts as a safety-valve by means of which a surplus of gas may be removed.

Guyénot states that the emission of air-bubbles before the destruction of this connection, set in at a pressure-decrease of ± 4.5 centimetres of mercury; immediately after the operation it took place only after a decrease of 12—14 centimetres of mercury.

In my preceding article (these Proceedings Vol. XXIII, p. 857) I took exception to the technics of Guyénot's experiments. I feel compelled to do the same now. Guyénot's method is open to various objections. It is based upon the most distal of the bones of Weber, the Tripus, being detached from the side of the air-bladder; the reaction of the fish is investigated immediately after the operation, and the fish is killed immediately after this investigation.

Why was only the connection between air-bladder and Tripus removed? Could not the air-bladder when it expands effect a pressure on the Tripus, which could be transmitted to the vestibulary apparatus by means of the rest of the organ of Weber? Why should the fishes be killed immediately after the operation? Was it absolutely impossible then that the retardation of the reflex was due to the shock? Why was it not verified, in the case of some fishes at least, that they reacted a few days after the operation exactly as they did immediately after?

These considerations induced me to test Guyénot's experiments.

In two ways I tried to disrupt the connection in question. First by making a ventral median section; thus I reached the body-cavity and by moving a little hook past liver, intestine and genitals I tried to destroy the connection. The sinus venosus rendered this operation very difficult and the results were unsatisfactory, or rather they agreed perfectly with those of GUYÉNOT.

The second way resembles much that of GUYÉNOT. Sideways behind the head a longitudinal cut was made in the muscles just where the Tripus is situated. I reached the fossa auditoria of WEBER, felt my way by means of a thin hook until I felt the Tripus move, then I caught firmly hold of it, detached it carefully from its connection with the air-bladder on one side and the other bones of WEBER on the other, and removed it *from the body*. Of course this was done on either side.

The connection was now entirely removed.

The results of these experiments are very striking. *Whenever the removal of the connection had been effected without giving rise to hemorrhage during the operation, the pressure-decrease required to bring about an emission of air-bubbles was no greater or hardly any greater than before the operation.* Only when the general condition of the fish was a bad one, and *immediately*, after the operation, a retardation was to be observed. Sometimes indeed, a retardation could be observed in fishes which had only been submitted to a beginning of an operation, which, moreover, had nothing to do with the organ of WEBER, or the muscles innervating the sphincter. If, besides, we keep in view how long the retardation of the reflex manifested itself after narcosis or after the recovery from the effect of an electric current, we may be sure that GUYÉNOT's results must be due to the shock.

Hence we conclude that the experiment of GUYÉNOT *cannot be adduced in support of the theory of* HASSE *c. s. regarding the function of the air-bladder and the organ of* WEBER.

To obtain greater certainty I also interrupted the hypothetical reflex course in another spot.

If the sphincter-reflex is affected by the elimination of the organ of WEBER, this must also be the case if the connection between brain and labyrinth is destroyed. Therefore I twice attempted to cut the nervus octavus in tenches on one side and twice on both sides. Technically this operation presented few difficulties. The fishes remained alive for many days after the operation. Autopsy proved that the operation had succeeded. In none of these cases the emission of air-bubbles had been retarded after the operation. The function of the ductus-sphincter is entirely independent of the intact state of the labyrinth.

Hence the afferent part of the inhibitory reflex course is not found in the organ of WEBER. It will probably have to be looked for in the sensitive spinal nerve-ramifications, met with in the air-bladder.

The efferent part of the reflex passes along the Rami intestinales Vagi. This became evident when these two nerves were cut through. It is very probable that the tension and the relaxation of the sphincter are brought about by different nerves, just as in the case of the muscles of the bladder of mammals.

Here e.g. the sphincter internus is relaxed (tonus-inhibition) along the nervus pelvicus, whilst the nervus hypogastricus effects the contraction of this muscle.

What are the reasons for assuming such an antagonistic innervation also for the ductus sphincter? The grounds for this supposition are of two kinds and derived: 1 from experimental data, 2 from microscopic observations.

1. Experiments. The sphincter is innervated on both sides by a branch of the Ramus intestinalis Vagi. I have cut through this double "innervation in two ways viz. immediately behind the gill-cover, where the ramus intestinalis with the ramus lateralis bends away from the whole vagus group, and immediately near the sphincter (by making a median ventral cut). When the vagusbranches had been cut through near the gill-covers, the consequences, as regards the emission of air from the bladder, were the following: 1. the emission was considerably retarded, 2. when air-bubbles were emitted the emission no longer took place intermittently, but for a long time at a stretch.

Hence we must conclude that the vagus contains inhibitory fibres for the sphincter-tonus.

If the vagus-branch is cut through immediately near the sphincter the effect is different. The tonus-inhibition is not retarded, but is no longer intermittent either, and the tonus decreases more and more after the operation.

This result might be explained if it could be demonstrated that the vagus branch near the sphincter also contains fibres for the preservation of the tonus (e.g. sympathetic fibres) the cutting of which caused the tonus to disappear, thus entirely removing the inhibition-delay.

2. Microscopic observations. What can we gather from the topographic studies of Chevrel as regards the sympathetic nerve-system of fishes, and our own histological and microscopic-anatomical researches on sphincterinnervation?

Chevrel divides the sympathetic system of fishes into three parts; the cranial, the abdominal, and the caudal part. He describes the connection which the ganglia of the first part form with brain and gill-nerves and Ramus lateralis, and then describes how in the Labrax lupus the R. intestinalis vagi forms near the division of the Arteria coeliaca into Art. hepatoduodenale and Art. mesentero-spleniale, a strong Plexus coeliacus with the N. splanchnicus, which originates from the first abdominal sympathetic ganglion. No such plexus is mentioned by CHEVREL in the case of Cyprinoids. As the latter resembles Labrax in the main, there is no reason to assume that though not mentioned it should not be found here. The probability that the branch innervating the esophagus receives sympathetic fibres by means of the splanchnicus is therefore very great, and becomes practically a certainty if sympathetic fibres can be identified in the thinnest nerve-ramifications on the muscular fibres.

We know that in the striated muscle three kinds of nerve-endings may be met with. First the epilemmal sensible nerve-endings, secondly the hypolemmal endings connected with nerve-fibres possessing a myelin sheath, the so-called motoric endplates of KÜHNE, thirdly, much more delicately shaped networks, always originating, as far as we know, from the marrowless fibres, which are called accessory endplates. BOEKE describing this species takes them to be endings of sympathetic fibres.

From DE BOER's publications we have known for a few years that the sympathetic fibres maintain the tonus of the muscles.

The presence of accessory endplates in the sphincter ductus pneumatici has rendered in my opinion the antagonistic innervation very probable.

For the study of the motoric endplates I used the silver-impregnation of BIELSCHOWSKY as prescribed by BOEKE. The results, obtained for the present by this method, are made clear in fig. 1—3. Histological particulars concerning the course of the nerve-fibres and the shape of the endplates may be omitted here. The main point is that in the muscle closing the esophagus and ductus motoric end plates of 2 kinds may be met with.

The hypolemmal nerve-fibrils without a medullary sheath as far as they could be traced, were thinner than those with one. The endplates were less marked and mostly ended in simple loops.

Hence there are good reasons for assuming that the sphincter is innervated in two ways, that the stimulation of the nervus sympathicus keeps up the tonus, and that of the vagus removes it.

The easiest way of investigating the function of the ductus sphincter is to expose the fish to a modified air-pressure.

There are, however, also other stimuli which act upon the "inhibitory reflex", stimuli acting upon other senses than the hydrostatic organ of sense (the air-bladder filled with gas) are also amongst them.

The following were made to act upon fishes: light stimuli, vibrations of the water (whether they are to be viewed as sound or sensory stimuli I shall leave undiscussed for the present), stimulation of the static organ, chemical stimuli, enclosure in a narrow space (this must not be viewed as the stimulation of a certain organ of sense, but as a means of exciting terror).

a. Light-stimuli.

The fishes in the experimental basin nearly always went to the darkest part. If the basin is lighted up, they turn away from the light, but do not become restless. This is the case, however, if the basin is alternately lighted and darkened. If, for instance, the basin is alternately lighted and darkened about 120 times a minute, the fish begins to swim round uneasily, the respiration-rhythm rises from about 50 to about 90 a minute, the mouth is opened every now and then, and finally some air-bubbles escape.

b. Vibrations in the water. These are brought about by tapping (with a stick) against the experiment-bottle which was in the basin, and which contained the fish. The results agree with those mentioned under *a*.

c. Stimulation of the static organ.

If a fish is placed in a bottle completely filled with water, which is closed by means of a tight fitting stopper, and if the bottle is swiftly turned round in all directions, then the fish is compelled to correct continually its static position. Within a very short time such an animal emits a number of air-bubbles.

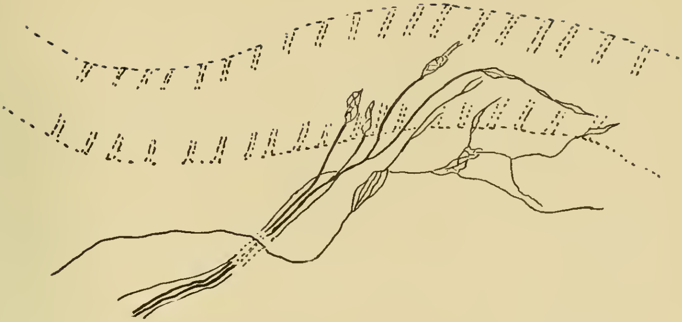
d. Chemical stimuli.

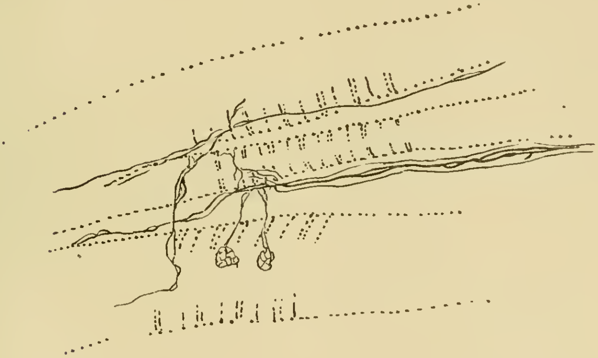
When fishes are narcotized in the water with ether or chloroform, they often emit air-bubbles.

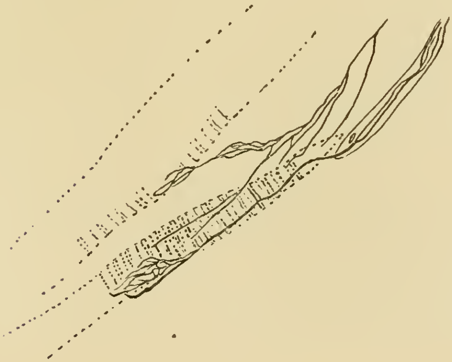
e. Fishes enclosed in a narrow space, which are, for instance, put in a jar below the surface of the water in the basin, emit a few air-bubbles, swimming up and down meanwhile in a state of great agitation.

We conclude from the preceding that as a result of greatly different sensory stimuli, besides swimming and respiratory movements, the opening of the sphincter also manifests itself as a reflex.

Finally I wish to point out that these experiments with various stimuli were also carried out with fishes that had been operated upon. Thus I hoped to obtain a clue as to the direction in which







we shall have to look for an interpretation of the organ of Weber, now that it has become evident that the view of Guyénot can no longer be held.

The results of these experiments may be summarized as follows:

1. When the vagus-branches are cut through, the fishes no longer emit air-bubbles, though they respond in a normal way to light-alternations, vibrations and static stimuli, by their swimming and respiratory movements.

2. *Destruction* of the *organ of* Weber results in fishes responding to light-stimuli (swimming, respiration, sometimes also air-bubble) but *not or very feebly* to vibrations.

3. When the N. octavus is cut through, the fishes respond (and that very violently) to changes in the light, but not to vibrations, nor (which need scarcely be mentioned) to static disturbances.

On comparing these results with those obtained formerly by means of pressure-modification, we obtain the following survey.

Fishes	Reaction on pressure-changes	Light alternation	Vibrations	Static disturbances	Narcosis	Enclosure in narrow space
Normal fish	+ +	+ +	+ +	+ +	+ +	+ +
Vagus has been cut on both sides	+ −	+ −	+ −	+ −	+ −	+ −
Destruction of organ of Weber	+ +	+ (+)	− −	+ +		
N VIII has been cut on both sides	+ +	+ +! +	− −	− −		

[The first sign denotes reaction caused by swimming- or respiratory movements, the second by the opening of the sphincter.]

Very curious is the disappearance of reactions to vibrations as opposed to their remaining after pressure-modifications, when the organ of Weber has been destroyed and the N VIII has been cut through.

The sensitiveness of fishes to vibrations causing sound-sensations in man, has been proved by Piper, who derived actioncurrents from the N. octavus when the fish-labyrinth had been isolated, and by Parker, who at the action of sound saw a number of fishes gather at one side of the basin.

The Clupeides are very sensitive to vibrations. Would this perhaps be due to the special direct connection these fishes have between air-bladder and vestibulary apparatus?

I should say there are ample grounds for investigating if not the view of E. H. Weber, Nusbaum and Sidoniak and others, who see in the organ of Weber a means to transmit vibrations which the air-bladder receives from outside, to the vestibulary apparatus, must be preferred to that of Hasse, Bridge and Haddon, Guyénot, who wish to connect this organ with the hydrostatic function of the air-bladder.

Of course I do not for a moment lose sight of the importance of the air-bladder as a hydrostatic organ of sense.

In my opinion it is, however, quite possible that further investigations will prove that the air-bladder also serves to receive vibrations and that the organ of Weber has to transmit these vibrations to the perilymph of the vestibulary apparatus.

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(concerning all three inferior parts of this treatise).

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ERRATUM.

In the Proceedings of the Meeting of December 30, 1914.

p. 905 line 7 of the 2nd column of table III: for 20.10^5 read 21.06

(October 30, 1915.)

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

VOLUME XVIII

N°. 4—5.

President: Prof. H. A. LORENTZ.
Secretary: Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling, Dl. XXIII and XXIV).

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Petrography. — "*Pneumatolytic hornfels from the hill countries of Siak (Sumatra)*". By Dr. H. A. BROUWER. (Communicated by Prof. G. A. F. MOLENGRAAFF.)

(Communicated in the meeting of October 31, 1914).

The contact-phenomena described in a former communication,[1]) on the southwestern side of the granitic area of Rokan are marked by the occurrence, near the granites, of stratified granite-apophyses and schistose hornfels rich in felspar. From a preliminary examination of the hornfels near the contact with granites from the hill countries of Siak these rocks appear to show an entirely different

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[1]) H. A. BROUWER, "*On the granitic area of Rokan (Middle-Sumatra) and on contact-phenomena in the surrounding schists*", these Proc. Vol. XVII (1915), p 1190.

To the facts related there can be added that during an expedition along the Rokan Kiri when its level was low, also to the right side of the Rokan similar phenomena were observed on the south-western contact of the granites, as were described from the S^i Pakis. The first granites form an isolated little rock emerging from the water near the right bank, whereas about 15 m. down the river the contactmetamorphic schists with numerous granite-apophyses, which occur in alternating layers with the schists, are uncovered in the right bank of the river. Apophyses with a thickness varying from a few cm. to at least 1 m. were observed, the dip is again towards the granitic mass (e. g. Str. N. 20 W. dip N. O. 70° was measured). As a rule, the granite of the apophyses, just like near Pakis, is very rich in biotite and shows parallel texture; here too, at a short distance of the zone of apophyses, leucocratic granites with parallel texture are found, beds of coarse and fine-granular rocks sometimes alternate. The thickness of these beds varies from a few cm. to several dm., they have almost the same strike and dip as the hornfels and granite apophyses (e. g. Str. N. 30 W. dip N.O. 55°).

character; often the schistose structure has entirely disappeared, whereas "felspathisation" as a characteristic contact-phenomenon is missing. Tourmaline often occurs here in such large quantities at the contact of the granites, that for the greater part the rocks consist of this mineral. The tilted more or less schistose limestones with gradnations into sandstones, quartzites and hornfels of the Goenoeng Soeligi, on the border of the hill countries of Siak and the subdivision Boven Kampar of the government Sumatra's Westkust, are mainly covered to the North-East by sedimentary terrane. In the beds of the S^{ei} Lau and S^{ei} Rambei, which have their sources on the G^{g} Soeligi, however, similar rocks are repeatedly uncovered. Veins of quartz are numerous in these rocks. Near the top of the Goenoeng Soeligi, N.W. and N.N.W. strikes with N.E. dips of 65° and 70° were measured, whereas to the North-East side of the G^{g} Soeligi in the S^{ei} Lau, up the river from Kota Renah, N.W. strikes and N.E. dips of 50° to 60° were found.

The occurrence of detached pieces and of weathering-products of granite in the neighbourhood of Kota Renah (hill countries of Siak) has already been mentioned by Everwijn[1] (1864) whereas on a sketch-map of Rolker[2]) granite is indicated in the last right branch of the S^{ei} Kalemboi, a right branch of the S^{ei} Lau. Further pebbles of hornfels from the S^{ei} Lau have been collected and described by Verbeek[3]). The "big, rounded diorite-stones" too, which Everwijn found near and in the kampong Kota Renah, agree, judging from his microscopical description, with some of our hornfels.

The occurrence of cassiterite, although not met with in the material as yet examined, as a component of rocks in situ in the neighbourhood of Kota Renah is very probably in connection with the character and distribution of alluvial tin-ore in the S^{ei} Lau and its side-rivers. Coarse and fine ore occur mixedly, the ore being often very sharp-edged and sometimes intergrown with quartz, whereas it was not found in the upper part of the S^{ei} Lau.

The examined granites are rocks containing tourmaline and are free from biotite, they were collected in the right bank of the last

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1) R. Everwijn. Verslag van een onderzoekingsreis in het rijk van Siak. Jaarb. v. h. Mijnwezen v. N. O.-Indië 1874, and Natuurk. Tijdschr. v Ned. Indië, vol. XXIX, 1867

2) Charles M. Rolker. The alluvial tin-deposits of Siak, Sumatra. Trans. Americ. Institute of Mining Engineers, vol. XX (1891), p. 50.

3) R D. M. Verbeek. Topographische en Geologische Beschrijving van een Gedeelte van Sumatra's Westkust, Batavia 1883, p. 610, 612.

right side-river of the S^{ei} Kalemboi near the Kampong Kota Renah. Here we remark some tens of meters up the river, from the mouth, first a larger intrusion of granite, and a few meters farther a smaller intrusion which seems to be developed as a vein with N.W. strike and a breadth of 1.8 m.

Coarse-granular parts alternate with fine-granular ones and porphyritic structures are found too. Polysynthetically twinned felspars and untwinned ones, or felspars showing cross-hatching, can both dominate so as to exclude the others. Further constituents are quartz, muscovite, tourmaline and sometimes reddish-brown garnet, iron ore missing almost entirely and only occurring as very fine spots in the rocks. Further, some light-green chlorite was found in a few samples when microscopically examined. The plagioclase (chiefly albite) shows only polysynthetical twins, according to the albite-law. Whole crystals are sometimes characterised by cross-hatching. However, part of the crystals often is untwinned, entirely untwinned crystals also occurring. These untwinned parts sometimes show parallel extinction, often their direction of extinction in sections of the symmetrical zone was observed to cut in half the angle between the directions of extinction of the polysynthetical twins; the untwinned felspar often consists of irregular spots, which gradually pass into one another and extinguish to different sides of the twinning plane, their angle of extinction varying between the one of the distinctly limited lamels and the one of the homogeneously extinguishing parts mentioned above. These crystals apparently contain different graduations from microcline into orthoclase (extinction in sections perpendicular to the positive bisectrix of the obtuse angle = 5°). Similar graduations were described by the author in the microcline microperthites of Transvaal foyaites[1]; they support the truth of the conception of orthoclase as a microcline in which microscopically no twinning can be observed.

In the parts with porphyritic structure small crystals of muscovite, sometimes of quartz and felspar too, are to a small degree enclosed by the larger felspar-crystals. The form of the larger crystals of felspar, muscovite and quartz with respect to the groundmass, points to partly simultaneous crystallisation; in the groundmass the felspar often occurs in well developed elongated sections.

Varieties rich in garnet and tourmaline, near the contact with the hornfels, show a beautiful poikilitical structure. Large crystals of felspar include many small crystals of muscovite, of beautifully

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[1] H. A. BROUWER, Oorsprong en Samenstelling der Transvaalsche nephelien-syenieten. 's Gravenhage, 1910.

idiomorphic tourmaline and garnet and also of quartz and felspar. No ground-mass is observed here, the larger felspars closely adjoining each other and the small crystals of the other minerals and of felspar are disseminated in those larger crystals. The garnets are idiomorphic and microscopically colourless (in thicker sections they show a light rose colour). Exceptionally they are partly surrounded by a tourmaline-crystal, tourmaline-crystals enclosed by garnet also occurring occasionally. As a rule, tourmaline in the granites shows a beautiful zonar structure, with often rather distinct light-blue central part and a brown margin. Sometimes, between these zones an equally distinct one of intermediate colour is found, or the colours graduate into each other. Sometimes in zonar crystals a bluish central part is seen with a pale-blue margin and an intermediate zone of light-brown colour, differently coloured and repeatedly alternating zones also being observed in some crystals. It is remarkable that in the contiguous hornfels only brown and almost always homogeneously coloured tourmalines occur. In the pieces of hornfels of the S^{ei} Lau the zonar tourmalines were also found.

The contact-rocks have been examined near the contact with the granites. There they are dark to nearly black-coloured, and often even macroscopically a high percentage of mica can be seen, whereas between the granites and these rocks sometimes a rather narrow transition zone is found which is rich in tourmaline. At the very contact we often see a zone which for the greater part consists of tourmaline. Farther away from the granites, biotite occurs more frequently, the percentage of tourmaline decreasing at the same time. The biotitehornfels at the contact of the larger intrusion contain, as a rule, much tourmaline, whereas along the contact of a narrow tourmaline-bearing vein in the upper-Lau no tourmaline but only traces of biotite could be observed as a contactphenomenon in the schists, which for the rest were unaltered. The tourmaline of the hornfels is almost always of homogeneous structure and of a brown colour, exceptionally a marginal zone of darker brown colour also occurs, but zones of blue tourmaline like those found in the adjoining granites do not occur here. Garnet is often found in considerable quantity in the contact-rocks, especially near the granites.

Sometimes between the quartztourmaline-rocks and the biotite-hornfels a quartz-muscovite-zone was found of some mm.'s breadth containing a small quantity of tourmaline, the muscovite of the zone graduating farther from the contact into a mica of a pale brown colour.

So we can distinguish near the contact of the granites successively:

1. A quartz-tourmaline zone of varying thickness (sometimes not thicker than a few mm., sometimes entirely missing).

2. A quartz-muscovite zone with tourmaline, of some cm.'s breadth, which is most times missing.

3. A quartz-biotite zone which also occurs at the very contact of the granites.

In the *quartz-tourmaline zone* — partly perhaps a marginal facies of the granites — sometimes plenty of garnet and often in small quantity some muscovite and apatite occur together with the main constituents. The structure is sometimes beautifully poikilitic, larger tourmaline crystals, sometimes reduced to skeletons, enclosing numerous grains of quartz and sometimes also crystals of garnet and smaller crystals of tourmaline. This zone often shows a mosaic structure, which sometimes approaches to the hypidiomorphic granular structure, these various structures graduate into each other, and in the granular mixtures we sometimes see some larger crystals of tourmaline with poikilitic structure. Again, the garnet often encloses small quartz-crystals, even when it is itself enclosed by tourmaline. Often this mineral is troubled by numerous inclusions, partly very fine ore-spots. Occasionally, some irregularly limited and turbid felspar was observed in this zone, which poikilitically enclosed quartz and also muscovite. Between the granites and the quartz-tourmaline zone a strong contrast can be seen microscopically, due to the differences of structure, size of grain and constituent minerals. Between the quartz-tourmaline zone and the granites sometimes a narrow zone is observed, consisting of an aggregate of quartz-crystals only or of quartz-crystals intermixed with very little tourmaline and muscovite or of a quartz-muscovite-mixture with much muscovite.

The *quartz-muscovite-zone*, which on several places was found showing a thickness of some mm. only, between a quartz-tourmaline zone of the same thickness containing much garnet and some muscovite and a quartz-biotite-zone containing less garnet, insensibly graduates into the adjoining zones. In the quartz-muscovite zone tourmaline-crystals still occur, which farther from the contact disappear almost entirely. By the growing intensity of a brown colour, the muscovite graduates farther from the contact into a pale brown mica. The percentage of garnet is much smaller than in the quartz-tourmaline-zone and it remains almost constant in the quartz-biotite-zone.

The *quartz-biotite-zone* contains mostly tourmaline, sometimes muscovite and garnet. As a rule the quartz-tourmaline zone is between it and the contact, occasionally it also occurs at the very contact of the granites. Thus e. g. from a quartz-tourmaline-zone of 4 mm.'s breadth, the amount of biotite through a very narrow transitional zone may increase to a large percentage in a quartz-biotite-zone containing much tourmaline.

At $1^1/_2$ cm. from the contact this percentage of tourmaline is still considerable. The biotite is strongly pleochroic, from reddish-brown to almost colourless; the tourmaline is found in small crystals in the quartz-biotite-mixture, but for the greater part in larger crystals, which enclose numerous grains of quartz and also small crystals of garnet. This tourmaline with sieve-structure is sometimes idiomorphic but most times shows irregular forms; in the former case we often see flakes of biotite along the circumference of the crystal, from which it is evident that they have more recently crystallised. The garnet too is always idiomorphic with regard to biotite. In the quartz-biotite-mixture lath-shaped sections of biotite are sometimes rather numerous.

At another place near the contact we see that a small percentage of biotite in a mixture of larger tourmaline-crystals with sieve-structure, quartz and small garnets, has but slightly increased over a distance of 2 cm. Therefore the transitional zone to rocks containing more biotite is much broader there. The biotite is again reddish-brown and shows a strong pleochroism.

The presence of pale-brown mica in a quartz-biotite-zone, separated from the tourmaline by rocks bearing a quartz-muscovite-zone, has already been mentioned above.

If the quartz-tourmaline-zone does not exist, quartz-biotite hornfels are found at the very contact of the granites. Tourmaline-quartz-mixtures rich in garnet, and quartz-biotite-mixtures with tourmaline and containing little garnet, sometimes occur in the same section, both at the very contact. Sometimes, muscovite occurs in a small quantity together with biotite, and the contact-rock is sometimes separated from the granite by a narrow quartz-zone with or without muscovite. The tourmaline occurring in varying quantity forms small as well as larger crystals with sieve-structure. Small spots of ore occur in small quantity; in parts which have more or less elliptical forms and are free from tourmaline, the percentage of ore has slightly increased.

In a specimen of the western contact of the dyke-shaped intrusion, the quartz-tourmaline zone does not occur, and a fine-granular mixture of quartz, biotite and muscovite with rather many small idiomorphic tourmaline-crystals is seen. It is separated from the granites by a narrow zone of quartz. Some spots of ore occur in these rocks, very few larger quartz-crystals without inclusions being found in the fine-granular mixture. At the eastern contact of this intrusion, or very near to it, even muscovite bearing biotiteschists occurs, in which the schistose structure has been preserved.

The detached pieces of hornfels already described by **Verbeek**, which are found very frequently in the neighbourhood of Kota Renah (similar rocks being met with by me even in the upper stream of the S^ei^ Lau as rocks in situ) prove the great extension of rocks similar to those of the quartz-biotite zone which hitherto have been examined by us only near the contact. They often contain green amphibole. The other constituents are quartz, biotite, tourmaline, titanite, ilmenite, calcite and pyrite.

Again, numerous pebbles of rocks similar to the quartz-tourmaline-zone, were found in the rivers Lau and Pinggir, proving that these rocks occur also elsewhere and of more considerable thickness. Of the latter rocks, some with narrow veins of quartz were microscopically examined.

The veins of quartz often — and chiefly in the marginal zone — contain tourmaline, and are sometimes rich in muscovite. Occasionally in the marginal zone larger tourmaline-crystals (of sometimes several mm.'s length) are deposed more or less perpendicular to the plane of contact. As a rule, these tourmaline-crystals have a zonar structure, just like the tourmaline of the granites, and contrary to the tourmaline of the adjoining rocks, which most times has a brown colour. Bluey and brown varieties can both occur as a marginal zone, a repeated alternation of differently coloured zones also being found. Especially at the contact of a vein containing much muscovite, there could be clearly observed how a long crystal of tourmaline, which was interrupted in the marginal zone, continued at some distance in the fine-granular quartz-tourmaline-mixture of the adjoining rock, which points to a partly simultaneous crystallisation of the vein and the adjoining rock.

Like those of the granitic area of Rokan the contact-phenomena described above show a pneumatolytic character. The phenomena in the first mentioned area point to such relations of pressure and temperature and to such a percentage of mineralisers as make granite apophyses possible to be formed in alternating layers with the surrounding rocks, and these rocks to be imbibed with mineralisers. The missing of felspathisation in the contact rocks of the hill countries of Siak can be explained by crystallisation at lower temperature and pressure, and a lower percentage of mineralisers (especially of the alkalies), which occurred in sufficient quantity to make the magma crystallise as a granite, but not in sufficient quantity to cause felspathisation in the adjoining rocks. To match this supposition, the large extension of the granitic area of Rokan and the occasional occurrence of small outcrops of granite in the hill countries of Siak point to the fact that in the first mentioned area the granite and the contact-rocks have been uncovered to a lower level by erosion.

Physics. — "*A Confirmation of the Principle of Relativity*". By Dr. H. K. DE HAAS. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of June 26, 1915).

The following considerations founded on a negative result of an experimental research[1]) concerning the question: "does gravitation require time for its extension in space?" corroborate one of the principal theses of the principle of relativity with a greater degree of accuracy, than is possible for *light*. Any effect resulting at any moment from the relative motion of matter and ether, diametrically opposed to the motion of 30 km. + or — the component of the motion toward the apex in the direction of these 30 km. per second twelve hours later, can be excluded as regards gravitation, with an accuracy of $\left(\frac{1}{10,000}\right)^{0,1/2}$.

At the extremities of a torsion-balance two balls of equal weight were hung, one of platinum (sp. gr.: 21·5), the other of paraffin (sp. gr.: 0·87).

The constants of the apparatus were:

Weight:	Grams:	Moment of inertia (cm². gr.)
Platinum ball	11·6628	2189
Paraffin ball	11·6612	2199
Beam	2·1670	145
2 hooks (at ends of beam)	2 × 0·0364	14
Suspension-hook + mirror		± 3
		Q = 4550

The distance from the hooks at the extremities to the (middle) suspension hook: 13·70 cm. ± 0·01

The half period: $\vartheta = 340'' \pm 1$.

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[1]) For details see: Reports of the lectures delivered by members of the *Bataafsch Genootschap* at Rotterdam. Vol. 1, 1915.

The distance between the mirror, which was attached to the beam, and by which the ray of light was reflected, and the film, on which the movements of the ray of light were photographed, was: 410 cm. ± 0·5.

It can be calculated from the formula $\vartheta = \pi \sqrt{\frac{Q}{K(57 \cdot 3^\circ)}}$ that 1 mm. permanent deviation of the distinctly observable image on the film corresponded to a horizontal force normal to the beam ot $3 \cdot 45 \times 10^{-6}$ dynes on one of the balls or, of $2 \cdot 96 \times 10^{-7}$ dynes per gram of mass of one ball.

The film was moved vertically about 3·4 mm. per hour, by means of a registering timepiece, for 86 hours at a stretch, behind a narrow horizontal slit in a light-proof case.

Every hour an illuminating apparatus, set in motion electrically by means of a clock-work, flashed a ray of light on the slit in such a way that a time-line, divided into min. was registered.

After many difficulties, caused by a sensitiveness to various disturbances, which proved relatively great, and which prevented the balance from acquiring a position of steady equilibrium, we succeeded in registering nearly straight lines on several films, the deviation from straight lines being less than 1 mm.

If we consider that an effect of the "ether wind" would be perceptible to the left in the morning, to the right in the evening, or the reverse, a force exerted on one of the balls, or more exact: a difference of force, exerted on the two balls of $1 \cdot 48 \times 10^{-7}$ dynes per gram, may be considered excluded. It was shown that not even so small a force was released, though the ether rushed through a field of trillions of dynes of intermolecular attraction: for the field of gravitation in one gram of platinum possesses trillions of dynes!

The order of magnitude (of the number of dynes) of total intermolecular attraction cannot be directly calculated for paraffin and platinum, but it can be indirectly approximated from the total amount of intermolecular attraction in 1 cm^3. of water; the physical constants of paraffin and platinum required for a direct calculation, are unknown. We base our indirect calculation on the supposition, that the attraction between the molecules of liquids and of solids is equal, if the specific density is equal. The comparatively small amount of heat, necessary to melt ice, and the slight linear contraction of melting ice, permit of this supposition. An error in this calculation for water and ice of double or half the amount is improbable.

For water the force with which the outer layer of molecules is drawn inward is 10700 atmospheres or $1·085 \times 10^{10}$ dynes per cm.^{2} (VAN DER WAALS).

The more central molecules attract each other no less; they also attract each other with a force of $1·085 \times 10^{10}$ dynes, because the sphere of action of this attraction does not extend beyond the diameter of one molecule. The radius of this sphere (r) is stated as $1·5 \times 10^{-8}$ cm. (MINKOWSKI), the diameter of a molecule being $2·9 \times 10^{-8}$.

There are about $3·45 \times 10^7$ molecules to a cm., hence there is the same number of layers. In the three directions of the sides of 1 cm^3 of water, we find $3 \times 1·085 \times 10^{10} \times 3·45 \times 10^7 = 1·12 \times 10^{18}$ dynes of total intermolecular force. That the sphere of action is smaller than the diameter of one molecule, on which the correctness of the amount $1·12 \times 10^{18}$ is based, may be verified by considering the amount of heat necessary to evaporate 1 gram of water or even of ice (0·62 calorie) as a measure of the work required to split up 1 gram into loose molecules. This work amounts to 260 K.gr.m., for 1 gram of ice, or $2·6 \times 10^{10}$ erg. From the equation $2·6 \times 10^{10}$ erg $= 3 \times 1·085 \times 10^{10}$ dynes $\times 3·45 \times 10^7 \times r$, we find $r = 2·31 \times 10^{-8}$, hence *smaller* than the diameter of one molecule.

How much attraction do we find in platinum or in paraffin?

VAN DER WAALS states that the intermolecular pressure is proportional to the sp. gr^2. This is also true of the sum of the attractions. In balls of the same size it is therefore also proportional to the sp. gr^2, but in balls of the same weight, to the sp. gr.^{1}, provided there are equal numbers of layers of molecules per cm.^{1}, which however is not the case. The sp. gr. of platinum being 21·5 and the molecular weight 194, it can be calculated that there are 1·26 × the number of molecules in water per cm^1. In like manner it can be calculated for paraffin, sp. gr. 0·87 and molecular weight ($C_{22}H_{22}$) 286, that it contains per cm.^{1} 0.38 × the number of molecules in water per cm.^{1}.

In 1 gram of water we found the total intermolecular attraction to be 1.12×10^{18} dynes, we derive from this for

1 gram of platinum $1·12 \times 10^{18} \times 21·5 \times 1·26 = 30·5 \times 10^{18}$ dynes
1 gram of paraffin $1·12 \times 10^{18} \times 0·87 \times 0·38 = 0·37 \times 10^{18}$ dynes
in platinum per gram an excess of 30×10^{18} dynes.

If the motion of the ether through the two balls had caused any aberration, we might reasonably assume that of the $0·37 \times 10^{18}$ dynes per gram of paraffin an equal fraction had been diverted as of $0·37 \times 10^{18}$ dynes in platinum; aberration-angles and aberration-components, which may accompany them, are exclusively based on ratios of velocity, and not on ratios of distance. The equal amounts of aberration, which might be released from $0{\cdot}37 \times 10^{18}$ dynes (platinum and paraffin), can never be demonstrated by means of a torsion-balance, as this apparatus is fundamentally unsuitable for this purpose.

But the torsion-balance would not fail to indicate any possible variation of direction, i.e. aberration of the excess of 3×10^{19} dynes per gram of platinum.

Of these 3×10^{19} dynes of attraction only $\frac{2}{3}$ are to be taken into consideration for aberration, viz. only the sum of all the forces in the 2 directions normal to the motion, but no forces parallel to the direction of translation.

Let us now take into account that every single line of force, acting at its extremities on two molecules, consists of two forces, each equal to the tension along that line of force. It is true, that, when the molecules are at rest, those two forces are exactly equal and exactly opposed; their *sum* as such is *nihil.* But if there were any effect of aberration, the aberration-components, though resulting from opposed forces, would each be parallel to the direction of motion; hence they would be mutually parallel and both point in the same direction. Their *sum* would manifest itself in the experiment.

For example: let us imagine two equal molecules, A and B, attracting each other, when at rest, with a force K along the joining line AB. If these molecules travel through the ether in a direction normal to the joining line, and if gravitation requires time for its extension, the agent acting on A will no longer reach point A along BA, but along a diverging direction, forming an angle with AB (conceived in the plane passing through AB and through the direction of translation). The action which is not directed along the joining line AB would produce a force-component $\perp AB$ in A, but in B an equal component of force will originate, and the components of the two will have the same direction in spite of their arising from forces of opposite directions.

We presume, in this experiment, that $\frac{2}{3} \times 2 \cdot 3 \times 10^{19}$ dynes of attraction per gram are present in the platinum ball, of which the presence of $1{\cdot}48 \times 10^{-7}$ dynes of aberration-component is excluded in our straight registered line; not even $1{\cdot}48 \times 10^{-7}$ to 4×10^{19} dynes, i. e. not $\frac{1}{2{\cdot}7 \times 10^{26}} \times$ the total complex of forces manifested itself outside the system.

In virtue of our mode of derivation, we shall assign no value to the factor 2·7, and we shall round off our figures to powers of ten.

It follows from the straight registered line that the "ether wind" did *not* cause the direction of the intermolecular forces to deviate from the direction required by NEWTON: an angle, namely, deviating from the joining line, of the value $\frac{1}{10^{26}}$ can be excluded: a deviation between the direction indicated in the law of NEWTON, namely the joining line, and the direction of attraction through the relative ether motion of 2 × 30 km. per sec. remains *below* this amount of $\frac{1}{10^{26}}$; the deviation, provided there be one, amounts to less than 1 micron at a distance of 100 light-centuries.

Chemistry. — *"Investigations on the Temperature-Coefficients of the Free Molecular Surface-Energy of Liquids from* —80° *to* 1650° *C."* **XIII.** *The Surface-Energy of position-isomeric Benzene-Derivatives.* By Prof. Dr. F. M. JAEGER and Dr. JUL. KAHN.

(Communicated in the meeting of September 25, 1915)

§ **1.** For the purpose of investigating the influence of the chemical constitution of the liquids on the magnitude and on the temperature-coefficients of the free surface-energy, we also made a series of measurements with a number of benzene-derivatives, which are to each other in relation of position-isomerides. The problem considered seemed to us of yet greater importance, because i. a. in the already previously mentioned paper of FEUSTEL[1]), some position isomerides were studied with this same purpose, and this author as a result of his experiments concluded, that the surface-tensions of such isomeric substances did not differ from each other in any appreciable degree. His conclusion, founded only on a relatively small number of data, seemed to us not too probable, judging from some experience already gathered by us in the course of these investigations: for the μ-t-curves, determined by the first of us in the cases of *dimethyl-resorcinol* and *dimethyl-hydroquinone*[2]), and also of *mesitylene* and *pseudocumene*[3]), appeared to be clearly different for the two pairs of isomerides.

Therefore it seemed of importance to extend such a comparison of the magnitude of the surface-tension to a greater number of such position-isomeric derivatives.

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[1]) FEUSTEL, Drude's Annalen **16**, 61. (1905).

[2]) F. M JAEGER, these Proceedings. **23**, 357, (1914).

[3]) F. M. JAEGER, these Proceedings, **23**, 408, 409, (1914).

In the following paper we therefore publish the measurements made with 36 position-isomeric substances: *ortho-*, *meta-*, and *para-Dinitrobenzene*; *meta-*, and *para-Fluoronitrobenzene*; *ortho-*, *meta-*, and *para-Chloronitrobenzene; meta-*[1]), and *para-Dichlorobenzene*; 1-2-4, 1-3-4- and 1-4 2-*Dichloronitrobenzenes*; *ortho-*, *meta-*, and *para-Bromonitrobenzene; ortho-*, and *meta-Jodonitrobenzene; ortho-*[2]), and *para-Nitrotoluene*; *ortho-*, *meta-*, and *para-Nitrophenol*; *ortho-*[3]), and *para-Nitroanisol*; *ortho-*, and *para-Cresol; ortho-*, and *para-Chloroaniline*; *meta-*, and *para-Nitroaniline*; 3-*Nitro-*, and 5-*Nitro-ortho-Toluïdine*, and 3-*Nitro-para-Toluïdine;* and finally the cyclic derivatives: *sylvestrene* and *terebene*.

The purification of these compounds, as well as the determination of the density, occurred in the same way as formerly described. In the case of some compounds evaporating rapidly already at the meltingpoint, these determinations could not be made with satisfactory exactitude.

§ 2.

I.

ortho-Dinitrobenzene: 1-2-$C_6H_4(NO_2)_2$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
126°	1.279	1705.0	38.4	1.305	979.2
140	1.230	1639.8	36.9	1.291	947.8
155	1.183	1580.0	35.6	1.276	923.4
176	1.125	1499.8	33.6	1.259	877.6
194.4	1.082	1442.5	32.3	1.245	849.9
209.1	1.034	1378.4	30.9	1.235	817.5

Molecular weight: **168.05**.

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

Under a pressure of 30 mm. the substance boils at 194° C.; the meltingpoint was 117° C.

At 120° C. the density was: 1.3119; at 140° C.: 1.2915; at 160° C.: 1.2737.
At t° C. in general: $d_{4^\circ} = 1.3349 - 0.001215\,(t - 100^\circ) + 0.00000325\,(t - 100^\circ)^2$.

The temperature-coefficient of μ oscillates somewhat round a mean value of: **1.95** Erg pro degree.

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[1] F. M. Jaeger, these Proceedings, **23**, 411, (1914).

[2] F. M. Jaeger and M. J. Smit, these Proceedings, **23**, 387, (1914)

[3] F. M. Jaeger and Jul. Kahn, ibidem, **23**, 400, (1914).

II.

meta-Dinitrobenzene: $_{(1,3)}C_6H_4\,(NO_2)_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
94°.8	1.410	1880.3	42.3	1.361	1048.9
114.9	1.342	1788.9	40.2	1.340	1007.2
136	1.264	1688.5	38.1	1.316	966.1
155	1.209	1611.7	36.1	1.295	925.3
175.5	1.149	1532.1	34.3	1.271	890.3
191.2	1.103	1471.2	32.9	1.248	864.5
204.5	1.069	1425.0	31.8	1.235	841.4

Molecular weight: **168.05**.

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The substance boils at 291° C. under a pressure of 756 mm.; it melts at 91° C. At 120° C. the density was: 1.3349; at 140 C.: 1.3149; at 160° C.: 1.2957. At t° C.: $d_{4^\circ} = 1.3557 - 0.00106\,(t - 100^\circ) - 0.000001\,(t - 100^\circ)^2$.

The temperature-coefficient of μ is originally: **2.05** Erg; afterwards it decreases slowly to about: **1.71** Erg pro degree.

III.

para-Dinitrobenzene: 1-4 $C_6H_4\,(NO_2)_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes	
176°.2	1.139	1518.5	34.4
196.5	1.080	1439.8	32.6
210	1.043	1391.0	31.5
226	1.007	1342.5	30.4

Molecular weight: **168.05**.

Radius of the Capillary tube: 0.04529 cm.
Depth: 0.1 mm.

The compound melts at 172° C.; it is very volatile and sublimes readily.

IV.

meta-Fluoronitrobenzene: $C_6H_4(NO_2)_{(1)}F_{(3)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
*0°	1.274	1698.7	40.1	1.348	890.4
29.9	1.193	1590.9	37.1	1.314	837.9
47.8	1.137	1515.6	35.3	1.293	805.9
64.5	1.083	1444.4	33.6	1.274	774.7
80.8	1.031	1374.5	32.1	1.256	747.2
104.5	0.961	1281.1	29.7	1.232	700.3
122	0.914	1218.3	28.2	1.215	671.1
151.5	0.822	1095.9	25.4	1.187	613.9
178	0.741	988.0	22.8	1.160	559.6
196	0.697	929.4	21.4	1.145	529.8

Molecular weight: **141.04**.

Radius of the Capillary tube: 0.04777 cm.; with the measurements indicated by *, it was: 0.04839 cm.
Depth: 0.1 mm.

The liquid boils constantly at 197.°5 C. and a pressure of 760 mm. It solidifies on cooling very soon, and melts then at −1° C. At the boilingpoint χ is about: 21.2 Erg pro cm². The specific weight at 25° C. was: 1.3189; at 50° C.: 1.2905; at 75° C.: 1.2632; at t°: $d_{4^\circ} = 1.3484 \quad 0.001202\,t + 0.00000088\,t^2$.

The temperature-coefficient of μ oscillates round a mean value of **1.82** Erg pro degree.

V.

para-Fluoronitrobenzene: $C_6H_4(NO_2)_{(1)}F_{(4)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
24.5°	1.284	1711.7	38.4	1.325	862.5
31	1.269	1689.0	37.6	1.319	847.1
46.8	1.201	1601.1	35.9	1.301	816.2
60.4	1.149	1531.8	34.3	1.288	785.1
74.2	1.096	1461.2	32.8	1.270	757.8
89.3	1.050	1399.8	31.3	1.254	729.3
110	0.968	1292.8	29.0	1.229	684.4
124	0.931	1240.5	27.7	1.213	659.9
140.3	0.868	1157.8	25.9	1.193	623.9
156	0.805	1076.0	24.3	1.172	592.3
174.5	0.747	996.6	22.3	1.152	549.8
194.1	0.688	913.4	20.3	1.125	508.5

Molecular weight: **141.04**.

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The substance boils at 203.°5 C. under a pressure of 755 mm.; its meltingpoint is 26°.5 C. The specific gravity at 30° C. was: 1.3204; at 50° C.: 1.2986; at 75° C.: 1.2691. At t° in general: $d_{4^\circ} = 1.3509 - 0.0010275\,t - 0.00000078\,t^2$.

At the boilingpoint χ has the value: 19.3 Erg. The temperature-coefficient of μ is about **2.09** Erg pro degree, as a mean value.

VI.

ortho-Chloronitrobenzene: $C_6H_4(NO_2)_{(1)}Cl_{(2)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
31°.2	1.387	1849.8	41.6	1.355	990.8
46	1.330	1777.5	39.9	1.340	957.4
61.2	1.279	1706.2	38.3	1.323	926.9
73.5	1.227	1638.7	36.9	1.304	901.6
89	1.176	1567.8	35.1	1.285	866.1
110	1.102	1470.2	32.9	1.270	818.2
124	1.056	1408.4	31.5	1.256	789.2
140	0.999	1330.9	29.6	1.237	749.1
155.5	0.960	1277.5	28.3	1.222	722.1
175	0.877	1171.0	26.1	1.199	674.5
194.5	0.824	1098.5	24.3	1.177	635.7
209.1	0.797	1062.0	23.5	1.159	621.2

Molecular weight: **157.50.** Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

Under a pressure of 755 mm. the substance boils at 241°; it melts at 33 C
The density at 75° C. was: 1.3083; at 100° C.: 1.2812; at 125° C.: 1.2536.
At t° C. in general: $d_{4^\circ} = 1.3866 - 0.001014\,t - 0.0000004\,t^2$.

The temperature-coefficient of μ is up to 195° C. fairly constant and equal to **2.16** Erg pro degree as a mean value.

VII.

meta-Chloronitrobenzene: $C_6H_4(NO_2)_{(1)}Cl_{(3)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
46°.3	1.312	1749.7	39.3	1.339	943.4
60.5	1.258	1675.9	37.6	1.327	908.1
74.8	1.206	1608.4	36.1	1.308	880.3
90.3	1.148	1535.2	34.4	1.291	846.2
110	1.082	1442.4	32.2	1.272	799.9
124	1.037	1382.5	30.8	1.256	771.6
140.3	0.979	1304.4	29.2	1.237	739.0
155.2	0.928	1240.8	27.7	1.219	708.0
175.2	0.858	1147.0	25.7	1.194	666.0
194.2	0.806	1075.0	23.8	1.172	624.4
209.2	0.770	1026.6	22.7	1.154	601.7

Molecular weight: **157.50.** Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The compound boils at 236° C. under a pressure of 756 mm. It melts at 44°.5 C.
The density at 75° C. was: 1.3082; at 100° C.: 1.2816; at 125° C.: 1.2536; at t° C.: $d_{4^\circ} = 1.3788 - 0.00086\,t - 0.00000112\,t^2$.

The temperature-coefficient of μ between 46° and 194° C. is fairly constant; its mean value is: **2.19** Erg pro degree.

VIII.

para-Chloronitrobenzene: $C_6H_4(NO_2)_{(1)}Cl_{(4)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg. pro cm².
90°	1.147	1529.1	34.3	1.293	842.8
110	1.080	1439.8	32.3	1.272	802.4
125	1.029	1374.0	30.9	1.256	774.1
139.9	0.992	1322.0	29.6	1.242	747.2
155	0.937	1252.6	28.2	1.225	718.3
175.2	0.882	1177.6	26.4	1.204	680.3
194.4	0.835	1113.2	24.8	1.184	646.2
209.2	0.795	1059.9	23.5	1.169	617.6

Molecular weight: **157.50.** Radius of the Capillary tube: 0.04595 cm. Depth: 0.1 mm.

Under a pressure of 756 mm. the substance boils at 234° C.; it melts at 83°.5 C. The density at 85° C. was: 1.2998; at 110° C.: 1.2722; at 135 C.: 1.2457. In general at t C.: $d_{4^\circ} = 1.3285—0.00117\,(t—60\ ) + 0.00000088\,(t\ \ 60^\circ)^2$.

The temperature-coefficient of μ is fairly constant; its mean value is **1.88** Erg pro degree Celsius.

IX.

para-Dichlorobenzene: 1-4-$C_6H_4Cl_2$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular-Surface-energy μ in Erg pro cm².
60°.3	0.972	1294.7	29.4	1.242	708.6
82.6	0.903	1204.4	27.4	1.218	669.0
95.1	0.872	1161.3	26.3	1.205	646.8
114	0.816	1087.9	24.6	1.185	611.7
130.4	0.768	1024.0	23.1	1.168	580.0
144.5	0.727	970.0	21.9	1.153	554.6
166.5	0.671	894.6	20.1	1.130	515.9

Molecular weight: **146.95.** Radius of the Capillary tube: 0.04660 cm. Depth: 0.1 mm.

The para-Dichlorobenzene boils under a pressure of 755 mm. at 173.°5 C.; it melts at 52° C.

At 75° C. the specific gravity was: 1.2261; at 100° C.: 1.1983; at 125° C.: 1.1697. At t° C.: $d_{4^\circ} = 1.2531—0.001064\,(t—50^\circ)—0.00000064\,(t\ \ 50^\circ)^2$.

The temperature-coefficient of μ is constant: **1.83** Erg.

X.

1-2-Dichloro-4-Nitrobenzene: $C_6H_3Cl_{2(1,2)}(NO_2)_{(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
46°	1.340	1787.5	40.2	1.490	1025.4
61	1.294	1724.4	38.7	1.471	995.6
76.7	1.246	1660.5	37.2	1.454	964.5
95	1.217	1622.5	35.6	1.430	933.3
113.5	1.150	1533.2	34.0	1.407	901.1
136	1.074	1431.8	32.0	1.379	859.4
155.1	1.016	1355.0	30.3	1.356	823.0
177	0.948	1263.9	28.1	1.329	773.5
190.5	0.917	1217.9	26.8	1.313	743.7
204	0.867	1155.9	25.6	1.295	717.0

Molecular weight: **191.95**.

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The meltingpoint of the compound is 43° C. The specific gravity at 75° C. was: 1.4558; at 100° C.: 1.4266; at 125° C.: 1.3979. At $t°$ C.: $d_{4^\circ} = 1.5464 - 0.001238\,t + 0.0000004\,t^2$.

The temperature-coefficient of μ is rather constant; its mean value is: **1.96** Erg pro degree.

XI.

1-3-Dichloro-4-Nitrobenzene: $C_6H_3Cl_{2(1,3)}(NO_2)_{(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
35°	1.375	1833.1	41.3	1.487	1054.9
46.3	1.342	1787.4	40.1	1.475	1029.8
60.5	1.294	1724.4	38.8	1.460	1003.2
76.5	1.249	1665.7	37.3	1.443	972.0
95	1.176	1567.7	35.2	1.421	926.7
114.9	1.104	1475.1	33.3	1.399	885.8
136	1.042	1390.5	31.2	1.373	840.4
155.1	0.982	1308.6	29.2	1.350	795.4
176	0.929	1246.0	27.2	1.325	750.3
191	0.870	1158.7	25.7	1.305	716.2
204	0.823	1096.8	24.4	1.289	685.5

Molecular weight: **191.95**.

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

Under a pressure of 15 mm. the boilingpoint is 154° C. The meltingpoint 34° C. The specific gravity was hydrostatically determined: at 75° C. it was: 1.4434; at 100° C.: 1.4149; at 125° C.: 1.3856. At t C. it was in general: $d_{4^\circ} = 1.5241 - 0.001028\,t - 0.00000064\,t^2$.

The temperature-coefficient of μ has a mean value of **2.16** Erg pro degree.

XII.

1-4-Dichloro-2-Nitrobenzene: $C_6H_3\,Cl_{2(1,4)}\,(NO_2)_{(2)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
60.5°	1.281	1705.6	38.3	1.455	992.6
76	1.234	1645.2	37.1	1.438	969.0
95	1.172	1564.1	35.3	1.416	931.5
115	1.118	1491.1	33.6	1.393	896.4
136	1.053	1403.8	31.5	1.368	850.6
155	0.986	1314.4	29.5	1.344	806.0
177.5	0.938	1247.0	27.5	1.315	762.4
190.2	0.886	1181.2	26.4	1.298	738.3
204	0.840	1119.3	25.0	1.281	705.3

Molecular weight: **191.95.**

Radius of the Capillary tube: 0.04595 cm
Depth: 0.1 mm.

The compound boils at 267° C., and melts at 55° C. The specific weight at 75° C. was 1.4390; at 100° C.: 1.4102; at 125° C.: 1.3804. In general at t°C.: $d_{4°} = 1.5194 - 0.001012\,t - 0.0000008\,t^2$.

The temperature-coefficient of μ is fairly constant; its mean value is **2.01** Erg pro degree.

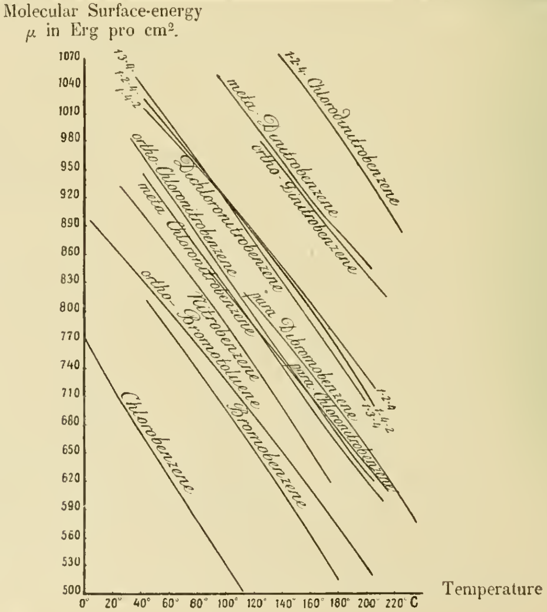

Fig. 1.

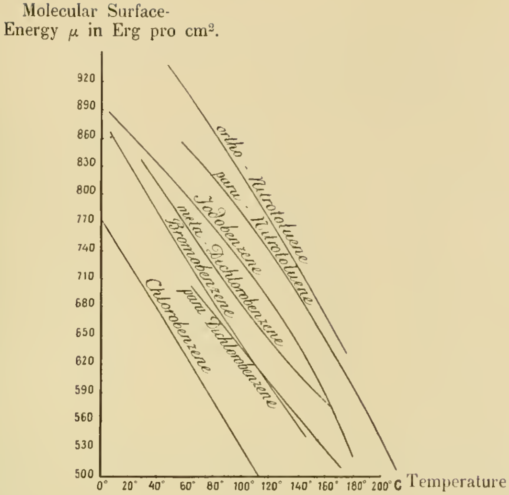

Fig. 2.

XIII.

ortho-Bromonitrobenzene: $C_6H_4Br_{(1)}(NO_2)_{(2)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
46°.3	1.405	1876.2	42.0	1.669	1027.5
61	1.353	1802.7	40.1	1.651	988.1
76.5	1.303	1734.3	38.4	1.632	953.6
95.2	1.220	1627.3	36.3	1.608	910.4
116	1.156	1540.8	34.2	1.582	867.1
136.2	1.076	1437.3	32.0	1.556	820.3
155.2	1.018	1358.0	30.1	1.532	779.7
176.3	0.950	1266.6	28.1	1.505	736.6
191	0.908	1210.0	26.9	1.484	711.7
204.5	0.867	1155.9	25.6	1.468	682.2

Molecular weight: **201.96.**

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The substance boils at 258°.5 C. under a pressure of 756 mm. it melts at 43° C.

The specific gravity at 75° C. was: 1.6333; at 100° C.: 1.6020; at 125° C.: 1.5703. In general at t° C.: $d_{4^\circ} = 1.6642 - 0.001228(t-50^\circ) - 0.0000032(t-50^\circ)^2$.

The temperature-coefficient of μ is fairly constant; its mean value is 2.19 Erg pro degree.

XIV.

meta-Bromonitrobenzene: $C_6H_4\,Br_{(1)}\,(NO_2)_{(3)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
61°.5	1.347	1798.8	39.9	1.650	983.6
74	1.296	1730.0	38.6	1.634	957.8
89	1.256	1672.9	37.1	1.616	927.4
110	1.164	1556.4	34.9	1.590	881.9
124	1.137	1512.8	33.4	1.572	850.4
139.8	1.085	1445.6	32.0	1.553	821.4
156	1.032	1376.4	30.6	1.532	792.6
175	0.961	1303.0	28.8	1.506	754.5
194.4	0.910	1212.6	26.9	1.480	713.0
209	0.888	1179.3	25.9	1.459	693.0

Moleculair weight: 201.96. Radius of the Capillary tube: 0.04595 cm. Depth: 0.1 mm.

Under a pressure of 755 mm. the substance boils at 251° C.; it melts at 56°.5 C. At 75° C. the density is: 1.6329; at 100° C.: 1.6024; at 125° C.: 1.5710. In general at $t°$ C.: $d_{4°} = 1.6625 - 0.001166\,(t-50°) - 0.00000072\,(t-50°)^2$.

Up to 195° C. the temperature-coefficient of μ is fairly constant; its mean value is: 2.04 Erg pro degree.

XV.

para-Bromonitrobenzene: $C_6H_4Br_{(1)}\,(NO_2)_{(4)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Molecular Surface-energy χ in Erg pro cm².
127°	1.116	1488.6	34.2
140.3	1.085	1445.9	33.1
155	1.025	1367.3	31.5
178	0.956	1274.5	29.3
194.5	0.908	1211.3	27.8
209.3	0.870	1159.9	26.6

Moleculair weight: 201.96. Radius of the Capillary tube: 0.04595 cm. Depth: 0.1 mm.

Under a pressure of 758 mm. the compound boils at 254° C.; it melts at 127° C. At 140° already it sublimes rather rapidly against the colder parts of the capillar tube.

XVI.

ortho-Iodonitrobenzene: $C_6H_4 J_{(1)}(NO_2)_{(2)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
61°	1.448	1930.5	43.1	1.938	1097.1
76.5	1.400	1866.5	41.7	1.916	1069.6
95.2	1.339	1784.5	39.8	1.890	1030.2
114.1	1.280	1706.2	38.0	1.863	993.1
136	1.209	1611.7	35.8	1.832	946.1
155.5	1.150	1533.1	34.0	1.805	907.5
176	1.085	1445.4	31.9	1.775	861.0
191	1.037	1382.5	30.6	1.754	832.5
205	1.004	1338.5	29.5	1.734	808.7

Molecular weight: **248.90**.

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The substance boils at 162°.5 C. under a pressure of 18 mm. it melts at 50° C. The specific gravity at 75° C. is: 1.9186; at 100° C.: 1.8831; at 125° C.: 1.8475. At t° C.: $d_{4°} = 1.9541 - 0.001422(t-50°)$.

The temperature-coefficient of μ has a mean value of **1.98** Erg per degree.

XVII.

meta-Iodonitrobenzene: $C_6H_4 J_{(1)} NO_{2(3)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
*25.7°	1.564	2086.2	47.3	1.981	1186.8
*41.1	1.509	2010.7	45.4	1.960	1147.2
*59.8	1.449	1929.4	43.4	1.935	1106.1
*83	1.362	1815.4	41.0	1.902	1056.9
95	1.324	1765.7	39.8	1.885	1032.2
110	1.273	1696.8	38.2	1.864	998.1
124.5	1.224	1632.2	36.8	1.842	969.2
140.2	1.181	1572.8	35.3	1.821	936.8
156.1	1.124	1498.7	33.7	1.797	902.3
170	1.084	1444.0	32.4	1.775	874.7
185.5	1.038	1381.6	30.9	1.752	841.5
198	0.999	1330.8	29.8	1.732	817.7
215	0.957	1276.3	28.6	1.688	798.4

Molecular weight: **248.96**.

Radius of the Capillary tube: 0.04644 cm.; with the observations indicated by *, it was 0.04660 cm.
Depth: 0.1 mm.

Under a pressure of 14 mm. the boilingpoint was 153° C.; the substance melts at 36° C. It can remain in an undercooled state during a very long time, and crystallises extremely slowly.

At 50° C. the density was: 1.9477; at 75° C.: 1.9131; at 100° C.: 1.8778. In general at t° C.: $d_{4°} = 1.9816 - 0.001342(t-25°) - 0.00000056(t-25°)^2$.

Up to 198° C. the temperature-coefficient of μ is fairly constant and has a mean value of: **2.16** Erg pro degree.

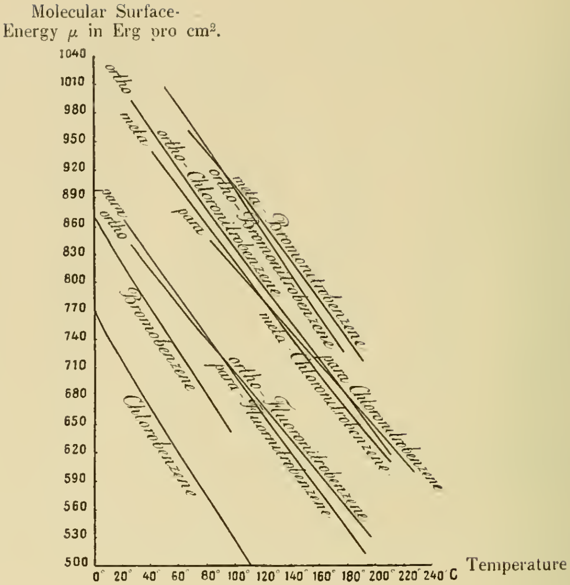

Fig. 3.

XVIII.

para-Nitrotoluene: $CH_3 \cdot {}_{(1)}C_6H_4 \cdot (NO_2)_{(4)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
60°.2	1.166	1554.5	35.5	1.112	879.4
83.5	1.101	1467.8	33.5	1.098	836.9
95	1.069	1424.9	32.5	1.086	817.9
115	1.007	1343.3	30.6	1.066	779.7
130.1	0.956	1274.6	29.0	1.054	744.5
144.5	0.908	1210.3	27.5	1.040	712.3
166	0.827	1102.5	25.0	1.017	657.0
180.2	0.782	1042.9	23.6	0.995	629.6
194.5	0.738	982.8	22.1	0.973	598.4
214.6	0.659	876.9	19.9	0.954	546.0

Molecular weight: **137.1.**

Radius of the Capillary tube: 0.04660 cm.
Depth: 0.1 mm.

The compound boils at 236° C. under a pressure of 755 mm.; the melting-point was 57°.5 C.

The density at 75° C. was: 1.1038; at 100° C.: 1.0817; at 125° C.: 1.0576. At t° C.: $d_{4^\circ} = 1.1239 - 0.000764\,(t-50^\circ) - 0.0000016\,(t-50^\circ)^2$.

The temperature-coefficient of μ is originally (up to 95°) about **1.77** Erg; afterwards it becomes fairly constant and equal to **2.30** Erg pro degree.

XIX.

ortho-Nitrophenol: $C_6H_4(OH)_{(1)}(NO_2)_{(2)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
52°	1.289	1718.5	38.0	1.281	864.7
70	1.246	1660.0	36.6	1.264	840.3
90.2	1.185	1580.5	34.8	1.243	807.9
108	1.134	1512.4	33.1	1.224	776.4
124.3	1.029	1374.4	31.2	1.206	739.1
140.1	1.014	1352.3	29.5	1.195	703.1
156	0.955	1272.1	27.5	1.179	661.4
170	0.888	1184.4	25.6	1.153	624.9
185.7	0.805	1073.2	23.0	1.135	567.3
204	0.730	973.2	20.7	1.113	517.3

Molecular weight: 139.05.

Radius of the Capillary tube: 0.04644 cm.
Depth: 0.1 mm.

The substance melts at 45° C. Under a pressure of 760 mm. it boils at 214°.5 C. Above 200° C. a brown colouring is produced by gradual decomposition.

The density at 75° C. was: 1.2583; at 100° C.: 1.2323; at 125° C.: 1.2052. At t° C.: $d_{4^\circ} = 1.2832 - 0.000974\,(t-50^\circ) - 0.00000088\,(t-50^\circ)^2$.

The temperature-coefficient of μ increases evidently with rise of temperature: between 52° and 70° C.: **1.35** Erg; between 70° and 90°: **1.60**; between 90° and 108° C.: **1.77**; between 108° and 140° C.: **1.84**; between 140° and 170° C.: **2.61**; and between 170° and 204° C.: about **3.20** Erg pro degree. Probably a gradual decomposition of the substance occurs here, causing this increase of $\frac{\partial\mu}{\partial t}$ at higher temperatures.

XX.

meta-Nitrophenol: $C_6H_4(OH)_{(1)}(NO_2)_{(3)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
110°	1.354	1805.1	40.0	1.273	914.0
125	1.338	1783.8	39.5	1.259	909.2
140.1	1.316	1754.5	38.8	1.249	897.9
155.2	1.272	1701.5	37.9	1.237	882.8
170	1.247	1662.4	36.7	1.222	861.8
185.6	1.196	1594.4	35.1	1.207	831.0
201	1.146	1523.2	33.1	1.191	790.7
218	1.051	1401.2	30.6	1.174	738.0

Molecular weight: 139.05.

Radius of the Capillary tube: 0.04644 cm.
Depth: 0.1 mm.

The carefully purified substance melts at 96° C.

The density at 100° C. was: 1.2797; at 125° C.: 1.2588; at 150° C.: 1.2359. At t° C.: $d_{4^\circ} = 1.2797 - 0.000716\,(t-100^\circ) - 0.0000016\,(t-100^\circ)^2$.

The temperature-coefficient of μ increases rapidly with rise of temperature: between 110° and 140° C. it is: about **0.50** Erg; between 140° and 155° C.: **1.00**; between 155° and 170° C.: **1.41**; between 170° and 186° C.: **1.97**; between 186° and 201° C.: **2.61**°; and between 201° and 218° C.: **3.1** Erg pro degree. It is rather probable, that this fact is connected with a gradual decomposition of the substance.

XXI.

para-Nitrophenol: $C_6H_4(OH)_{(1)}(NO_2)_{(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0 C.	in Dynes			
117°	1.497	1996.0	43.3	1.273	989.4
130.5	1.452	1936.9	42.0	1.262	965.3
145.5	1.408	1877.1	40.6	1.249	939.6
162	1.353	1815.3	39.1	1.234	912.2
176.5	1.311	1747.8	37.7	1.222	885.3
196.5	1.241	1654.4	35.6	1.205	843.8

Molecular weight: **139.05.** Radius of the Capillary tube: 0.04529 cm.
Depth: 0.1 mm.

The compound melts at 113° C. It sublimes rapidly and the measurements are thus made much more difficult by the gradual reduction of the cross-section of the capillary tube by the layers of crystals deposed there within. The specific gravity at 120° C was: 1.2703; at 140° C.: 1.2532; at 160° C.: 1.2361. At t° C.: $d_{4^\circ} = 1.2874 - 0.000855(t - 100^\circ)$.

The temperature-coefficient of μ is somewhat oscillating round a mean value of **1.81** Erg pro degree.

XXII.

para-Nitroanisol: $CH_3O_{(1)} . C_6H_4 . (NO_2)_{(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm mercury of 0° C.	in Dynes			
60°.5	1.342	1789.2	40.9	1.216	1027.3
83	1.280	1706.2	39.1	1.194	994.1
95	1.243	1659.4	38.0	1.183	972.1
115.2	1.187	1582.5	36.1	1.165	932.9
130.6	1.148	1528.2	34.6	1.149	902.5
144.5	1.096	1459.5	33.1	1.137	869.4
167.2	1.014	1351.9	30.7	1.115	817.0
180.1	0.968	1291.8	29.3	1.101	786.3
194.5	0.909	1214.1	27.6	1.086	747.5
220	0.814	1085.9	24.5	1.059	674.7

Molecular weight: **153.06.** Radius of the Capillary tube: 0.04660 cm.
Depth: 0.1 mm.

Under atmospheric pressure the boilingpoint is 259° C. The substance melts at 55° C.

The density was at 75° C.: 1.2012; at 100° C.: 1.1775; at 125° C.: 1.1535; at t° C.: $d_{4^\circ} = 1.2246 - 0.00093(t - 50^\circ) \quad 0.00000024(t - 05^\circ)^2$.

The temperature-coefficient of μ increases gradually with rising temperature: it is between 60° and 83° **1.49** Erg; between 83° and 95° C.: **1.93**; between 95° C. and 131° C.: **1.97**; between 131° and 180° C.: **2.35**; between 180° and 195° C.: **2.69**; and between 195° and 220° C.: **2.80** Erg.

XXIII.

ortho-Cresol: $CH_{3(1)} \cdot C_6H_4\,(OH)_{(2)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
40°.3	1.142	1522.5	34.8	1.033	772.6
54.5	1.107	1475.8	33.7	1.019	755.0
75.6	1.047	1395.9	32.0	1.002	725.0
95	0.993	1323.3	30.3	0.987	693.5
116.2	0.918	1224.8	28.0	0.971	647.8
135	0.864	1152.0	26.3	0.956	614.8
151.5	0.814	1085.5	24.7	0.946	581.5
176	0.711	947.9	21.5	0.930	511.9

Molecular weight: **108.06**.

Radius of the Capillary tube: 0.04670 cm.
Depth: 0.1 mm.

Under a pressure of 755 mm. the ortho-cresol boils at 190°.2 C.; it melts at 30° C. The specific weight at 25° C. is: 1.0458; at 50° C.: 1.0236; at 75° C.: 1.0027. At $t°$ it is: $d_{4°} = 1.0693 - 0.000966\,t + 0.00000104\,t^2$.

XXIV.

para-Cresol: $CH_{3(1)} \cdot C_6H_4\,OH_{(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
25°.6	1.135	1514.9	34.5	1.030	767.4
41	1.100	1465.4	33.2	1.018	744.3
60.2	1.042	1389.2	31.6	1.004	715.0
83	0.981	1309.0	29.7	0.984	685.3
95	0.946	1261.8	28.7	0.975	658.2
114.3	0.898	1195.5	27.0	0.961	629.0
130.5	0.849	1132.4	25.7	0.950	603.3
144.5	0.809	1079.1	24.6	0.942	580.8
166	0.746	994.2	22.6	0.927	539.3
180.9	0.701	926.6	21.0	0.918	504.4
194.5	0.639	851.9	19.2	0.910	463.9

Molecular weight: **108.06**.

Radius of the Capillary tube: 0.04660 cm.
Depth: 0.1 mm.

The substance boils at 200° C. under a pressure of one atmosphere. It melts at 37° C. The specific weight at 25° C. was: 1.0309; at 50° C.: 1.0102; at 75° C.: 0.9905; at $t°$ C.: $d_{4°} = 1.0526 - 0.000888\,t + 0.0000008\,t^2$.

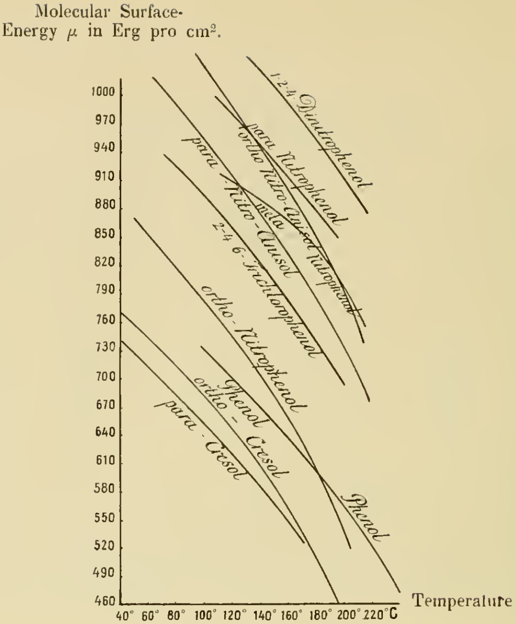

Fig. 4.

XXV.

ortho-Chloroaniline: $C_6H_4Cl_{(1)}(NH_2)_{(2)}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
* −19°	1.444	1926.0	45.7	1.259	993.0
* 0	1.379	1839.2	43.6	1.239	957.6
29.7	1.300	1733.3	40.5	1.208	904.6
47.8	1.240	1653.7	38.6	1.190	870.8
64.8	1.180	1574.2	36.7	1.174	835.5
80.9	1.130	1507.3	35.1	1.160	805.5
104.5	1.055	1406.8	32.7	1.140	759.1
125.1	0.977	1302.1	30.2	1.124	707.8
151.8	0.934	1245.2	28.8	1.103	683.5
177.5	0.883	1176.4	27.2	1.085	652.6
196.5	0.848	1130.4	26.1	1.073	630.9

Molecular weight: 127.52. Radius of the Capillary tube: 0.04777 cm.; with the observations, indicated by *, it was: 0.04839 cm. Depth 0.1 mm.

The liquid boils under a pressure of 760 mm. at 210°.5 C. It can be strongly undercooled, but after solidification it melts again at 0° C. At the boiling-point χ has a value of: 25.3 Erg pro cm².

At 28°.5 C. the density is: 1.2178; at 50° C.: 1.1890; at 75° C.: 1.1660. At t° C.: $d_{4^\circ} = 1.2388 - 0.001047\,t + 0.000001\,t^2$.

The temperature-coefficient of μ is below 125° C. fairly constant and has a mean value of 1.97 Erg.: Afterwards it decreases to about 1.1 Erg pro degree.

XXVI.

para-Chloroaniline: $C_6H_4 . (NH_2)_{(1)} . Cl_{(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
74.6°	1.322	1762.5	37.8	1.166	864.5
90.6	1.262	1682.5	36.1	1.151	832.8
104.1	1.221	1627.9	34.9	1.139	810.7
121	1.166	1554.5	33.3	1.124	780.4
130.4	1.144	1525.2	32.6	1.116	767.7
151	1.073	1431.1	30.6	1.097	728.8
170	1.015	1353.2	28.9	1.080	695.6
185	0.981	1307.7	27.9	1.067	676.9

Molecular weight: **127.52**.

Radius of the Capillary tube: 0.04374 cm.
Depth: 0.1 mm.

The compound was often recrystallised from mixtures of chloroform and ether. The beautiful colourless crystals melt at 70° C.; the substance boils at 232° C. The specific gravity at 70° C. is 1.1704; at 100° C.: 1.1432. At 170° the liquid becomes coloured deeply violet; the measurements therefore were no longer continued. At the boilingpoint χ must have a value not very far deviating from 25,0 Erg. The density at t° can be calculated from: $d_{4^\circ} = 1.2337 - 0.000903\, t$.

The temperature-coefficient of μ decreases a little with increasing temperature: between 74° and 91° C. it is about **1.98** Erg; between 170° and 185° C.: **1.24** Erg, oscillating thus round a mean value of about: **1.64** Erg pro degree.

XXVII.

meta-Nitro-Aniline: $C_6H_4 (NH_2)_{(1)} NO_{2(3)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
124.2°	1.410	1879.8	42.7	1.206	1006.7
140.5	1.357	1809.7	41.2	1.192	979.0
157	1.266	1684.5	39.7	1.177	951.4
170	1.274	1698.4	38.5	1.166	928.4
186.2	1.221	1631.6	37.0	1.152	899.4
201.3	1.184	1577.4	35.6	1.139	872.0

Molecular weight: **138.07**.

Radius of the Capillary tube: 0.04644 cm.
Depth: 0.1 mm.

The beautifully yellow coloured and well crystallised substance melts at 112° C.; while the liquid is heated above 200° C., it is gradually tinged brownish by progressive decomposition, and therefore the measurements were no further continued. Under the pressure of one atmosphere, the liquid boils at 286° C. according to the data given in literature; however it must be decomposed partially already at that temperature.
At 120° C. the density was: 1.2095; at 140° C.: 1.1921; at 160° C.: 1.1747. At t° C. in general: $d_{4^\circ} = 1.2269 \quad 0.00087 (t - 100^\circ)$.

The temperature-coefficient of μ is fairly constant; its mean value is: **1.74** Erg pro degree.

XXVIII.

para-Nitroaniline: $C_6H_4(NH_2)_{(1)}(NO_2)_{(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes	
151°	1.601	2135.3	46.7
171.5	1.535	2048.4	44.8
184.5	1.496	1993.6	43.6

Molecular weight: **138.07.** Radius of the Capillary tube: 0.04374 cm.
Depth: 0.1 m m.

The beautiful, orange-yellow crystals melt at 147° C. The substance is so volatile above 180°, that reliable measurements were no longer possible.

XXIX.

3-Nitro-ortho-Toluïdine: $CH_{3(1)} \cdot C_6H_3 \cdot (NH_2)_{(2)} \cdot (NO_2)_{(3)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
105°	1.370	1826.5	39.2	1.186	996.8
121.5	1.323	1764.9	37.9	1.171	972.0
130	1.295	1726.5	37.0	1.164	952.7
151	1.231	1641.5	35.2	1.144	916.8
170	1.166	1549.7	33.4	1.128	878.2
184.8	1.124	1499.7	32.1	1.115	850.6
201.2	1.077	1435.8	30.7	1.101	820.3

Molecular weight: **152.08.** Radius of the Capillary tube: 0.04374 cm.
Depth: 0.1 mm.

The compound melts at 96° C. At 100° C. the density was: 1.1900; at 120° C.: 1.1722; 140° C.: 1.1546. At $t°$ C.: $d_{4°} = 1.1900 - 0.0008815\,(t - 100°)$.

Originally the temperature-coefficient of μ is somewhat increasing: from 1.27 Erg at 130° C. to **1.71** Erg at 151° C. Then it remains fairly constant, with a mean value of about: **1.9** Erg per degree.

XXX.

5-Nitro-ortho-Toluïdine: $CH_{3(1)} . C_6H_3 (NH_2)_{(2)} . (NO_2)_{(5)}$.

Temperature in ° C.	Maximum Pressure *H*		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0 C.	in Dynes			
142°	1.477	1969.1	43.0	1.157	1115.1
151	1.444	1925.1	41.1	1.150	1070.2
170.5	1.333	1777.1	37.9	1.135	995.5
184.5	1.279	1705.5	36.3	1.122	960.9

Molecular weight: **152.08.**

Radius of the Capillary tube: 0.04374 cm.
Depth: 0.1 mm.

The beautiful yellow crystals melt at 128° C. Above 180° C. the volatility of the compound was too great, to make any reliable measurements possible.

XXXI.

3-Nitro-para-Toluïdine: $CH_{3(1)} . C_6H_3 . (NH_2)_{(4)} . (NO_2)_{(3)}$.

Temperature in ° C.	Maximum Pressure *H*		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
121°	1.274	1698.5	36.4	1.164	969.1
130.5	1.248	1664.2	35.7	1.156	943.1
151	1.134	1511.8	33.1	1.137	865.7
170.5	1.094	1458.6	31.2	1.120	807.0
185	1.045	1393.2	29.8	1.107	767.3

Molecular weight: **152.08.**

Radius of the Capillary tube: 0.04374 cm.
Depth: 0.1 mm.

The substance melts at 117° C. Above 180° C. the compound is so volatile, that reliable measurements were hardly any more possible. The specific gravity at 120° C. was: 1.1645; at 140° C.: 1.1468; at 160° C.: 1.1292. At t C.: $d_{4^\circ} = 1\ 1821 - 0\ 000882\,(t - 100\ )$.

The temperature-coefficient of μ is abnormally great; its mean value is about: **3.08** Erg per degree.

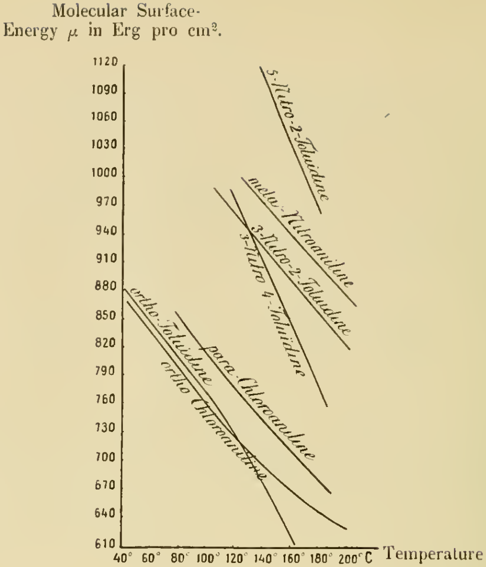

Fig. 5.

XXXII.

Sylvestrene: $C_{10}H_{16}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
—70°	1.139	1518.5	35.7	0.923	979.2
—20	0.964	1285.5	30.1	0.891	860.2
0	0.908	1210.5	28.3	0.878	816.8
25.8	0.833	1110.2	25.9	0.859	758.5
41	0.792	1055.9	24.6	0.847	727.2
55.5	0.736	981.2	23.2	0.841	689.1
80.4	0.682	909.8	21.2	0.827	636.7
92	0.654	872.3	20.3	0.820	613.2
116.2	0.582	776.3	18.0	0.807	549.6
*136	0.546	728.1	16.4	0.797	504.8
*149.5	0.507	676.7	14.6	0.790	452.1

Molecular weight: 136.13.

Radius of the Capillary tube: 0.04792 cm.; with the observations indicated by *, the radius was: 0.04670 cm.
Depth: 0.1 mm.

Under a pressure of 21 mm. it boils at 63°.5 C.; under atmospheric pressure at 177° C. The specific gravity at 25° C. was: 0.8599; at 50° C.: 0.8409; at 75° C.: 0.8209; at $t°$ in general: $d_{4°} = 0.8779 - 0.0007\,t - 0.0000008\,t^2$.

The temperature-coefficient of μ is between —70° and 136° C. fairly constant; its mean value is: 2.28 Erg pro degree. Above 136° it increases rapidly and becomes 3.9 Erg.

XXXIII.

Terebene: $C_{10}H_{16}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
−74°	1.131	1508.6	35.8	0.956	976.2
* −22	0.968	1290.4	30.7	0.912	863.9
* 0	0.906	1208.2	28.7	0.893	819.0
29.9	0.825	1099.3	25.9	0.868	753.2
46.8	0.775	1033.2	24,3	0.853	714.9
58.3	0.744	991.9	23.4	0.844	693.4
86.3	0.673	896.9	21.1	0.820	637.4
102.7	0.626	834.9	19.6	0.806	598.9
118	0.573	764.6	17.9	0.793	552.9
127.4	0.558	743.9	17.4	0.786	540.6
153	0.499	665.4	15.5	0.764	494.0
170	0.449	599.3	13.9	0.749	446.0

Molecular weight: **136.13**. Radius of the Capillary tube: 0.04839 cm.; in the measurements indicated by *, the radius was 0.04867 cm.; Depth: 0.1 mm.

Under a pressure of 761 mm. the liquid boils at 170° C.; at the boilingpoint the value of χ is about 13.7 Erg pro cm². Even at —79° C. the compound is not crystallised, but the liquid is turbid then. Probably it is a mixture of isomerides.

The specific gravity at 25° C. is: 0.8721; at 50° C.: 0.8509; at 75° C.: 0.8298. At t° in general: $d_{4^\circ} = 0.8932 - 0.000846\,t$. The temperaturecoefficient of μ is in mean: **2.16** Erg pro degree, and fairly constant.

§ **3.** If we now review the results here obtained, it will appear in first instance that such position-isomeric substances at the same temperatures do *not* possess the same surface-energy in general, as was formerly occasionally supposed. One cannot deny that the μ-t-curves, and especially those of the aromatic hydrocarbons, if substituted by halogen-atoms or nitro-groups, often closely approach each other: so e.g. with *o*- and *m-Dinitrobenzene*, with *o*-, *m*- and *p-Chloronitrobenzene*; with *o*- and *m-Bromonitrobenzene*; with *o*- and *p-Fluoronitrobenzene*; and with 1-2-4-, 1-4-2-, and 1-3-4-*Dichloronitrobenzenes*. In the case of the nitrated *phenols* these curves deviate much more; but we must conclude this to be caused by differences of the internal structure of the mentioned compounds, which are undoubtedly connected with the presence of the *H*-atom in the *OH*-group. For while the mutual differences are rather great in the case of the substituted phenols themselves, these differences will be strongly diminished, if e.g. in the derivatives of polyvalent phenols *one* of

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the *OH*-groups is substituted by an oxalkyl-group, as e.g. with *monomethylresorcinol* and *guajacol.* These differences however are completely reduced to the size found in the case of the above mentioned substituted hydrocarbons, if *all H*-atoms of the *OH*-groups present are esterified: between *ortho-*, and *para-Nitroanisol* e.g. the deviation of the two curves is already much weaker, as in the case of *ortho-*, and *para-Nitrophenol* itself, while it is yet more considerably diminished in the case of *Veratrol*, *Dimethylhydroquinone*, where the μ-t-curves of the two last named substances even coincide almost over their full length. If we now observe so much stronger differences between e.g. *ortho-*, and *para-Nitrophenol*, than between their corresponding *anisols*, this could probably be considered as an indication, th t the internal equilibrium in the liquid between the molecules with the constitution of the pseudo-acid, and between those with the true nitrophenol-formula, may be situated in the case of the *ortho*-compound in such a way, that it much more approaches to the side of the pseudo-acid, than in the case of the *para*-compound: a circumstance probably caused by the more immediate vicinity of *OH*-groups and NO_2-radical in the case of the *ortho-nitrophenol.* In the case of the corresponding *anisols*, they might then be supposed to possess a quite analogous structure, no freely movable *H*-atom being any more present.

Even in the cases, where the μ-t-curves of such isomerides, approach each other relatively closely, it can be often observed, that the values of the temperature-coefficient $\frac{\partial\mu}{\partial t}$ are evidently different, which thus determines the steeper or flatter shape of the curves.

Besides in the case of the *phenols*, also somewhat greater differences may be stated between isomeric *aromatic bases*, and between the *cresols.* The abnormal shape of the curves with some of the considered bases, undoubtedly must be partially explained by the alterations and decompositions, which seem more easily to occur in the case of these compounds at higher temperatures, than with other substances. Finally we can draw attention to the fact, that within the series of the *halogennitrobenzenes*, just as within that of the *halogenated benzenes* themselves, the values of μ at the same temperatures appear to be the greater, the higher the atomic weight of the halogen-atom is. This fact is of course just opposite to that observed in the case of the molten halogenides of the alcali-metals.

A general rule considering the relative magnitude of μ in the case of *ortho-*, *meta-*, and *para-*monosubstitutionproducts, could not be formulated.

University-Laboratory for Inorganic and Physical Chemistry.

Groningen, August 1915.

Chemistry. — "*Investigations on the Temperature-Coëfficients of the Free Molecular Surface-Energy of Liquids from* —80° *C. to* 1650° *C.*" **XIV**. *Measurements of a Series of Aromatic and Heterocyclic Substances.* By Prof. Dr. F. M. Jaeger and Dr. Jul. Kahn.

(Communicated in the meeting of September 25, 1915).

§ **1.** In the present paper the results are published, obtained with the measurements of the surface-energy of the following 28 compounds; these measurements may be considered as a supplement of the formerly published researches with aromatic and cyclic derivatives: 1-2-4-*Chlorodinitrobenzene*; *para-Dibromobenzene*; *Iodobenzene*; *ortho-Bromotoluene*; *Phenol*; 1-2-4-*Dinitrophenol*; 2-4-6-*Trichlorophenol*; *para-Nitrophenetol*; 2-*Nitro-resorcine*; *Veratrol*; 4-5-*Dinitro-veratrol*; *Ethyl-Cinnamylate*; *Anisaldehyde*; *Benzophenone*; 3-4-3′-4′-*Tetra-chloro-benzophenone*; 2-4-2′-4′-*Tetrachlorobenzophenonebichloride*; *Monomethylaniline*; *Nitrosomethylaniline*; *Diïsobutylaniline*; *Diphenylamine*; *Dibenzylamine*; *Azoxybenzene*; *α-Dihydrocampholenic Acid*; *Ethyl-α-Dihydro-campholenate*; *α-Furfurol*; *Thiophene*; and *Piperidine*.

The specific gravities were determined in the way previously described, either by means of a dilatometer, or by the aid of the pycnometer, or finally in some cases by a hydrostatical method. Of some substances only such small quantities were available, that it appeared impossible to determine these specific weights with sufficient exactitude; or there were other causes, which prohibited these determinations in some cases. It is more especially the very rapid evaporation of many of the higher melting substances, which causes the formation of a crystalline layer round the fine platinum suspension-wire of the immersion-conus, and which of course must appear a serious obstacle for the exact determinations of the density required.

§ 2.

I.

1-2-4-Chlorodinitrobenzene: $C_6H_3Cl_{(1)}(NO_2)_{2(2,4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm²
	in mm. mercury of 0° C.	in Dynes			
60°.4	1.517	2021.3	45.5	1.515	1189.5
76.2	1.428	1954.8	43.9	1.497	1156.8
95	1.416	1884.4	42.2	1.477	1122.1
114	1.343	1791.0	40.4	1.455	1085.0
136	1.278	1703.8	38.3	1.432	1039.6
155.1	1.219	1623.9	36.4	1.412	997.3
175.5	1.158	1544.0	34.5	1.391	954.7
190	1.101	1467.8	32.9	1.378	916.2
204.2	1.057	1408.0	31.5	1.365	882.8

Molecular weight: 202.50.

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The substance melts at 51° C.

The specific gravity at 75° C. was: 1.4982; at 100° C.: 1.4706; at 125 C.: 1.4439. At t C.: $d_{4^\circ} = 1.5267 - 0.001158\,(t - 50\ ) + 0.0000007\,(t - 50^\circ)^2$.

The temperature coefficient of μ is fairly constant; its mean value is 2.23 Erg. pro degree.

II.

para-Dibromobenzene: 1-4-$C_6H_4Br_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
94°.8	1.069	1424.9	32.0	1.840	813.4
115	1.008	1345.6	30.3	1.807	779.5
130.1	0.967	1289.2	28.8	1.782	747.8
144.5	0.923	1229.4	27.4	1.756	718.5
168.5	0.850	1133.0	25.2	1.715	671.3
180	0.810	1078.8	23.8	1.694	639.2
194.5	0.757	1009.2	22.3	1.668	605.1
209	0.701	926.6	20.4	1.643	559.2

Molecular weight: 235.79.

Radius of the Capillary tube: 0.04660 cm.
Depth: 0.1 mm.

Under atmospheric pressure the boiling point is 216° C. The substance melts at 89° C. It sublimes already notoriously at rather low temperature (130°).

The density at 100° C. was: 1.8322; at 120° C.: 1.8000; at 140° C.: 1.7683. At t° C. it is calculated from: $d_{4^\circ} = 1.8649 - 0.0016475\,(t - 80^\circ) - 0.000000625\,(t - 80^\circ)^2$.

The somewhat oscillating temperature-coefficient of μ has below 195°C. a mean value of about: 2.15 Erg pro degree.

III

Iodobenzene : C_6H_5J.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
— 21°	1.375	1833.1	41.0	1.892	928.7
0	1.314	1751.6	39.1	1.861	895.5
25.4	1.233	1644.5	37.1	1.823	861.4
40.4	1.188	1584.5	35.7	1.801	835.7
54.1	1.144	1524.6	34.4	1.781	811.3
76.1	1.076	1434.7	32.3	1.747	771.6
95.1	1.015	1353.3	30.4	1.716	734.9
117.2	0.944	1260.5	28.2	1.683	690.6
135.1	0.857	1143.4	25.5	1.659	630.5
150.5	0.803	1070.6	23.9	1.637	596.2
176	0.704	938.6	20.7	1.598	524.7

Molecular weight: **203.96.**

Radius of the Capillary tube: 0.04670cm.
Depth: 0.1 mm.

Under a pressure of 13 mm. the liquid boils constantly at 79° C. under 760 mm. at 188°.5 C.; on heating it becomes slightly coloured. In solid carbondioxide and alcohol it solidifies into a hard crystalline mass, which melts at —26° C.; according to Timmermans at —31°.3 C. The specific gravity at 25° C. was: 1.8230; at 50° C.: 1.7852; at 100° C.: 1.7090. At $t°$ it can be calculated from: $d_{4^\circ} = 1.8606 - 0.0015\,t - 0.00000016\,t^2$.

The temperature-coefficient of μ increases regularly with rising temperature: between —21° C. and 76° C. its mean value is: **1.65**; between 76° C. and 150° C: **2.46**; and above 150° C.: **2.80** Erg. The μ-t-curve therefore is concave towards the t-axis.

IV

ortho-Bromotoluene : $CH_{3(1)} . C_6H_4Br_{(2)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
— 20°	1.236	1647.8	38.4	1.471	914.6
0	1.177	1569.3	36.5	1.447	878.9
25.8	1.102	1469.2	34.1	1.416	833.1
40	1.052	1402.3	32.5	1.399	800.4
55.5	1.002	1335.5	31.1	1.386	770.7
80	0.923	1231.2	28.6	1.352	720.6
92	0.886	1181.2	27.4	1.338	695.2
115.5	0.814	1085.1	25.1	1.310	645.8
*133.5	0.784	1045.0	23.6	1.288	614.1
*149.5	0.725	966.6	21.8	1.269	573.0
*175	0.634	845.2	18.9	1.239	504.7

Molecular weight: **170.98**

Radius of the Capillary tube: 0.04792 cm.; with the determinations indicated by *, it was: 0.04670 cm.
Depth: 0.1 mm.

Under a pressure of 755 mm. the liquid boils at 179° C. At —20° it becomes turbid, and solidifies at a somewhat lower temperature into a white crystalline mass, whose meltingpoint is: —27° C. The specific weight at 25° C. is: 1.4173; at 50° C.: 1.3876; at 75° C.: 1.3578; at $t°$: in general it is: $d_{4^\circ} = 1.4470 - 0.00119\,t$. The temperature-coefficient of μ oscillates round a mean value of **2.09** Erg pro degree.

V.

Phenol: C_6H_5OH.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
41°.2	1.207	1609.4	37.0	1.063	734.6
60.1	1.156	1538.9	35.2	1.043	707.8
82.1	1.090	1453.2	33.3	1.021	679.2
95.1	1.052	1400.8	32.0	1.019	653.5
115	0.980	1306.5	29.9	0.990	622.5
130.5	0.936	1245.6	28.3	0.979	593.6
144.5	0.868	1160.0	26.7	0.964	565.9
166	0.793	1057.2	24.1	0.951	515.4
180.5	0.719	958.6	21.8	0.940	469.8

Molecular weight: 94.05.

Radius of the Capillary tube: 0.04660 cm.
Depth: 0.1 mm.

The compound boils at 180°.5 C. under a pressure of 758 mm. The melting-point is 41° C. The specific gravity was determined by means of the hydrostatic method; at 50° C. it was: 1.0529; at 75° C.: 1.0272; at 100° C.: 1.0033. At t° C.: $d_{4^\circ} = 1.1097 - 0.001208\,t + 0.00000144\,t^2$.

The temperature-coefficient of μ is between 41° and 82° C.: **1.36**; between 82° and 166° C.: **1.94** Erg.; above 166° C it increases very rapidly.

VI.

1-2-4-Dinitrophenol: $C_6H_3(OH)_{(1)}(NO_2)_2$

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
125°.4	1.361	1813.3	41.1	1.426	1049.6
140	1.318	1757.1	39.9	1.411	1026.2
155.1	1.279	1705.5	38.7	1.396	1002.4
170	1.235	1645.9	37.3	1.380	973.7
185.8	1.177	1570.3	35.6	1.363	937.0
200.1	1.142	1511.6	34.2	1.348	906.8
215	1.091	1455.7	32.9	1.333	878.9

Molecular weight: **184,07**.

Radius of the Capillary tube: 0.04644 cm.
Depth: 0.1 mm.

The beautifully crystallised compound melts at 114° C. The specific gravity at 120° C. was: 1.4309; at 140° C.: 1.4106; at 160° C.: 1.3898. At t° C.: $d_{4^\circ} = 1.4507 - 0.000962\,(t - 100^\circ) - 0.00000062\,(t - 100^\circ)^2$.

The temperature-coefficient of μ has a mean value of about: **1.90** Erg per degree.

VII.

2-4-6-Trichlorophenol: $C_6H_2(OH).Cl_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
70°.2	1.202	1600.8	36.3	1.495	941.3
90	1.134	1522.4	34.7	1.466	911.6
109	1.095	1459.3	33.1	1.438	880.8
124.9	1.040	1387.7	31.6	1.414	850.4
140.2	0.998	1328.7	30.0	1.386	818.2
156	0.941	1256.2	28.6	1.360	789.9
170	0.897	1195.9	27.1	1.333	758.5
185.5	0.846	1127.9	25.5	1.308	722.8
196.5	0.803	1070.5	24.1	1.290	689.8

Molecular weight: **197.40**.

Radius of the Capillary tube: 0.04644 cm.
Depth: 0.1 mm.

Under a pressure of 760 mm. the substance boils at 246° C. It melts at 69°.5 C. and evaporates rapidly on heating above the meltingpoint. Above 196° the liquid gets darker by a gradual decomposition. At 75° C. the density was: 1.4901; at 100° C.: 1.4587; at 125° C.: 1.4294. At $t°$ C.: $d_{4°} = 1.5236 - 0.001382\,(t-50°) - 0.00000168\,(t-50°)^2$.

The temperature-coefficient of μ increases gradually with rise of temperature; between 70° and 109° C. it is about **1.57** Erg; between 109° and 185° C.: **2.07** Erg; and between 185° and 196°.5 C.: **3.02** Erg pro degree Celsius.

VIII.

para-Nitrophenetol: $C_6H_4(NO_2)_{(1)}.OC_2H_{5(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
70°.2	1.164	1549.0	35.3	1.171	963.9
90	1.096	1461.7	33.6	1.152	927.6
107.5	1.051	1401.7	32.2	1.111	910.6
124.5	1.004	1338.9	30.7	1.094	877.2
140	0.964	1284.1	29.3	1.079	844.9
157	0.914	1218.7	27.9	1.063	812.6
170	0.871	1162.9	26.7	1.051	784.0
185.6	0.840	1119.9	25.4	1.036	752.6
201	0.785	1048.8	24.1	1.020	721.5
220	0.747	994.2	22.6	1.002	684.6

Molecular weight: **167.08.**

Radius of the Capillary tube: 0.04644 cm.
Depth: 0.1 mm.

The beautifully crystallised compound melts at 60° C.; under atmospheric pressure it boils at 283° C. The specific gravity at 75° C. is: 1.1416; at 100° C.: 1.1176; at 125° C.: 1.0937. At $t°$ C.: $d_{4°} = 1.1656 - 0.00096\,(t-50°)$.

The temperature-coefficient of μ is fairly constant; its mean value is: **2.0** Erg pro degree.

IX.

2-Nitroresorcinol: $C_6H_3(OH)_2(NO_2)$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².
90°.7	1.276	1701.1	39.5
109.5	1.208	1610.6	37.4
125	1.150	1533.2	35.6
140	1.101	1466.6	34.0
156.2	1.037	1382.5	32.1
169.2	0.988	1317.8	30.6
185.5	0.940	1253.2	29.1

Molecular weight: **139.05.**

Radius of the Capillary tube:
0.04644 cm.
Depth: 0.1 mm.

The substance crystallises in bloodred crystals, and melts at 85° C. At higher temperatures it is very volatile. Above 180° C. the liquid becomes gradually darker by oxydation and decomposition; thus the determinations were no longer continued. (Added in the English translation.)

X

Veratrol: $C_6H_4(OCH_3)_2$ (1.2).

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
* 0°	1.345	1793.7	42.5	1.105	1062.4
29.9	1.209	1611.8	37.7	1.077	958.6
47.3	1.143	1524.0	35.6	1.059	915.4
64.5	1.083	1444.2	33.7	1.044	874.9
81.2	1.026	1367.9	31.9	1.029	836.2
104.5	0.945	1260.2	29.3	1.009	778.2
124.8	0.879	1172.3	27.2	0.989	732.1
151.5	0.795	1058.2	24.4	0.967	666.6
178	0.719	958.8	22.1	0.943	614.0
196	0.678	904.3	20.8	0.928	584.1

Molecular weight: **138.1**

Radius of the Capillary tube: 0.04777 cm.; with the measurements indicated by * it was: 0.04839 cm.
Depth: 0.1 mm.

Under a pressure of 759 mm. the boilingpoint is 206° C. In a refrigerant mixture it solidifies rapidly, and melts then again at +22° C. At the boiling point χ will have about the value: 19.9 Erg pro cm². The specific gravity at 25° C. was: 1.0812; at 50° C.: 1.0570; at 75° C.: 1.0325; at $t°$: $d_{4^\circ} = 1.1051 - 0.00095\,t - 0.00000024\,t^2$.

The temperature-coefficient of μ is between 0° and 30° C. very great: **3.47** Erg; between 30° and 150° it remains fairly constant, or only slowly decreasing from **2.42** to **2.36** Erg. Between 150° and 176° it decreases: **1.98** Erg, and between 176° and 196° C.: **1.66** Erg. The curve thus is slightly concave.

XI

4-5-Dinitro-Veratrol: $CH_3O.C_6H_2(NO_2)_2.OCH_3$.

Temperature in 0° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
130°.8	1.349	1798.3	41.0	1.326	1268.0
144.5	1.307	1742.5	39.7	1.312	1236.5
167.2	1.236	1648.0	37.5	1.287	1183.1
182	1.178	1570.8	35.7	1.270	1136.3
194.5	1.125	1499.3	34.0	1.251	1093.1
208	1.042	1389.2	31.5	1.241	1018.2

Molecular weight: **228.06**. Radius of the Capillary tube: 0.04660 cm.
Depth: 0.1 mm.

The compound was recrystallised from chloroform or ethylacetate; the long, yellow needles melt sharply at 130°.5 C. On heating above ca. 160° C., the liquid becomes gradually brownish. The specific gravity is at 140° C.: 1.3164; at 160° C.: 1.2948; and at 180° C.: 1.2726. At $t°$ C.: $d_{4°} = 1.3374 - 0.001035\,(t - 120°) - 0.00000075\,(t - 120°)^2$. The temperature-coefficient of μ increases rapidly with the temperature: between 130° and 167° C. it is: **2.32** Erg; between 167° and 182° C.: **3.17** Erg; between 182° and 194° C.: **3.45** Erg. Above 198° C. the increase grows rapidly, to about **5.5** Erg at 208° C., indicating a decomposition setting in.

XII.

Ethyl-Cinnamylate: $C_6H_5\,.\,CH:CH\,.\,COO\,(C_2H_5)$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
25°.7	1.164	1552.6	36.5	1.045	1113.6
40.5	1.111	1481.5	34.8	1.032	1070.7
55.8	1.064	1418.5	33.3	1.018	1033.8
80	0.994	1325.2	31.0	0.997	975.9
92	0.956	1274.5	29.8	0.987	944.4
116.5	0.883	1176.9	27.5	0.966	884.1
*136	0.854	1139.2	26.0	0.953	843.5
*149.5	0.819	1092.1	24.9	0.941	814.6
*176	0.732	976.4	22.2	0.922	736.3
*194.8	0.694	925.0	21.0	0.909	703.1

Molecular weight: **176.1**. Radius of the Capillary tube: 0.04792 cm.; in the measurements indicated by *, it was: 0.04670 cm.
Depth: 0.1 mm.

Under a pressure of 755 mm. the liquid boils at 269° C.; at 158° C. under a pressure of 21 mm. On cooling it solidifies soon and melts again at + 6°.5 C. The rapid decrease of the χ-t-curve above 194° C. indicates doubtless a beginning decomposition. The specific weight at 25° C. is: 1.0457; at 50° C.: 1.0234; at 75° C.: 1.0018. At $t°$ it is calculated from: $d_{4°} = 1.0687 - 0.000934\,t + 0.00000056\,t^2$.

The temperature-coefficient of μ oscillates in a somewhat irregular way round a rather considerable value of: **2.41** Erg pro degree.

XIII.

Anisaldehyde: $CH_3O_{(1)} . C_6H_4 . COH_{(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
0°	1.489	1984.7	44.9	1.142	1087.2
24.5	1.386	1847.8	41.8	1.120	1025.4
31.5	1.364	1818.9	40.9	1.114	1006.9
46.5	1.299	1741.1	39.5	1.101	980.1
61	1.268	1682.9	38.0	1.088	950.3
74.2	1.205	1609.3	36.5	1.077	919.0
90.3	1.159	1545.8	34.8	1.063	883.9
101	1.132	1506.8	33.7	1.054	860.8
124	1.052	1400.8	31.3	1.030	811.9
140.2	0.996	1327.8	29.8	1.022	777.0
154.2	0.946	1262.3	28.4	1.009	746.9
175	0.882	1177.6	26.5	0.993	704.3
194.1	0.822	1095.7	24.5	0.977	658.3
210	0.770	1027.2	22.9	0.963	621.2

Molecular weight: **136.07**.

Radius of the Capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The aldehyde boils under a pressure of 751 mm. at 246° C. At −12° it solidifies and melts again at +2°.5 C.; according to Walden, the meltingpoint is −2° C. The density at 25° C. is: 1.1199; at 50° C.: 1.0980; at 75° C.: 1.0764. In general at $t°$: $d_{4°} = 1.1421 - 0.000894\,t + 0.00000024\,t^2$.

The temperature-coefficient of μ oscillates round a mean value of **2.06** Erg pro degree.

XIV.

Benzophenone: $C_6H_5 . CO . C_6H_5$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
50°.3	1.397	1862.5	40.0	1.087	1215.5
65	1.341	1787.9	38.4	1.075	1175.5
75	1.317	1755.9	37.7	1.067	1160.0
91	1.255	1673.5	35.9	1.055	1112.8
104.1	1.214	1618.6	34.7	1.039	1086.7
121	1.165	1558.7	33.2	1.028	1047.1
130.5	1.138	1518.0	32.5	1.021	1029.7
151	1.076	1435.7	30.7	1.003	984.3
171.8	1.015	1349.9	28.9	0.985	937.8
184.3	0.977	1303.1	27.8	0.973	909.5
200	0.925	1234.5	26.3	0.960	868.1

Molecular weight: **182.08**.

Radius of the Capillary tube: 0.04374 cm.
Depth: 0.1 mm.

The compound was purified by repeated crystallisation from alcohol. It melts at 48°.5 C.; its metastable form at 26°5 C. Under atmospheric pressure the boilingpoint is 305° C. The specific gravity at 50° C. is: 1.0869; at 75° C.: 1.0669; at 100° C.: 1.0464. At $t°$ C.: $d_{4°} = 1.1064 - 0.00077(t - 25°) - 0.0000004\,(t - 25°)^2$.

The temperature-coefficient of μ has a mean value of **2.27** Erg per degree.

XV.

3-4-3′-4′-Tetrachlorobenzophenone:
$C_6H_3Cl_2 . CO . C_6H_3Cl_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes	
154°	1.134	1511.7	35.1
170	1.090	1453.1	33.7
186.5	1.037	1382.4	32.1
201.8	0.993	1323.6	30.7
220	0.948	1263.7	29.3

Molecular weight: **319.88.** Radius of the Capillary tube: 0.04644 cm.
Depth: 0.1 mm.

The colourless, beautifully crystallised substance melts at 142° C.

The quantity available did not allow the determination of the specific weight of the liquid.

XVI.

2-4-2′-4′-Tetrachlorobenzophenone-Dichloride: $C_6H_3Cl_2 . CCl_2 . C_6H_3Cl_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
156°	1.037	1382.5	31.2	1.442	1270.7
170	1.002	1358.7	30.6	1.429	1253.8
185.5	0.994	1325.2	29.9	1.415	1233.2
199.2	0.969	1291.9	29.1	1.401	1208.2
218	0.943	1253.2	27.9	1.390	1164.5

Molecular weight: **374.80.** Radius of the Capillary tube: 0.04644 cm.
Depth: 0.1 mm.

The compound, which crystallises in beautiful, colourless crystals, melts at 140° C. At 145° C. the specific weight was: 1.4523; at 165° C.: 1.4336; at 185° C.: 1.4146. At t° C.: $d_{4^\circ} = 1.4570 - 0.0009425\,(t - 140^\circ)$. The temperature-coefficient of μ increases rather rapidly with rise of temperature: between 156° and 170° C. it is: **1.21** Erg; between 170° and 185° C.: **1.33** Erg; between 185° and 199° C.: **1.82** Erg; and between 199° and 218° C.: **2.32** Erg per degree.

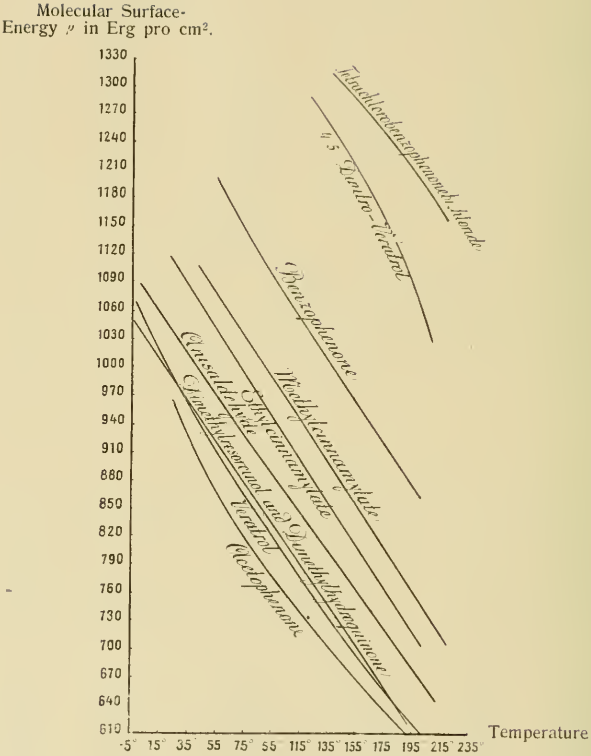
Molecular Surface-Energy γ in Erg pro cm².
1330
1300
1270
1240
1210
1180
1150
1120
1090
1060
1030
1000
970
940
910
880
850
820
790
760
730
700
670
640
610
-5° 15° 35° 55 75° 55 115° 135° 155° 175 195 215° 235°
Temperature
Tetrachlorobenzophenonchloride
4.5 Dinitro-Veratrol
Benzophenone
Methylcinnamylate
Ethylcinnamylate
Anisaldehyde
Dimethylresorcinol and Dimethylhydroquinone
Veratrol
Acetophenone

Fig. 1.

XVII.

Monomethylaniline: $C_6H_5 . NH(CH_3)$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
*—18°	1.332	1775.8	42.2	1.033	931.2
* 0	1.268	1690.5	40.1	1.015	895.3
29.8	1.174	1565.8	36.7	0.985	835.9
49.3	1.106	1474.5	34.6	0.965	799.0
65	1.058	1410.9	33.0	0.952	768.9
80.9	1.005	1339.8	31.3	0.936	737.6
104.5	0.934	1245.2	29.0	0.915	693.8
122	0.879	1172.3	27.3	0.899	660.9
152	0.791	1055.0	24.5	0.872	605.3
178.8	0.713	950.4	22.0	0.850	552.9
195	0.672	895.9	20.7	0.837	525.6

Molecular weight: **107.08**

Radius of the Capillary tube: 0.04777 cm.; with the observations indicated by *, it was: 0.04839 cm.
Depth: 0.1 mm.

The substance boils constantly at 195°.5 C. under a pressure of 759 mm. After strongly undercooling it solidifies and melts afterwards at −57° C. The specific weight at 25° C is: 0.9898; at 50° C.: 0.9656; at 75° C.: 0.9420; at $t°$ C.: $d_{4^\circ} = 1.0146 - 0.001004\, t + 0.00000048\, t^2$.

The temperature coefficient of μ is fairly constant; its mean value is: **1.90** Erg pro degree.

XVIII

para-Nitro-Monomethylaniline: $C_6H_4 . (NHCH_3)_{(1)} . NO_{2(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
155.2	1.525	2032.7	46.3	1.201	1167.5
170	1.469	1958.2	45.2	1.189	1147.5
186	1.440	1919.7	43.7	1.175	1117.5
199	1.373	1830.3	41.5	1.165	1070.5
210	1.324	1765.7	40.1	1.156	1037.2

Molecular weight: **152.08.**

Radius of the Capillary tube: 0.04644 cm.
Depth: 0.1 mm.

The yellow crystals, which possess a beautiful pink lustre, melt at 152° C. Above 190° the liquid becomes gradually darker tinged; therefore the measurements were no longer continued. The specific gravity at 160° C. was: 1.1968; at 180° C.: 1.1807; at 200° C.: 1.1643. At t C.: $d_{4^\circ} = 1.2049 - 0.0008125\, (t - 150^\circ)$. The temperature-coefficient of μ increases very rapidly with rise of temperature: from **1.3** Erg at 155° C. to **3.3** Erg at 210° C. Evidently the above mentioned decomposition must be considered the cause of this phenomenon.

XIX.

Nitrosomethylaniline: $C_6H_5.N(NO)CH_3$.

Temperature in 0° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm mercury of 0° C.	in Dynes			
* 0°	1.439	1919.1	45.7	1.143	1106.0
* 30.4	1.356	1808.1	43.0	1.117	1056.8
46.9	1.314	1752.4	41.4	1.099	1028.5
58.6	1.280	1707.0	40.3	1.092	1005.4
85.9	1.190	1587.1	37.5	1.068	949.6
103.3	1.132	1508.6	35.6	1.054	909.4
117.6	1.079	1438.3	33.9	1.041	873.2
127.4	1.048	1397.0	32.9	1.033	851.8

Molecular weight: **136.08**.

Radius of the Capillary tube: 0.04839 cm.; in the observations indicated by *, it was: 0.04867 cm.
Depth: 0.1 mm.

The substance boils constantly at 128° C. under a pressure of 760 mm. In a mixture of ice and salt it solidifies, and melts afterwards at + 13° C. Above 125° C. the liquid becomes gradually brownish by slow decomposition. The specific gravity at 25° C was: 1.1213; at 50° C.: 1.0995; at 75° C.: 1.0779. At t° C.: $d_{4^\circ} = 1.1430 - 0.000868\,t$.

Originally the temperature-coefficient of μ increases with rise of temperature from **1.63** Erg at 0° C. to **1.99** Erg at 30° C. Then it remains fairly constant at **2.27** Erg pro degree.

XX.

Diïsobutylaniline: $C_6H_5 . N\,[CH_2 . CH\,(CH_3)_2]_2$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
—18°	(1.118)	(1490.0)	(37.0)	0.949	(1332.6)
0	1.049	1398.1	32.8	0.932	1195.6
26	0.959	1278.5	29.9	0.909	1108.2
40.7	0.908	1210.3	28.3	0.899	1056.7
55.7	0.864	1151.9	26.9	0.885	1015.0
80.2	0.800	1066.6	24.8	0.866	949.3
92.5	0.700	1026.7	23.9	0.860	919.1
115.5	0.711	947.4	22.1	0.847	858.6
*135.3	0.678	903.6	20.5	0.836	803.4
*149.2	0.642	856.6	19.4	0.832	762.7
*175.9	0.577	769.2	17.4	0.823	689.1
*195.8	0.530	706.6	15.9	0.818	632.2

Molecular weight: **205.11**.

Radius of the Capillary tube: 0.04792 cm.; in the measurements indicated by *, the radius was: 0.04670 cm.
Depth: 0.1 mm.

The substance boils under a pressure of 21 mm. at 146° C. It remains in liquid condition down to — 20° C., but is then very viscous; at — 79° C. it becomes glassy, but does not crystallise. Under atmospheric pressure the liquid boils at 250° C. The specific gravity at 25° C. is: 0.9099; at 50° C.: 0.8901; at 75° C.: 0.8725. At t° in general: $d_{4^\circ} = 0.9319 - 0.000924\,t + 0.00000176\,t^2$.

The temperature-coefficient of μ is in the beginning (below 41° C.) almost **3.43** Erg, afterwards very constant: **2.73** Erg pro degree. It is therefore rather great, also at higher temperatures.

XXI.

Diphenylamine: $(C_6H_5)_2\,NH$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
60°.5	1.284	1710.7	38.6	1.054	1143.3
76.8	1.230	1639.5	37.0	1.039	1106.4
95	1.171	1570.4	35.2	1.025	1062.1
114.2	1.103	1472.8	33.4	1.010	1017.8
136	1.041	1389.4	31.4	0.993	967.7
155	0.991	1321.2	29.7	0.980	923.4

Molecular weight: **169.89.** Radius of the capillary tube: 0.04595 cm.
Depth: 0.1 mm.

The substance boils at 179° C.; under a pressure of 12 mm. The melting-point is 54° C. Above 150° C. the liquid is soon coloured darkly; the measurements therefore were no longer continued. The density at 75° C. was: 1.0412; at 100° C.: 1.0210; at 125° C.: 1.0022. In general at $t°$ C.: $d_{4°} = 1.0628 - 0.000892\,(t-50°) + 0.00000112\,(t-50°)^2$.

The temperature-coefficient of μ is constant, and **2.31** Erg pro degree.

XXII.

Dibenzylamine: $(C_6H_5\,CH_2)_2\,NH$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
−18°.5	1.413	1883.6	43.3	1.060	1410.6
0	1.340	1787.8	41.1	1.045	1351.7
25.1	1.254	1683.5	38.5	1.024	1283.5
41.5	1.204	1603.9	36.7	1.011	1234.0
56	1.158	1543.7	35.4	0.999	1199.6
71	1.117	1489.2	34.1	0.988	1164.3
84.8	1.071	1437.3	33.1	0.977	1138.4
100	1.039	1385.1	31.7	0.963	1101.0
*116	1.026	1367.9	30.3	0.950	1061.9
*130.5	0.977	1305.1	28.9	0.938	1021.5
*146	0.931	1242.6	27.5	0.925	981.1
*162.5	0.900	1200.9	26.2	0.912	943.6
*176	0.853	1135.9	24.9	0.901	904.0
*196.8	0.803	1069.2	23.4	0.884	860.4
*209.5	0.772	1024.6	22.4	0.873	830.6
*228	0.713	949.4	20.7	0.858	776.4

Molecular weight: **197.10.** Radius of the Capillary tube: 0.04676 cm.; in the measurements indicated by *, the radius was 0.04529 cm.
Depth: 0.1 mm.

Under a pressure of 19 mm. the amine boils constantly at 186° C. At — 70° it becomes a transparent glassy mass, but does not crystallise. The specific gravity was volumetrically determined: at 0° C. it was 1.045; at 25° C.: 1.024; at 50° C.: 1.004. Generally: $t°$ C.: $d_{4°} = 1.045 - 0\,00082\,t$.

The temperature-coefficient of μ is oscillating round a mean value of: **2.53** Erg pro degree Celsius.

XXIII.

Azoxybenzene: $C_6H_5 . N_2O . C_6H_5$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
55.8°	1.296	1725.4	39.3	1.133	1228.8
70.6	1.257	1676.0	38.3	1.121	1206.1
85	1.219	1625.2	37.1	1.110	1176.0
100	1.181	1579.9	35.9	1.098	1146.3
*115	1.180	1572.0	34.7	1.087	1115.4
*130.5	1.139	1519.0	33.5	1.074	1085.5
*145.5	1.085	1448.8	32.1	1.063	1047.3
*162	1.050	1400.0	30.8	1.050	1013.2
*176	1.017	1355.4	29.7	1.039	983.9
*196.9	0.950	1265.5	27.7	1.022	927.7
*211	0.906	1210.1	26.6	1.011	897.3
*226	0.833	1110.5	24.2	1.000	822.4

Molecular weight: **198.1**. Radius of the Capillary tube: 0.04676 cm.; in the measurements indicated by *, this radius was: 0.04529 cm.
Depth: 0.1 mm.

At 36° C. the substance melts; the liquid is of a clear yellow colour. The specific gravity at 50° C. was 1.1373; at 75° C.: 1.1177; at 100° C.: 1.0982. In general at t° C.: $d_{4^\circ} = 1.1764 - 0.000782\,t$.

The temperature-coefficient of μ increases gradually with rise of temperature: between 56° and 71° it is: C. **1.53** Erg; between 71° and 100° C: **1.96** Erg; between 100° C. and 162° C.: **2.16** Erg; between 162° and 211° C.: **2.31** Erg and above 211° C. increasing very rapidly, up to about **4.98** Erg per degree at 226° C., decomposition evidently setting in.

XXIV

α-Dihydrocampholenic Acid: $C_5H_6(CH_3)_3.CH_2.COOH$

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes	
— 21°	(1.752)	(2335.8)	(54.4)
0	1.102	1468.9	34.3
25	1.008	1344.7	31.4
40.3	0.960	1280.5	29.9
54.1	0.915	1220.5	28.5
75.5	0.861	1147.5	26.8
95	0.813	1083.8	25.3
115	0.758	1010.7	23.6
134.3	0.723	963.6	22.5
150.5	0.684	912.2	21.3
175.5	0.636	847.9	19.8
195.3	0.607	809.4	18.9

Molecular weight: **170.14**. Radius of the Capillary tube: 0.04670 cm.
Depth: 0.1 mm

At — 79° the liquid becomes a glassy mass, but does not crystallise. At — 20° and 0° C. also it is already very viscous.

The quantity of the liquid was too small to permit the determination of its specific gravity.

XXV.

Aethyl-α-Dihydrocampholenate: $C_5H_6(CH_3)_3 \,.\, CH_2 \,.\, COOC_2H_5$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0 C.	in Dynes			
— 21°	1.020	1359.9	31.0	0.961	1082.0
0	0.964	1284.8	29.3	0.945	1034.2
25.3	0.893	1190.6	27.1	0.924	971.0
40.4	0.859	1145.2	26.0	0.912	939.8
54.1	0.822	1095.9	24.9	0.901	907.3
75.5	0.768	1023.9	23.2	0.884	856.2
95.5	0.714	951.9	21.5	0.869	802.5
115.2	0.673	896.2	20.2	0.852	764.0
134.8	0.620	826.5	18.6	0.837	711.9
153	0.577	769.2	17.3	0.822	670.2
176.1	0.517	689.5	15.4	0.804	605.4
194	0.456	607.9	13.5	0.789	537.4

Molecular weight: **198.18.**

Radius of the Capillary tube: 0.04670 cm.
Depth: 0.1 mm.

Under a pressure of 20 mm. the colourless liquid boils at 147° C. At — 79° C. it gets turbid and very viscous, but does not crystallise. The specific gravity at 0° C. is: 0.9445; at 25° C.: 0.9250; at 50° C.: 0.9045. At t° C.: $d_{4^\circ} = 0.9445 - 0.0008\,t$.

Below 176° C. the temperature-coefficient of μ is relatively constant, with a mean value of: **2 46** Erg pro degree.

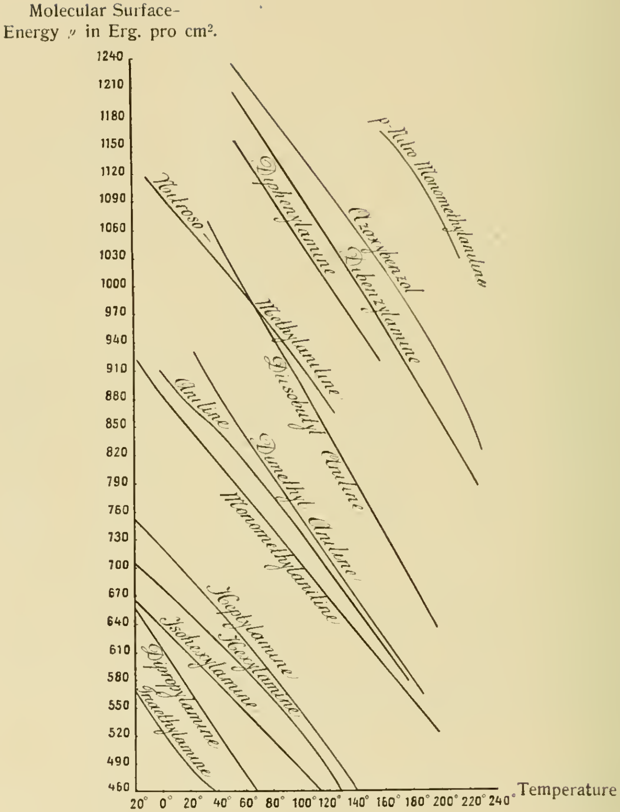
Molecular Surface-Energy γ in Erg. pro cm².
1240
1210
1180
1150
1120
1090
1060
1030
1000
970
940
910
880
850
820
790
760
730
700
670
640
610
580
550
520
490
460
20°
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°
200°
220°
240°
Temperature
p-Nitro Monomethylaniline
Azoxybenzol
Dibenzylamine
Diphenylamine
Nitroso-
Methylaniline
Diisobutyl Aniline
Aniline
Dimethyl Aniline
Monomethylaniline
Heptylamine
Hexylamine
Isohexylamine
Dipropylamine
Triaethylamine

Fig. 2.

XXVI.

Furfurol: $\alpha\cdot C_4H_3O.\,C^{H}_{O}$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
*—22°	1.437	1915.8	45.7	1.211	921.8
* 0	1.368	1824.5	43.5	1.185	869.8
29.9	1.289	1719.3	40.7	1.151	806.3
46.8	1.214	1618.5	38.3	1.133	745.2
58.3	1.171	1561.2	37.0	1.119	713.9
86.5	1.072	1429.0	33.8	1.089	645.4
102.3	1.017	1355.5	32.0	1.074	599.3
117.7	0.961	1281.2	30.2	1.060	557.4

Molecular weight: **96.03**. Radius of the Capillary tube: 0.04839 cm.; in the observations indicated by *, it was: 0.04867 cm.
Depth: 0.1 mm.

The liquid boils at 162° and 761 mm. mercury. The substace crystallises in a bath of solid carbondioxide and alcohol, and melts then again at —31° C.; according to Walden at —36° C Above 100° C. the liquid is rapidly oxydized, and gets a brownish colour. At the boilingpoint, the value of χ can only differ slightly from: 25.4 Erg pro cm². The specific gravity at 25° C. was: 1.1563; at 50° C.: 1.1287; at 75° C.: 1.1023; at t°: $d_{4^\circ}=1.1851-0.001176\,t+0.00000096\,t^2$.

The temperature-coefficient μ is almost constant, and has the mean value: **2.70** Erg pro degree; it is rather high.

XXVII.

Thiophene: C_4H_4S.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg pro cm².	Specific gravity d_{0}	Molecular Surface-energy μ in Erg pro cm².
*—19°	1.134	1512.3	36.0	1.110	644.6
* 0	1.057	1409.5	33.5	1.087	608.3
29.9	0.939	1252.3	29.5	1.051	547.8
47.3	0.874	1165.5	27.4	1.032	515.1
58.7	0.834	1111.8	26.1	1.006	499.0
87	0.732	975.4	22.8	0.987	441.5

Molecular weight: **84.10**. Radius of the Capillary tube: 0.04839 cm.; in the measurements indicated by *, this radius was: 0.04867 cm.
Depth: 0.1 mm.

The liquid boils constantly at 87° C. under a pressure of 770 mm. In a bath of solid carbondioxide and alcohol, the substance crystallises, and melts at —29°.8 C.; according to Tsakalotos the meltingpoint is —37°.1 C. At the boilingpoint χ has the value: 22.8 Erg pro cm².

At 0° C. the specific gravity is: 1.0873; at 25° C.: 1.0573; at 50° C.: 1.0285. At t° C.: $d_{4^\circ}=1.0873-0.001224\,t+0.00000096\,t^2$.

The temperature-coefficient of μ is fairly constant, with a mean value of: **1.90** Erg pro degree.

XXVIII

Piperidine: $C_5H_{10} > NH$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity d_{4°	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
* —19°	1.041	1388.6	32.8	0.900	680.8
* 0	0.973	1297.7	30.6	0.882	643.7
29.4	0.876	1168.0	27.1	0.855	582.0
48	0.813	1084.3	25.1	0.838	546.3
64.5	0.753	1004.8	23.2	0.823	511.1
80.9	0.703	937.8	21.6	0.808	481.7
104.5	0.628	837.4	19.2	0.786	436.2

Molecular weight: **85.10**

Radius of the Capillary tube: 0.04777 cm.; in the observations indicated by *, it was: 0.04839 cm. Depth: 0.1 mm.

Under a pressure of 760 mm. the base boils at 108° C. On cooling it crystallises, and melts afterwards at —9° C.; according to Mascarelli this temperature would be —13° C.; at the boiling point χ is about: 19.7 Erg pro cm². The specific gravity at 0° C. is: 0.8820; at 25° C.: 0.8586; at 50° C.: 0.8359. At t° C.: $d_{4^\circ} = 0.8821 - 0.00092\,t$. The temperature-coefficient of μ is fairly constant: its mean value can be fixed upon **1.98** Erg pro degree.

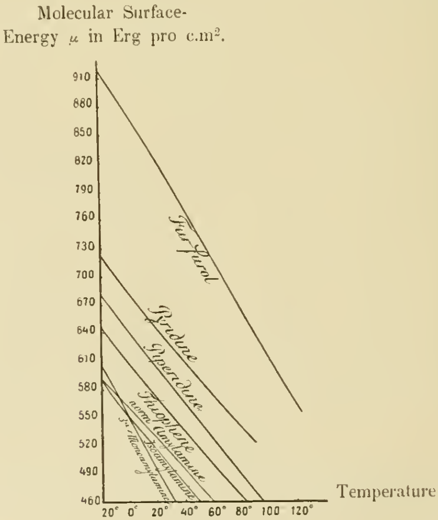

Fig. 3.

§ **3**. In connection with these data we can make the following remarks.

The substitution of the bromine in *bromobenzene* by iodine, makes the value of μ at the same temperatures increase, just as we formerly observed with the substitution of chlorine by bromine in the *chlorobenzene*. This behaviour is evidently opposite to what was formerly stated in the case of the molten halogenides of the alcalimetals. In agreement with our previous experiences, the substitution of H in the benzene-nucleus by CH_3, makes the value of μ increase (*bromobenzene* and *o-bromotoluene*); and the same holds good for the substitution of H by a NO_2-group, by *halogenides*, or by the *azoxy*-radical; in general by substitution of H by radicals built up from strongly electronegative atoms. This seems to be a general rule. An analogous phenomenon is observed, if aromatic hydrocarbon-radicals substitute the H-atoms: a comparison of the *hexyl*-, or *heptylamines* with *diphenyl*-, and *dibenzylamine* makes this very evident, and just in the same way a comparison of *acetophenone* and *benzophenone*. The μ-t-curve for *ethylcinnamylate* lies beneath that for *methylcinnamylate*, and the same is the case with *monomethylaniline* in comparison with *aniline* itself. On the contrary, the value of μ for *aniline* is very much increased by substitution of the H of the amino-group by two *isobutyl*-radicals.

The addition of hydrogen in *pyridine*, this thus being transformed into *piperidine*, makes the μ-t-curve of the former compound fall; for *thiophene* it lies beneath that for *piperidine*.

Some curves for *amylamines* are reproduced here also for the purpose of comparison. This is connected on the one hand with the substitution of the atom $\diagdown S \diagup$ in *thiophene* by the combination: $-N=\overset{|}{C}H-$, and perhaps on the other hand with the presence of the unsaturated C-atoms in *pyridine*, in comparison with those in *piperidine*. However it must be remarked here at once, that evidently this last may not be considered a general rule, as for instance the curve of *benzene* lies lower than that for *cyclohexane*. Certainly a number of constitutive influences are superposed one upon the other, thus prohibiting the statement of the precise connection between the value of μ and the degree of saturation of the C-atoms in this case, to a more or less degree.

We intend to finish here untill a later date the investigation of organic compounds with the series here described.

University Laboratory for Inorganic
and Physical Chemistry.

Groningen, August 1915.

Physics. — *The second virial coefficient for rigid spherical molecules, "whose mutual attraction is equivalent to that of a quadruplet placed at their centre"*. By Dr. W. H. Keesom. Supplement No. 39*a* to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes).

(Communicated in the meeting of September 25, 1915).

§ 1. This Communication forms a continuation of the investigation started in Suppl. N°. 24 (April '12, these Proceedings June '12), the aim of which is to derive, on different suppositions concerning structure and mutual interaction of the molecules, the first terms in the development of the equation of state into ascending powers of v^{-1} as functions of the temperature, in order to compare them with the available experimental material. It is obvious that in this problem it is indicated to proceed step by step from the simplest to more complicated suppositions.

In Suppl. N°. 24*b* § 6 the second virial coefficient, i. e. B in the equation of state:

$$pv = A\left(1 + \frac{B}{v} + \frac{C}{v^2} + \ldots\right) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

was derived for rigid spheres of concentric structure, which carry a doublet at their centre, or whose mutual attraction is equivalent to that of such doublets. In a following paper it will be shown i. a., that the limitation to molecules of concentric structure, observed there, can be omitted as far as concerns the derivation of B.

In Suppl. N°. 25 (Sept. '12) I then showed that the way in which the second virial coefficient of hydrogen between — 100° and + 100° C. depends on the temperature agrees with that which was derived for doublet-molecules of that structure.

Meanwhile it has, however, become evident especially by Debije's[1]) investigation concerning dielectric constant and refractive index, that the molecules of the diatomic elementary gases do not possess a moment such as that of a doublet. The next step in the theoretical development of the equation of state now seems to be, that the next term of the development of the attractive potential outside the spherical molecule into spherical harmonics, i. e. that of the degree —3, is considered to be present alone. The corresponding surface harmonic of the second order reduces to the zonal harmonic of the second order for diatomic molecules, which in this paper as in Suppl.

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[1]) Cf. P. Debije, Physik. ZS. 13 (1912), p. 97. W. C. Mandersloot, Thesis for the Doctorate, Utrecht 1914, p. 56. N. Bohr, Phil. Mag. (6) 26 (1913), p. 866.

No. 24 we treat as bodies of revolution as regards their fields of force. So we are led to the problem to deduce the second virial coefficient for a system of rigid spheres, whose attraction is equivalent to that of a quadruplet with two coinciding axes, and which is obtained when two doublets are placed along the same line with two homonymous poles towards one another and their distance approaches zero with maintenance of a finite quadruplet-moment [1]).

We place ourselves in this communication on the standpoint of classical mechanics. The quantum theory only intervenes in so far as the fact that according to that theory the rotations of a diatomic molecule about one of its principal axes of inertia in consequence of the smallness of the corresponding moment of inertia is not influenced appreciably by the heat motion, is accounted for in our treatment according to the principles of classical mechanics by considering such a molecule as a body of revolution. We do not consider here an influence, as given by the quantum theory, on the rotations about the two other principal axes of inertia nor a possible influence on the translational motion. If perhaps the bearing of the results obtained in this paper is limited by this circumstance, still they are in any case applicable to molecules for which these two principal moments of inertia and eventually the molecular weight in connection with the temperature region which is to be considered are sufficiently large.

§ 2. As we explained in § 1 we will consider here the molecules as rigid spheres of concentric structure [2]), with at their centre a quadruplet which consists of two doublets whose axes lie in the same line and have opposite directions, and which approach each other indefinitely preserving, however, a finite quadruplet-moment.

For calculating the second virial coefficient we have again to consider, just as in Suppl. N°. 24 *a* and *b*, pairs of molecules which at a given moment lie in each other's sphere of action. The mutual position of a pair can be specified in a way corresponding to that followed in Suppl. N°. 24*b* § 6 in discussing the doublets, viz. by the following coordinates (Fig. 1):

1st. the distance r between the centres;

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[1]) J. C. MAXWELL. Electricity and Magnetism. 3rd ed. Vol. I, p. 197.

[2]) This expression is meant to indicate that the density is uniformly distributed over concentric spherical layers. Yet the following deduction of B is also valid if the density is distributed symmetrically about an axis, if this axis coincides with the axis of the quadruplet. The result is, as far as regards B, even more general and is also valid, if the density is distributed arbitrarily.

2nd. the angles θ_1 and θ_2, which the axes of the quadruplets make with the line which joins the centres. For a closer definition of these angles we choose in each molecule arbitrarily one of the two equivalent directions on the axis as the positive direction; we choose further as the positive direction on the line which joins the centres the direction from the molecule whose position is determined by the angle considered, towards the other molecule; θ_1 and θ_2 are then the angles, from 0 to π, between the positive directions;

3rd. the angle φ between two half-planes each of which contains the positive direction of the axis of one of the quadruplets and the line joining the centres. This angle is further specified as in Suppl. N°. 24*b* § 6, and goes from 0 to 2π.

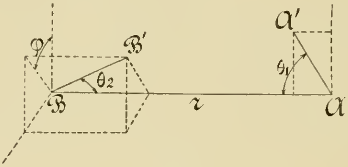

Fig. 1.

The method of Suppl. No. 24*b* § 6 may then be applied immediately to the problem dealt with here. It gives for the specific heat at constant volume in the Avogadro-state, assuming that the spheres are smooth:

$$\gamma_{vA} = {}^5/_2\, R,$$

and for the second virial coefficient:

$$B = \tfrac{1}{2}\, n \left(\tfrac{1}{3}\pi\sigma^3 - P'\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where:

$n =$ the number of molecules in the quantity of gas for which the equation of state is derived,

$\sigma =$ the diameter of the molecule and

$$P' = \tfrac{1}{2} \int\limits_{\sigma}^{\infty}\int\limits_{0}^{\pi}\int\limits_{0}^{\pi}\int\limits_{0}^{2\pi} \left(e^{-hu_{b1}} - 1\right) r^2 \sin\theta_1 \sin\theta_2\, dr\, d\theta_1\, d\theta_2\, d\varphi \quad . \quad . \quad (3)$$

In this formula

$$h = \frac{1}{kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

k is Planck's well known constant, whereas u_{b_1} is the potential energy of the pair of quadruplets indicated by the index 1, when the potential energy is put $= 0$ for $r = \infty$. Its value is given by:

$$u_{b1} = \tfrac{3}{4}\frac{\mu_2^{\,2}}{r^5}\{1 - 5\cos^2\theta_1 - 5\cos^2\theta_2 - 15\cos^2\theta_1\cos^2\theta_2 + + 2\,(4\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos\varphi)^2\}, \quad . \quad . \quad . \quad . \qquad (5)$$

if μ_2 represents the moment of the quadruplet.

We introduce:

$$v = \tfrac{3}{4}\frac{\mu_2^{\,2}}{\sigma^5}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

then $v =$ the potential energy, when two molecules are touching each other, the axes of the quadruplets being at right angles to each other and to the line joining the centres.

We put further

$$\Psi = 1 - 5\cos^2\theta_1 - 5\cos^2\theta_2 - 15\cos^2\theta_1\cos^2\theta_2 + 2\,(4\cos\theta_1\cos\theta_2 + + \sin\theta_1\sin\theta_2\cos\varphi)^2,$$

or:

$$\Psi = A + B\cos\varphi + C\cos 2\varphi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

if

$$\left.\begin{aligned} A &= 2\,(1 - 3\cos^2\theta_1)\,(1 - 3\cos^2\theta_2) \\ B &= 16\sin\theta_1\cos\theta_1\sin\theta_2\cos\theta_2 \\ C &= \sin^2\theta_1\sin^2\theta_2, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

so that

$$u_{b1} = v\frac{\sigma^5}{r^5}\Psi.$$

Developing $e^{-hu_{b_1}} - 1$ into a series of ascending powers of hu_{b1}, and integrating in (3) according to r, we obtain [1]):

$$P' = \tfrac{1}{2}\sigma^3\sum_{n=1}^{n=\infty}(-1)^n\frac{1}{5n-3}\frac{1}{n!}(hv)^n\int_0^\pi\!\!\int_0^\pi\!\!\int_0^{2\pi}\Psi^n\sin\theta_1\sin\theta_2\,d\theta_1 d\theta_2 d\varphi \quad . \qquad (9)$$

If for the sake of brevity we write $[\Psi^n]$ for the integral in (9) and correspondingly:

$$\left.\begin{aligned} [A^pB^{2q}C^r] &= \int_0^\pi\!\!\int_0^\pi A^pB^{2q}C^r\sin\theta_1\sin\theta_2\,d\theta_1\,d\theta_2 \\ [\cos^r\varphi\cos^s 2\varphi] &= \int_0^{2\pi}\cos^r\varphi\cos^s 2\varphi\,d\varphi, \end{aligned}\right\} \quad . \quad . \quad . \quad . \qquad (10)$$

observing that $[\cos^{2l-1}\varphi] = 0$, $[\cos^{2l-1}2\varphi] = 0$, $[\cos^{2l-1}\varphi\cos^m\varphi] = 0$ l and m being positive integers, we find:

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[1]) The quantities n, p, q, r, s, which we introduce temporarily in this § have a meaning different from that in the other part of this paper and in Suppl. No. 24.

$$\left.\begin{aligned}
&[\Psi^n] = 2\pi\,[A^n] + \\
&+ \binom{n}{2}[A^{n-2}\,B^2]\,[\cos^2\varphi] + \binom{n}{2}[A^{n-2}\,C^2]\,[\cos^2 2\varphi] + \\
&+ \binom{n}{3}\binom{3}{1}[A^{n-3}\,B^2\,C]\,[\cos^2\varphi\,\cos 2\varphi] + \\
&+ \binom{n}{4}[A^{n-4}\,B^4]\,[\cos^4\varphi] + \binom{n}{4}\binom{4}{2}[A^{n-4}\,B^2C^2][\cos^2\varphi\cos^2 2\varphi] + \\
&\qquad\qquad + \binom{n}{4}\binom{4}{4}[A^{n-4}\,C^4]\,[\cos^4 2\varphi] + \\
&+ \binom{n}{5}\binom{5}{1}[A^{n-5}B^4C][\cos^4\varphi\cos 2\varphi] + \binom{n}{5}\binom{5}{3}[A^{n-5}B^2C^3][\cos^2\varphi\cos^3 2\varphi] \\
&+ \binom{n}{6}[A^{n-6}B^6]\,[\cos^6\varphi] + \binom{n}{6}\binom{6}{2}[A^{n-6}\,B^4\,C^2]\,[\cos^4\varphi\,\cos^2 2\varphi] + \\
&\qquad\qquad + \binom{n}{6}\binom{6}{4}[A^{n-6}\,B^2\,C^4]\,[\cos^2\varphi\,\cos^4 2\varphi] + \\
&\qquad\qquad + \binom{n}{6}\binom{6}{6}[A^{n-6}\,C^6]\,[\cos^6 2\varphi] + \\
&+ \;.
\end{aligned}\right\} . (11)$$

If we write:

$$\left.\begin{aligned}
A &= 2A_1\,A_2, & A_1 &= 1 - 3\cos^2\theta_1 \\
B &= 16\,B_1B_2, & B_1 &= \sin\theta_1\,\cos\theta_1 \\
C &= C_1C_2, & C_1 &= \sin^2\theta_1
\end{aligned}\right\} \quad .\;.\;(12)$$

then

$$[A^p\,B^{2q}\,C^r] = 2^{p+8q}\left\{[A_1^p\,B_1^{2q}\,C_1^r]\right\}^2 \quad .\;.\;.\;.\;(13)$$

where the square brackets in the second member now refer to θ_1 only:

$$[\;.\;.\;.\;] = \int_0^\pi .\;.\;.\;\sin\,\theta_1\,d\theta_1.$$

One finds

$$\left.\begin{aligned}
&[A_1^pB_1^{2q}C_1^r] = 2^{p+q+r+1}\,\frac{(p+q+r)!}{(2p+4q+2r+1)(2p+4q+2r-1)\ldots(2q+1)} \\
&\qquad \left\{1 - \binom{p}{1}\frac{2q+1}{p+q+r} + \binom{p}{2}\frac{(2q+1)(2q+3)}{(p+q+r)(p+q+r-1)} - \ldots\right\},
\end{aligned}\right\} . (14)$$

from which formula also the special cases: $[A_1^p]$, $[A_1^pB_1^{2q}]$ etc., may be derived.

Of these expressions $[A_1^p]$ can be calculated more easily from the following relation:

$$[A_1^p] = (-1)^p\,\frac{2^{p+1}}{2p+1} + \frac{2p}{2p+1}\,[A_1^{p-1}] \quad .\;.\;.\;.\;(15)$$

Further:

$$\left.\begin{aligned}
&[\cos^{2q}\varphi] = [\cos^{2q} 2\varphi] = 2\pi \,.\binom{2q}{q}.\frac{1}{2^{2q}}\,,\\
&[\cos^{2q}\varphi\cos^{2r}2\varphi] = 2\pi.\frac{1}{2^{q+2r}}\left\{\binom{2r}{r}+\binom{q}{2}.\frac{1}{2^{2}}\binom{2r+2}{r+1}+\binom{q}{4}.\frac{1}{2^{4}}\binom{2r+4}{r+2}\dots\right\}\\
&[\cos^{2q}\varphi\cos^{2r-1}2\varphi] = 2\pi\,.\frac{1}{2^{q+2r}}\left\{\binom{q}{1}\binom{2r}{r}+\binom{q}{3}\frac{1}{2^{2}}\binom{2r+2}{r+1}\dots\right\}.
\end{aligned}\right\} \quad .(16)$$

These formulae give finally:

$$\left.\begin{aligned}
P' = \tfrac{4}{3}\pi\sigma^{3}\Big\{&\frac{16}{15}(hv)^{2} - \frac{128}{735}(hv)^{3} + \frac{18176}{37485}(hv)^{4} - \frac{262144}{419265}(hv)^{5} +\\
&+ 0{,}2360\,(hv)^{6} - 0{,}1355\,(hv)^{7} + 0{,}1019\,(hv)^{8}\dots\Big\}\,,
\end{aligned}\right\} \quad .(17)$$

so that

$$\left.\begin{aligned}
B = \tfrac{1}{2}n\,.\tfrac{4}{3}\pi\sigma^{3}\{&1 - 1.0667\,(hv)^{2} + 0.1741\,(hv)^{3} - 0.4738\,(hv)^{4} +\\
&+ 0.6252\,(hv)^{5} - 0.2360\,(hv)^{6} + 0.1355\,(hv)^{7} - 0.1019\,(hv)^{8}\dots\}
\end{aligned}\right\} \quad .(18)$$

§ 3. For the lower temperatures, e. g. at the BOYLE-point (the temperature at which $B = 0$), this series converges very slowly, so that for them the terms given above are not sufficient.

At the inversion point of the JOULE-KELVIN effect for small densities the term with $(hv)^{8}$ in (18) amounts to about $^{1}/_{800}$ of B_{∞} ($= b_{W\infty}$), the value to which B would approach for $T = \infty$, if the equations found here remained valid. Hence for the inversion point just mentioned and for higher temperatures, the terms given above may be considered to be sufficient, assuming that none of the following terms is unexpectedly large. At $0.75\ T_{inv(\rho=0)}$ the above mentioned term amounts to $^{1}/_{80}$ of B_{∞}, so that on the same assumption we may reckon upon an accuracy of about 1°/₀ (of B_{∞}).

I have not succeeded in deducing a series which is more suitable for lower temperatures.

Just as for the (spherical) molecules, which bear a doublet at their centre, so also for the quadruplets the term with T^{-1} is absent in the series for B. Whereas, however, for the doublets all odd powers are absent, here the higher odd powers appear in the series, although the coefficient of T^{-3} is still relatively small [1].

Above $3\,T_{inv(\rho=0)}$ with an accuracy of $^{1}/_{1000}$ and above $1.2\ T_{inv(\rho=0)}$ with an accuracy of $^{1}/_{100}$, the first two terms in (18) are sufficient. The dependence of B on temperature then agrees with the suppo-

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[1] The questions under what conditions in general the term with T^{-1}, as also the higher odd powers disappear from B will be dealt with in a following paper (Suppl. No. 39*b*).

sition that in VAN DER WAALS' equation b_W is independent of T and a_W is proportional to T^{-1}. The latter assumption was already made by CLAUSIUS, with a view to the vapour pressures of carbon dioxide. A relation agreeing with

$$B = B_\infty \left(1 + \frac{b_2}{T^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

(with a negative value of b_2) was also found by D. BERTHELOT[1]) to be suitable to represent the compressibility at densities near the normal. In these investigations the approximate validity of that relation was extended to much lower temperatures than those indicated above. It will appear in the next §, that equation (18) actually agrees with an equation of the form (19) down to an appreciably lower temperature than those indicated above.

§ 4. For the purpose of a closer comparison between the second virial coefficients of quadruplet-bearing molecules and of doublet-bearing molecules we shall introduce as a reduction temperature a temperature which is specific for each gas[2]). According to what was said in § 3 about the region in which equation (18) is applicable the inversion temperature of the JOULE-KELVIN-effect at small densities is a suitable one for this purpose. This temperature is found from the relation:

$$B - T\frac{dB}{dT} = 0,$$

or

$$B + hv\frac{dB}{d(hv)} = 0.$$

Equation (18), and Suppl. N°. 24b equation (59) give respectively, for quadruplets:

$$hv_{inv(\rho=0)} = 0.576,$$

for doublets:

$$hv_{inv(\rho=0)} = 0.969.$$

If we call $\dfrac{T}{T_{inv(\rho=0)}} = t_{(inv)}$, it follows further, that:

for quadruplets:

$$\left.\begin{aligned} B = B_\infty \{1 &- 0.3539\, t_{(inv)}^{-2} + 0.03327\, t_{(inv)}^{-3} - 0.05215\, t_{(inv)}^{-4} + \\ &+ 0.03964\, t_{(inv)}^{-5} - 0.00862\, t_{(inv)}^{-6} + 0.00285\, t_{(inv)}^{-7} - 0.00123\, t_{(inv)}^{-8} \ldots\} \end{aligned}\right\} (20)$$

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[1]) D. BERTHELOT. Trav. et Mém. Bur. Internat. des Poids et Mesures, t. 13 (1907).

[2]) Cf. H. KAMERLINGH ONNES and W. H. KEESOM. Die Zustandgleichung. Math. Enc. V 10. Leiden Comm. Suppl. No. 23 § 28a.

for doublets:

$$B = B_\infty \{1 - 0.3130\, \mathfrak{t}_{(inv)}^{-2} - 0.01175\, \mathfrak{t}_{(inv)}^{-4} - 0.00044\, \mathfrak{t}_{(inv)}^{-6} \ldots\} \quad (21)$$

Table I contains some values calculated from (20) and (21) respectively.

TABLE I.

$\frac{T}{T_{inv.\,(\rho=0)}}$	B/B_∞			
	quadr.	doublets	V. D. WAALS	CLAUSIUS-BERTHELOT
0.75	0.413	0.404	0.333	0.407
1	0.660	0.675	0.5	0.667
1.5	0.847	0.859	0.667	0.852
2	0.914	0.921	0.75	0.917
3	0.961	0.965	0.833	0.963
4	0.978	0.980	0.875	0.979

The table also gives some values calculated from the equation

$$B = B_\infty \left\{1 - 0{,}5\, \mathfrak{t}_{(inv)}^{-1}\right\}, \quad \ldots\ldots \quad (22)$$

which follows from VAN DER WAALS' equation with constant a_W, b_W and R_W, and some values calculated from the equation

$$B = B_\infty \left\{1 - \tfrac{1}{3}\, \mathfrak{t}_{(inv)}^{-2}\right\}, \quad \ldots\ldots \quad (23)$$

which is obtained from CLAUSIUS' and BERTHELOT's assumption: $a_W \sim T^{-1}$.

As appears from table I, the difference between the values of B for quadruplets and for doublets is small in the temperature region considered here, i. e. above 0.75 $T_{inv.\,\rho=0}$, viz. smaller than 1°/₀ of B_∞, or 2.3°/₀ of B.

Hence the circumstance of a diatomic molecule possessing or not possessing a doublet, has but a small influence on the dependence of B on temperature in this temperature region. This leads one to expect that in the considered region of temperature and density the equation of state of diatomic compound gases and that of diatomic elementary gases will not be easily distinguished from each other.

From table I it appears further, that the values of B for quadruplets and for doublets both deviate very little from equation (23), viz. over the whole region above 0.75 $T_{inv.(\rho=0)}$ less than 0.6°/₀ of the value of B_∞, and less than 1.5°/₀ of the value of B.

§ 5. *Hydrogen.* Values of B for a diatomic gas in the temperature region for which the terms given in (18) and (20) are sufficient are only known as yet for hydrogen. For this substance in view of its small molecular weight one has to pay particular attention to a possible modification of the molecular translational motion according to the quantum theory. According to it a correction ought to be applied to the values of pv, before the equation of state in the form (1) would be applicable. As that correction depends on other powers of v than occur in the second member of (1), a conclusion about that influence might be drawn for the temperature region to be considered here from the agreement or disagreement between the values of B calculated according to (1) without a quantum-correction from measurements at higher pressures and from such at densities near the normal one. The available experimental material [1]), however, does not yet enable us to apply this test. Meanwhile as mentioned above we will disregard a possible influence for the temperature region under consideration. We shall also leave out of account the possible influence on the value of the second virial coefficient of those deviations from the equipartition laws, which according to EUCKEN's measurements of the specific heat are shown by the rotations about the axes at right angles to the line joining the atomic centres, at least in the lowest part of the temperature region under consideration.

In Suppl. N°. 25 (Sept. '12) it was shown that the dependence of B on the temperature for temperatures above —100° C. agrees with that which was derived for spherical molecules carrying a doublet. From the agreement found in § 4 between the latter and that for spherical molecules carrying a quadruplet in the temperature region specified there it follows immediately that the values of B for hydrogen in the temperature region under consideration ought to be found in agreement with the dependence on temperature which we derived for quadruplets.

To test this B/B_{inv} for hydrogen was represented in a diagram as a function of $T/T_{inv(\rho=0)}$ and compared with the values calculated from (20) and (21) respectively. The values of B for hydrogen at —140°, —104°, 0° and 100° C. were taken from KAMERLINGH ONNES and BRAAK [2]), that for B at 20° C. from SCHALKWIJK [3]) and from KAMERLINGH ONNES, CROMMELIN and Miss SMID [4]). The temperature of

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[1]) Cf. W. J. HAAS, Comm. N⁰. 127*a* (April '12) § 4.

[2]) H. KAMERLINGH ONNES and C. BRAAK, Comm N⁰. 100 *a* and *b* (Nov. '07).

[3]) J. C. SCHALKWIJK. Thesis Amsterdam 1902. p. 116, also Leiden Comm. N⁰. 78 p. 22.

[4]) H. KAMERLINGH ONNES, C. A. CROMMELIN and Miss E. J. SMID. Comm. N⁰. 146*b* (June '15).

the inversion point for the JOULE-KELVIN effect at small densities (200.6° K.) was taken from the calculations by J. P. DALTON [1]). B_{inv} the value of B for the just mentioned temperature, was calculated from the special reduced equation of state for hydrogen, communicated in Comm. N°. 109*a* § 7.

In this manner no sufficient agreement was, however, obtained, neither with the quadruplet-equation, nor with the doublet-equation; the value for 100° C. deviates pretty considerably from the calculated curves.

This is to be ascribed chiefly to the value, which is assumed for $T_{inv(\rho=0)}$. The special equation of state used for the calculation of $T_{inv(\rho=0)}$ appears to give a somewhat less perfect agreement with experiment in this region than elsewhere, and this fact has a considerable influence on the result obtained for $T_{inv(\rho=0)}$ in consequence of the circumstance that for the determination of $T_{inv(\rho=0)}$ the value of dB/dT is of great importance.

A value of $T_{inv(\rho=0)}$ was therefore subsequently deduced with the aid of an equation which shows a good agreement in this region of temperatures; for this purpose an equation of the form (19) was chosen, and its constants were derived from the experimental data. From the results of KAMERLINGH ONNES and BRAAK we obtained: $T_{inv(\rho=0)} = 194.5$, $B_{N_{inv}} = 0.000465$.

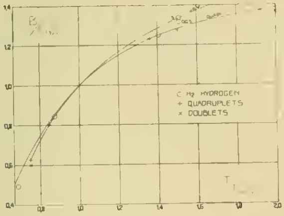

Fig. 2.

Fig. 2 shows what agreement is obtained with these values of the constants [2]). For comparison the curve following from VAN DER WAALS' equation with constant a_W, b_W and R_W is also represented.

It appears now that, as expected, for the temperature region under consideration the values of B for hydrogen can be made to agree with the equation derived for spherical molecules carrying a quadruplet, just as well as with the equation derived for doublets.

From the value found for B_{inv} we obtain for σ [3]):

$$\sigma = 2{,}32.10^{-8} \text{ cm.}$$

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[1]) J. P. DALTON. Comm. N°. 109*a* (March 1909).

[2]) The values taken from the measurements by SCHALKWIJK, and by KAMERLINGH ONNES, CROMMELIN and Miss SMID are indicated by S and OCS respectively.

[3]) From $B_{N\,inv} = 0.000465$, and $B_{inv}/B_{\infty} = 0.660$ (table I), follows $B_{N_\infty} = 0.000705$. $A_{N\,0^\circ C.} = 0.99942$ then gives $B_{\Theta\infty} = 0.000705$. $B_{M_\infty} = 0.000705 \times 22412 = 15.80 = \frac{1}{2} N \,.\, \frac{4}{3} \pi\sigma^3$. With $N = 6.06.10^{23}$ according to MILLIKAN one obtains for the dia-

From $T_{inv(\rho=0)}$ then follows: [1]

$$v = 1,53.10^{-14}$$

and using this value one obtains from (6) for the moment of the quadruplet:

$$\mu_2 = 2,03.10^{-26} \quad [\text{electrostatic units} \times \text{c.m}^2.].$$

If the quadruplet is assumed to consist of two positive charges e at a distance d from each other, and midway between them a charge $-2e$, so that $\mu_2 = \frac{1}{2} ed^2$, and if further $e =$ the charge of an electron $= 4.77.10^{-10}$ (MILLIKAN), one finds

$$d = 0,92.10^{-8} \text{ cm.},$$

a value whose order of magnitude agrees properly with what the distance of the positive nuclei of the two hydrogen atoms within the molecule [2]) may be expected to be. It is to be kept in view, however, that, properly speaking, with this distance of the charges it would not be allowable to assume the charges to be situated infinitely near to one and the same point, as is done in this paper. By taking account of this circumstance one would presumably find a smaller value of d.

§ 6. *Résumé.*

1. For a system of rigid spherical molecules, whose mutual attraction is equivalent to that of a quadruplet situated at their centres the second virial coefficient is developed in a series of ascending powers of T^{-1}.

2. Above 0.75 $T_{inr(\rho=0)}$ the dependence of B on the temperature for spherical molecules carrying a quadruplet nearly coincides with that for molecules carrying a doublet and for both differs but little from the relation $B = B_\infty \left\{1 - {}^1/_3\, \mathfrak{t}^{\,2}_{(inr)}\right\}$.

3. The values of B for hydrogen from —100° to +100° C. may be represented with sufficient accuracy by the equation derived for spherical molecules carrying a quadruplet.

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meter of the molecule the value mentioned in the text. For the meaning of the indices N, ə and M, cf. H. KAMERLINGH ONNES and W. H. KEESOM, "Die Zustandsgleichung", Math. Enz. V 10, Leiden Comm. Suppl. N⁰. 23, Einheiten b.

1) Calculated from $T_{inv(\rho=0)} = 194.5$, $h_{vinr} = 0.576$ (§ 4), equation (4), and $k = 1,37.10^{-16}$.

2) According to P. DEBIJE, München Sitz. Ber. 1915, p. 1, that distance amounts to $0.604.10^{-8}$ cm. DEBIJE's hydrogen molecule is, however, strongly paramagnetic (its magnetic moment corresponds to 10 WEISS magnetons) so that the magnetic properties of hydrogen are not represented accurately by this model, unless one would assume with SOMMERFELD, ELSTER- and GEITEL jubilee volume 1915, p. 549, that the electrons in the hydrogen molecule in circulating in circular orbits do not exert a magnetic action, and hence behave quite differently from the electrons which in the experiment of EINSTEIN and DE HAAS cause the magnetic moment of the iron molecules.

Anatomy. — "*The vagus-area in Camelopardalus Giraffe*". By Dr. H. A. Vermeulen. (Communicated by Prof. C. Winkler).

(Communicated in the meeting of September 25, 1915).

Lesbre, in his exhaustive treatise: "Recherches anatomiques sur les Camélidés" (*Archives du Muséum d'Histoire naturelle de Lyon*, Vol. VIII. 1903), wrote that no nervus accessorius spinalis occurs in these animals, and that the nervus laryngeus inferior does not follow the usual recurrent course, but emerges together with the nervus laryngeus superior from the vagus stem. Lesbre endeavoured to explain the latter circumstance by expressing the supposition that the usual course of the nervus recurrens would be useless by reason of the unusual length of neck in the Camelidae; and he expressed the desirability at the same time of the above relations being also studied in the giraffe, whereby support might be found for his assumption, if similar proportions were found in this extremely long-necked animal.

On a microscopical examination of the vagus area in Camelidae, I saw that the nucleus accessorii spinalis is indeed present, and that especially in the caudal third portion, the nucleus ambiguus is but poorly developed in these animals. I also found several remarkable relations, particularly of vagus and accessorius nuclei of Camelidae [1]) which roused in me the desire to examine what the circumstances might be in the giraffe. I was able to examine one part only of the central nervous system of this class of animal, and was enabled to do so by the courtesy of Dr. C. U. Ariëns Kappers, Director of the Central Institute for Brain Research, at Amsterdam, who kindly placed part of the material there at my disposal. This consisted of the brain stem and a piece of the first cervical segment of one specimen, and the first and second segments of another specimen. In the latter preparation the nervi accessorii Willisii could be seen perfectly intact in their usual course between the roots of the two first cervical nerves, so that in this respect the giraffe differs here at least, from the Camelidae. Of the portion of cervical cord and vagus area of the former preparation about 2500 sections of 18 μ have been coloured with cresil violet. From a part of the second preparation alternating series have been made according to Weigert Pal and Van Gieson, while the other part, for the fibre course, has been treated after Sheldon's method.

The illustrations given in this paper are, with the exception of

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[1]) H. A. Vermeulen. The vagus area in Camelidae. Kon. Acad. van Wetensch. at Amsterdam. Meeting of 27th February 1915. Vol. XVII.

the schemata, traced from microphotos made in the above-mentioned Institute.

The dorsal motor vagus nucleus. In no other mammal I have ever examined, does such a large part of this nucleus lie in the closed portion of the oblongata. In the horse, the ox and the sheep $^2/_5$ of this nucleus lie spinally from the calamus, in the pig and the dog it is nearly equally divided between the closed and the open parts of the oblongata, in the goat, the lama and the camel $^3/_5$, and in the giraffe no less than c.c. $^4/_5$ are situated spinally from the calamus (series of 1295 sections, 1007 of which spinal and 278 frontal from the calamus) (fig. 1). It makes its appearance with a few cells at the usual place, dorso-laterally from the canalis centralis. Some scores of sections frontally it is still poorly developed, and not unfrequently is entirely absent. In spite of its defective development, its appearance in this region varies. Sometimes a few cells are seen, clustered in a small group, while again we see a greater number, several of which have shifted into a more ventral level, or we see a narrow row of cells running horizontally and spreading laterally. Where in these last cases the cells, which in former sections lay

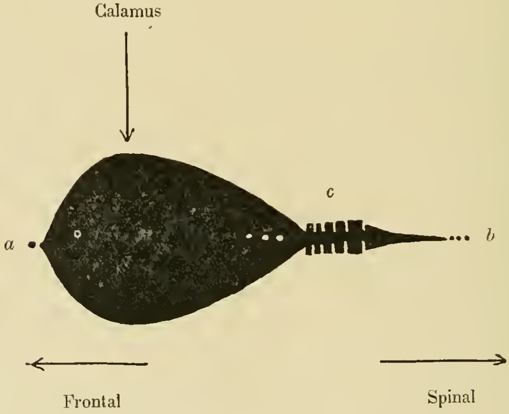
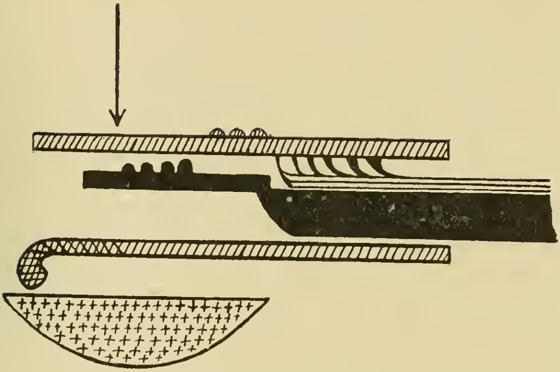


Fig. 1. Dorsal motor vagus nucleus of Giraffe.
a. Separate cell-group at the frontal pole.
b. Separate cell-groupe at the spinal pole.
c. Increases by fusion with nucleus XI.
o o o nucleus motorius commissuralis vagi.



EXPLANATION OF THE MARKS.

↓ = Calamus ▨ = Oliva inferior ▦ = Nucleus IX

▧ = Nucl. X ≡ = Nucl. XI ■ = Nucl. XII + Cervical I

Fig. 2.

Fig. 3. Union of nucleus dorsalis motorius vagi with nucleus accessorii; shifting of vaguscells in a more ventral level.

mostly medial, have disappeared in one or two sections, we are struck by the strongly lateral position of the cell group in the direction of nucleus XI on the border of the anterior and posterior horns. Further frontally we see the significance of this, for very speedily the nucleus accessorii appears at this place, and we notice in 11 consecutive sections a complete merging of the accessorius and dorsal-motor vagus nucleus (fig. 3), such as I have shown, though in a lesser degree, in the camel and the lama. In the same region there are also constant cells belonging to the vagus group, which have sunk into a more ventral level; in general these more ventrally situated cells are longer than those of the vagus type, and in this respect bear more resemblance to those of the nucleus XI. (fig. 3). After the dorsal motor vagus nucleus has separated from the accessorius nucleus and the latter at this place has disappeared, except for a few cells, the former numbers 15—16 cells, frequently to be seen more or less clearly arranged in two rows one above the other. Rather more frontally the nucleus XI manifests itself again more strongly and shortly after it is clearly seen to unite with the vagus nucleus in question. This time too they separate again, and the accessorius nucleus disappears entirely or almost entirely, after which the dorsal motor vagus nucleus appears as a loosely built group of cells, containing on an average 20 cells. The whole is more or less oval, with the blunt pole pointing laterally. Striking is the large size of the cell type in this region; ventrally shifted cells are no longer to be seen. A few sections more frontally the cell type becomes smaller again, and the nucleus decreases considerably in size, containing in many sections not more than 3 or 4 cells, the accessorius nucleus, however, soon appears again, and the process of uniting with the vagus nucleus is gone through for the third time. Now, however, the two nuclei are but a short time united, and only in a few sections is the closer connection between X and XI to be seen. Simultaneously, however, vagus cells have shifted into a more ventral level. The whole process, viz. the decrease in size of nucleus X dorsalis, then a union with the accessorius nucleus, accompanied by a spreading of the vagus cells into a more ventral region, takes place twice more, though in lesser degree. In the giraffe the union of the dorsal motor vagus nucleus with the accessorius nucleus thus successively occurs at five consecutive places. (fig. 2). This takes place before anything can be seen of the tongue nucleus. From this moment the dorsal motor vagus nucleus occurs constantly; it is loosely built and egg-shaped, with the blunt pole pointing ventro-laterally, and contains 20—25, mostly large cells (maximal 50 μ); a peculiarity here is, that sometimes the laterally situated cells are of a larger type than those lying more medially. As in the lama and the camel, the cell groups from the right and left come right to the raphe and soon we see here too a commissural motor vagus nucleus appear, as I have described in the lama and camel. It appears near the spinal pole of nucleus XII, is less developed than in Camelidae and not constant in appearance (fig. 1, 2 and 4).

Whenever the tongue nucleus is well developed, the dorsal motor vagus nucleus becomes much compacter and its ventro-

Fig. 4. Nucleus motorius commissuralis vagi. *c*. Canalis centralis

lateral part grows out into a curved point. Its base is then directed medio-dorsally, so that it more or less assumes the form of a sickle. In a great number of sections we see that many cells have shifted ventrally, so that not unfrequently an actual bridge has been formed between it and the nucleus hypoglossi. It contains in this region 90—100 cells (fig. 5). More frontally the ventro-lateral pole sinks more and more, and the nuclei diverge to right and left. The development of the nucleus is not equal everywhere. At times it is remarkably strong, with a large type of cell predominating. At other places the number of cells is much smaller and the cell group shows gaps. In a following region the form of the nucleus is irregular, as, besides the cells which have moved ventrally, some cells have also dropped out in a dorso-lateral direction; these are frequently classed in separate cell groups. Near the calamus the nucleus becomes clumsy in form, separate localisations can now be clearly seen, owing to cell groups severing

Fig. 5 Sickle-shaped dorsal motor vagus nucleus; connection with nucleus XII.

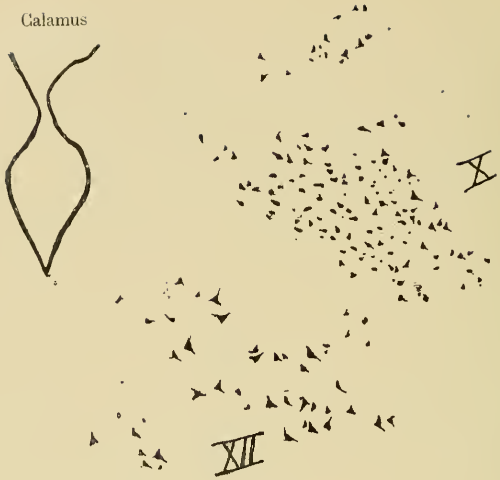


Fig. 6.

Fig. 7.

dorso-medially and dorso-laterally from the large body (fig. 6). That these groups belong to the vagus nucleus we learn from the sections immediately frontal from the calamus, where it is seen that the nucleus enlarges in the above direction by means of cells, which unite with these cell groups. Also the ventro-lateral point stretches further out (fig. 7); not unfrequently this is broken, so that the most distal portion appears as a separate cell group. On this level many cell groups have as many as c.c. 200 cells. Further frontally the ventro-lateral point disappears, the dorso-lateral one becomes thicker, till the nucleus is triangular in form with a broad base in the direction of the ependyma. Now two or three independent cell-groups frequently appear in the latero-dorsal portion, sometimes quite separate from the chief nucleus, again connected with it by a few cells. (fig. 8) These can be seen even when the chief nucleus has become considerably smaller, which takes place at first medially; simultaneously the number of cells in the whole nucleus decreases, so that it becomes looser. According as the nucleus decreases in size, the cell-type becomes smaller, till finally this cell-type, for this nucleus is a large one, is no longer seen in the ventro-lateral, i.e. the oldest, portion. In the giraffe it is remarkable that 20 sections more frontally from the place where the dorsal motor vagus nucleus entirely disappeared,

Fig. 8.

it reappears as a small cell-group which is seen for about 40 sections and then disappears definitively.

Nucleus ambiguus. In general the ambiguus is well developed in the giraffe. In the most spinal portion alone, it is small, contains 8—12 cells only. On this level I have been able to show repeatedly and more distinctly than was the case in the camel and the lama, the simultaneous presence of the nucleus dorsalis vagi, the nucleus accessorii and the ambiguus. Near the spinal pole of the tongue nucleus, however, the ambiguus of the giraffe has often grown to a powerful nucleus which, though varying in size, is seen to be constant in numerous sections. In the strongest development at this place we see a loosely built nucleus of about 45 large cells, all arranged in a ventro-lateral direction (fig. 9). Frequently the ventro-lateral part is noticeably more developed than the rest. This portion soon grows out medially in a nearly horizontal direction with a particularly large cell-type, till the whole has more or less the form of an equilateral triangle, with the fewest cells in the centre and at the medial side (fig. 10). Sometimes in successive sections we see mainly the basis of the triangle, so that the nucleus then appears as a horizontal column consisting of extremely large cells. In circa 300 successive sections the ambiguus in this region is clearly visible in the form described above, after which it varies very much, sometimes being altogether absent: in the most places, however, it is present in various forms, though less well developed than before; we can distinguish two separate cell groups, a medio dorsal and a ventro-lateral (nucleus laryngeus and nucleus cardiacus of Kosaka and Yagita) or only the ventro-lateral part of it, sometimes attached to these we see scattered cells which impart to the whole a sort of form of a triangle in which the nucleus is seen more spinally. We now see it growing gradually till it gets near the calamus,

Fig. 9.

Fig. 10.

and assuming the same forms as before. First a large loose group, in which as many as 50 cells may be counted, and then the triangle with all its derivatives, now mainly the base, again the base with the lateral side or the whole triangle. Sometimes the three corners are sharply defined by fine groups of cells, while here the characteristic shape of the ambiguus with its dorso-medial and ventro-lateral parts is also present. In the calamus there is again a decrease to 8—12 cells lying in ventro-lateral direction, while from the calamus to the frontal pole of nucleus XII, the development is much less marked than spinally from the calamus. The greatest number of cells contained here by the ambiguus is 18—20, sometimes it is altogether absent. At the frontal pole of the tongue nucleus we see very clearly in few sections the sinking of a few ambiguus cells into a more ventral level, and very soon the huge frontal bulging makes its appearance. This grows to an irregular oval form, with a maximum of 110 cells, the majority being large, genuine ambiguus cells. As in the lama and the camel the cells here are not crowded together but lie rather scattered. Ventrally from this large group is a smaller one, consisting principally of cells of a much smaller type. Whether this group too belongs to the ambiguus I do not venture to assert (fig. 2 and 11). As usual the bulging of the ambiguus begins to decrease at the frontal pole of the dorsal motor vagus nucleus and soon after decreases rapidly. Ten sections before its final disappearance it has still 25 cells. In this animal the frontal pole of the ambiguus stretches 46 sections frontally from the dorsal motor vagus nucleus (fig. 2), and reaches over a stretch of 12 sections the region of the nucl. facialis. The remainder of the ambiguus then lies dorso-medially from the caudal pole of nucl. VII.


Fig. 11.

Nucleus accessorii. In this series the first XI cells can be seen on the border of the anterior and posterior horns, 1188 sections spinally from the appearance of the nucleus motorius dorsalis vagi. These increase and a group of 14 cells is soon present, of a smaller type than the large motor cells of the anterior horn. It rapidly decreases in size and soon disappears altogether at this place. Cells of a similar type appear however in several sections, dorso-laterally from the canalis centralis, further lateral than where the dorsal motor vagus nucleus will presently appear; in other sections similar cells are to be seen still further lateral in the grey matter, directly medial from the angle between the anterior and posterior horns. Thereupon the XI nucleus again appears at the sharply defined place described above, and we can see how frontal horn cells of the lateral group have risen so high that they lie in the grey matter between the anterior and posterior horns and form a whole with nucleus XI, so that the impression is repeatedly conveyed as if the XI nucleus at that place is reinforced by frontal horn cells in its most ventral part, or that the XI nucleus itself continues ventrally along the lateral border of the frontal horn (fig. 12). More frontally the XI nucleus developed very differently, sometimes minimally, only to appear again stronger than before. It then contains as many as 32 cells. At the point of greatest development it is pear-shaped, with the point projecting laterally into the substantia reticularis; many cells exhibit a larger type than formerly, and here also a contact with frontal horn elements can be observed repeatedly (fig. 13).

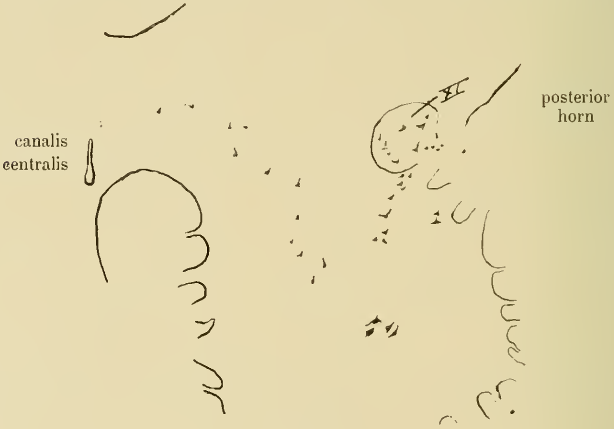


Fig. 12.

When the nucleus again commences to decrease, we frequently see that only the most lateral portion is developed, so that in these sections it lies exclusively in the substantia reticularis: in other places we see that only the middle part of the whole has disappeared and that the nucleus then consists of a medial and a lateral portion, the former at the usual place between the anterior and posterior horns: the latter lying lateral from it in the substantia reticularis (fig. 14).

Fig. 13.

Likewise in this region it can be seen that cells sometimes occur medially from the whole, in the so-called middle horn, dorso-lateral from the canalis centralis, as has been found before. Now follow scores of sections in which the XI nucleus is not present at the usual place, or but faintly indicated, though lateral frontal-horn cells with a strong upward tendency can be seen, or cells in a horizontal direction, lateral in the middle horn. This is followed again by a marked bulging and laterally by a growth of the XI nucleus in the substantia reticularis to a complex of a maximum of 38 cells, after which the reduction begins again under

Fig. 14.
a medial. *b* lateral part of × 1.

the same conditions as before. Locally again one medial and one lateral portion of the nucleus occurs, or either one of the two portions, or cells in the middle horn are seen. The contact with frontal horn cells is then present again. The same process repeats itself several times and the medial part, in the direction therefore of the place where the dorsal motor vagus nucleus will shortly appear, is frequently met with better developed than before. In this series we thus see in the first cervical segment, varying frequently at the place already mentioned, an extremely poor development of the accessorius nucleus, followed by a gradual strengthening and an outgrowth of it, both in a medial and in a lateral direction, together with a contact with front horn cells (or shifting in a ventro-lateral direction) till the dorsal motor vagus nucleus appears and the repeated merging of the latter with the XI nucleus begins, as has been mentioned in the description of the said vagus nucleus (fig. 2). The last union of the two nuclei occurs 40 sections spinally from the appearance of the first XII cells, in a region where the frontal horns are still well developed and nothing is to be seen of the oliva inferior.

Also in the Weigert-Pal, van Gieson and Sheldon series the XI nucleus was in the first cervical segment to be seen at the place already indicated. The ending of the nervus accessorii could be traced in many sections. Frequently we see several bundles leave through the processus posterolateralis of Ziehen, often three parallel to each other, first an upward arch, parallel to the distal portion of the posterior horn, and then laterally. These bundles do not leave the nucleus directly, but first take a medial curve before leaving grey matter. In a few preparations it was observed that fibres joined these bundles from a more centrally situated region, and also from a more ventrally situated region. Besides the above bundles fibres also leave the XI nucleus and a little further distally, directly i.e. without a central curve. Also in the 2nd. cervical segment efferent XI roots were to be seen, but far fewer in number and of poorer development than in the 1st. Only in a few sections could indications of the XI nucleus be demonstrated on the border of the anterior and posterior horns, though in several sections cells could be seen in the processus postero-lateralis, through which the efferent root takes its way. Judging from the great decrease in the efferent XI roots in the 2nd. cervical segment, it may be assumed that in the giraffe the nervus accessorius spinalis extends only to the 2nd. cervical segment, or perhaps a little further distally of it. In view, however, of the important function this nerve has undoubtedly to fulfil in this animal, it must not be considered impossible that the XI nucleus extends still further and that XI fibres with cervical nerves leave more distally, as is the case in the Camelidae, where a nervous accessorius spinalis is entirely absent.

Nucleus hypoglossi. Before the appearance of the XII nucleus the dorsal motor vagus nucleus is well developed and efferent XII fibres are visible; the direct continuation of nucleus XII out of the frontal horn grey matter can be clearly demonstrated in the giraffe as in the lama and the camel (fig. 2), typical large front-horn cells shift to a higher level and soon arrange themselves in a group of XII cells. In this series this occurs 496 sections spinally from the calamus. First a cell-group appears lying ventro-laterally from the canal and consisting of 6—10 cells; this group retains the same degree of development in many of the following sections. We see repeatedly cells in this area between the dorsal motor vagus nucleus and the tongue nucleus; they clearly belong to the vagus nucleus, in the first place by reason of their type, but in the second place because here there is always some distance between these ventral vagus cells and the tongue nucleus (fig. 15). After this the nucleus XII grows out, first dorso-laterally and then medially in the direction of the raphe. The nucleus then contains 30—35 large cells, the majority attain the maximum diameter of 85 μ; only in the dorsolateral group are

Fig. 15.

Fig. 16.

there often cells of a smaller type. Very shortly, in a more ventral region than where the first XII cells had occurred and medially from there a fourth group of cells appears, so that a large complex is formed, shaped like a slanting quadrilateral, containing 70—90 cells.

Here we can clearly distinguish a ventro-medial, a ventro-lateral, a dorso-medial and a dorso-lateral group. In many sections a few cells also occur in the centrum, while in all there are numbers of cells between the tongue nucleus and the dorsal motor vagus nucleus. Not unfrequently an actual bridge exists between the two nuclei (nucleus intermedius, fig. 16). Slightly more frontally both nuclei strike against the raphe and 168 sections spinally from the calamus a few XII cells appear in the raphe, whereupon a nucleus commissuralis hypoglossi makes its appearance (fig. 17). In this region many central cells appear in the irregular quadrilateral tongue nucleus. The commissural tongue nucleus does not seem to follow any continuous course, in a few consecutive sections it is present. Everywhere the connecting cells are met with between the tongue nucleus and the adjacent vagus nucleus. Now the XII nucleus begins to diminish in size, it becomes loose in structure, and shows gaps at different places, only the latero-dorsal and lateroventral portions remain constant, even commissural cells are now and again seen and not unfrequently the bridge to the dorsal motor vagus nucleus is complete. Then the central cells disappear entirely, and the latero-ventral portion also diminishes, so that it is mainly only the latero-dorsal part and the cells connecting with the vagus nucleus which are still properly visible. More frontally, more XII cells again appear and the irregular quadrilateral gradually reappears though in a less marked

Fig. 17.

degree than before; the centrum remains poor in cells. This process repeats itself for a third time; then practically all cells disappear, with the exception of the dorso-lateral portion and the connecting bridge with the X dorsalis; a few commissural cells still occur occasionally. In the calamus the grouping is different; the medial and dorso-lateral groups merge into an elongated triangular whole, the apex of which points ventrolaterally; ventrally from this lie the ventro-medial and the ventro-lateral groups, now fairly well on the same level (fig. 18).

Fig. 18.

Also in this region of the tongue nucleus a few cells can be observed in the raphe; they no longer show, however, the striking hypoglossus type, but have become much smaller. The former group is of the same shape as the nucleus hypoglossi in other animals, triangular in form and with a majority of large cells, it lies medially under the ependyma of the fourth ventricle; the ventral groups are different, occasionally they converge so that we see a second tongue nucleus ventrally from the usual tongue nucleus, built up of a fairly broad horizontal row of cells, the cell-type of which has grown smaller than of that lying dorsally (fig. 19); in general, however, the ventral tongue nucleus consists of a medial and a lateral portion. Between the lateral portion and the dorsal tongue nucleus we often find a few large XII cells (fig. 19); not unfrequently, however, the two main groups are quite separated from each other. The medial group of the ventral tongue-nucleus has shifted away from the raphe and simultaneously a small group of little cells appear between the tongue nucleus and the raphe (nucleus funiculi teretis) (fig. 19*a*); the bridge of connection with the vagus nucleus has vanished and in its place one or more small groups of cells have appeared (nucleus intercalatus Staderini) (fig. 19*b*). These

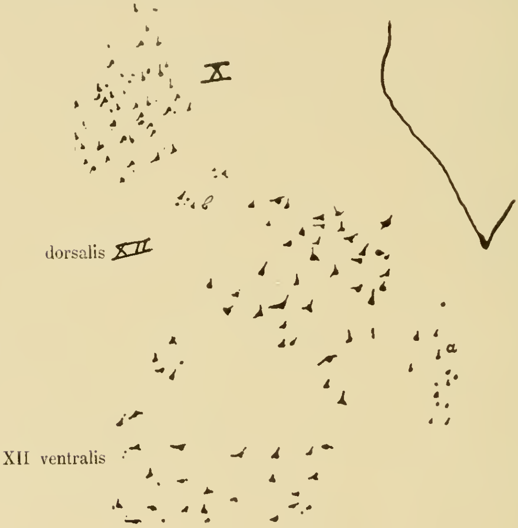


Fig. 19.

lie thus laterally from the dorsal tongue nucleus, i. e. between the latter and the dorsal motor vagus nucleus. Some cells of these last groups are of a larger type than those of the group next the raphe. The ventral tongue nucleus gradually diminishes: the cell type has grown smaller, the medial portion disappears first, the lateral portion, lying under the ventral point of XII. dorsalis remains longest in existence (fig. 20). The cell-group between the raphe has grown larger; it contains ± 30 cells, many of a larger type than these which first appear; soon similar cells also appear here in the raphe, so that the two small cellular nuclei are connected medially from the tongue nuclei by a group of cells. In this region too we often see tiny cells and little cell-groups between tongue and vagus nucleus. The distal nucleus soon completely disappears, but still further frontally the aspect changes again. The dorsal portion of XII. dorsalis vanishes, the lateral portion of XII. ventralis again appears, after which the latter combines with the rest of XII. dorsalis to make one large whole; the cell-group nearest the raphe has grown greatly, on the one hand it has extended medioventrally, on the other hand it has approached close to the ependyma; the little cell-groups between XII. and X. dorsalis occur inconstantly, not unfrequently a gradual parvo-cellular continuation of the nucleus funiculi teretis can be seen into the nucleus intercalatus Staderini over the tongue nucleus. The latter decreases rapidly in size; 168 sections frontally from the calamus it has disappeared; the ventrolateral portion remains longest in existence.

Fig. 20.

The oliva inferior of the giraffe appears in the latero-ventral region of the spinal pole of nucleus XII. and soon grows strongly in a medial direction, which medial portion presently curves upwards and begins to form a powerful lamel growing in a lateral direction. Very soon the olives from the right and left join at the raphe and a little further forward we can clearly see a connecting olive in the raphe. Near the calamus the olives have again receded from the raphe and the dorsal lamel loses itself in several cell-groups lying one behind the other, in which the celltype in general is larger than it was before. The strongly developed olive clearly bulges ventrally. It diminishes first laterally, then ventrally, and extends 360 sections frontally from the calamus, i.e. to just in front of the frontal end of the ambiguus (36 sections).

The nucleus reticularis inferior makes its appearance 85 sections spinally from the oliva inferior and dorso-laterally from it, with cells which for reticular elements are small. Frequently it breaks up into several cell-groups, locally we find also raphe cells in this spinal portion ; more frontally it extends over the olive in a medial direction, whereby the inclination towards the formation of cellclusters again shows itself, after which it begins to decrease in size spinally from the calamus ; the cell type becomes larger and the presence of raphe cells more constant. As far as the front poles of the vagus nuclei clusters of large cells next the raphe and of cells lying scattered laterally from it can be observed, after which the former groups become fewer and the latter still remain visible. In general the nucleus reticularis inferior is poorly developed in the giraffe.

As regards the occurrence of the commissural motor vagus nucleus in the giraffe, I refer to what I have remarked already in my paper to the Kon. Acad. v. Wetensch. at Amsterdam. on Jan. 18, 1915, The vagus area in Camelidae.

Although the presence of glands in the oesophagus and proventriculi of the giraffe has not yet been demonstrated, and this argument cannot as yet be advanced for an extension of the dorsal motor vagus nucleus with the commissural nucleus, yet the extreme length of the gullet in this animal, even more than in Camelidae, may be regarded as an argument in favour of the above opinion. The enormous development of the tongue nucleus and its extension with the commissural tongue nucleus has undoubtedly something to do with the extremely intensive use that the giraffe makes of its tongue as a prehensile organ ; as a rule this animal feeds on the leaves from the tops of high palm-trees, seizing them with its tongue and pulling them off. Regarding the significance of the presence of a commissural nucleus funiculi teretis and its direct passing into the nucleus intercalatus Staderini, I am not in a position to give fuller details. The strikingly strong development of a great part of the nucleus ambiguus spinally from the calamus furnished a strong contrast with the appearance of the nucleus at this place in Camelidae. I believe that a relation may be assumed between the short recurrent course of the nervus laryngeus inferior and the poor development of the nucleus ambiguus in its spinal third part in Camelidae. If this be so, one might conclude, judging from the strong development of the nucleus at this place in the giraffe, that the nervus recurrens, even in this animal in spite of its long neck, well deserves its name, in which case the highly exceptional conditions of this nerve in Camelidae have wrongly been connected by Lesbre with the unusually long neck of these animals.

As regards the conditions of the nucleus accessorii in the giraffe I wish to make the following observation. No agreement exists yet as to the position, extent and nature of this nucleus. Most observers are agreed upon the position of it in the first cervical segment, viz. about the level of its leaving the nervus accessorius, on the border of the anterior and posterior horns and their neighbourhood, or, according to the nomenclature of Waldeyer, in the lateral portion of the. middle horn. This position has already been fixed by Clarke. Roller and Darkewitsch believed that here also the XI nucleus was situated in the most ventro-lateral portion of the frontal horn. According to Dees only the most dorsal of the cells of this group belong to the cells of the accessorius nucleus, while only anterior horn roots arise in the ventral. He pointed out that in the cranial part of the first cervical segment the XI nucleus shifts to the anterior horn and then comes to lie sideways: Kaiser too indicates that spinally from the first cervical segment the XI nucleus shifts distally. According to Obersteiner the said nucleus lies first (5th cervical segment) dorso-lateral in the anterior horn, near its border; in a cerebral direction, however, it shifts centrally, to pass over into the nucleus ambiguus. Cajal indicates as the position of the XI nucleus, as regards the spinal portion, the lateral edge of the frontal horn, and more frontally the whole dorsal half of that. Kappers, found the nucleus on a frontal level, dorso-lateral from the canalis centralis, spinally more latero-ventral towards the border of anterior and posterior horns and finally latero-ventral from it. Langelaan also describes the nucleus in the dorso-lateral portion of the front horn, and from the illustration it appears that here too the boundary between the anterior and posterior horns is meant. Jacobsohn and Walter assume ascending cells from the medial group of frontal horn cells to the nucleus accessorii; Ziehen states that the nucleus in question, in the 1st cervical segment is formed by a pyramidal protrusion of the gray matter radiating at the base of the anterior horn into the substantia reticularis, which protrusion he names processus postero-lateralis cornu anterioris, and which he regards as a direct continuation of the dorso-lateral group of frontal horn cells.

From what I have found in consecutive series of lama, camel and giraffe, I believe I may conclude that spinally from the 1st. cervical segment the nucleus accessorii gradually ascends out of the latero-dorsal portion of the anterior horn, and thereby comes to lie on the border of the anterior and posterior horns and that, when once there, it can spread out both in a lateral direction into the substantia reticularis and into the processus postero-lateralis, and in a medial direction towards the central canal. The general opinion, and the one still expressed by Obersteiner in the latest edition of his text book, viz. that the nucleus XI continues frontally into the nucleus ambiguus, I am unable to share. In the first place I have demonstrated the direct transition of the nucleus accessorii and the nucleus motorius dorsalis vagi in Camelidae and much clearer still in the giraffe, and I have, moreover, shown in these animals, and especially in the last-mentioned, the simultaneous presence of ambiguus and nucleus XI. For the same reasons I consider the nomenclature in the atlas of Winkler and Potter (Anatomical Guide to Experimental Researches on the Cat's Brain plate 35) in which the nucleus of origin of the nervus accessorius spinalis is called nucleus ambiguus inferior, not a happy one. As regards the connection of nucleus XI with nucleus motorius dorsalis X in the spinal portion of the oblongata I may mention that the observation made by Kappers, who saw this union in embryos of sheep has been confirmed by myself in a calf's foetus ($4^1/_2$ months) and that I have again found undoubted indications of such a connection in a new-born lamb and in a new-born pig. (fig. 21)

As regards the spreading of the accessorius nucleus, it will be known that this varies very much in a spinal direction, according to the species of animal: the cerebral pole, however, is also described very differently. v. Gehuchten is of opinion that the frontal pole of this nucleus should lie in the first cervical segment. Darkewitsch, on the other hand, gave the distal third portion of the oliva inferior, thus quite in the hypoglossus region, v. Bunzl-Federn thinks it reaches as far as the rise of nucleus XII, while Grabower and Ziehen mention the region of the pyramidal decussation. (Ziehen, Nerven-system.)

In the giraffe this pole can be indicated directly behind the spinal end of the tongue nucleus and the oliva inferior. In any case it may be regarded as an established fact after what I have found in Camelidae, and so clearly and repeatedly confirmed in the giraffe, that the accessorius nucleus has also a bulbar part and that the difference between a nervus accessorius spinalis and bulbaris, challenged by Cajal and Kosaka, is correct.

The appearance of the nucleus XI, like that of the ambiguus, is very different; in continuous series of the 1st. cervical segment and

Fig. 21. Calf's foetus about $4^1/_2$ months.

of the region of it lying here cranially, i.e. at the place where the nucleus by reason of its position between anterior and posterior horns is most sharply defined and therefore easiest to follow, this can be seen very clearly and frequently in the neighbourhood of places where the nucleus is very strongly developed, it will be found that it is greatly reduced, often indeed quite absent. **Dees** has shown the so-called rosary-shaped development of the nucleus accessorii in longitudinal sections.

Also as regards the nature of the XI nucleus, various opinions exist. **Edinger** describes the motor bulbar nuclei as continuations of the frontal horn grey matter, which have been disturbed in their continuity, and explains the dorso-medial position, with respect to the ventral system of most of them as follows: owing to the upward rise of the central canal, the motory regions lying below rise too, whereby the sensory regions at the same time are pressed laterally. This conception cannot be disputed as regards the tongue nucleus. As for the glosso-pharyngeo-vago-accessorius system, however, the conclusion drawn by **Kappers** is in contradiction to it. On the basis of his phylogenetic and embryologic studies, KAPPERS came to the conviction that the nucleus accessorii and the ambiguus have nothing to do with the spinal system, but that both are direct continuations of the dorsal motor vagus nucleus; the accessorius nucleus exhibits hereby the peculiarity that it grows from its cerebral origin into the cervical cord, sometimes along almost its entire length. My confirmation of this position of the XI nucleus and the dorsal motor vagus nucleus in a calf's foetus, in ovis aries neonatus and sus scrofa domesticus neonatus, of what KAPPERS found in embryos of sheep, and especially the fact that the connection between these two nuclei is still to be found in Camelidae and so clearly and repeatedly in the giraffe, strengthen, in my opinion, KAPPERS' theory to no small extent. Other difficulties, however, present themselves with regard to this question.

BOLK has described that also anterior horn roots leave with the nervus accessorius, so that what has never yet been demonstrated in any other place in the animal body takes place here, viz. that visceromotor and somatomotor fibres unite. I have now observed that in the first cervical segment of the giraffe, cells from the anterior horn join the accessorius nucleus. The question is now whether these are genuine frontal horn cells or accessorius cells. Only from the first cervical segment do we find frontally, the XI nucleus at the sharply defined place, viz. or mainly at least, in the corner between the anterior and posterior horns; if we follow this nucleus spinally we see the connection with motor cells on the dorso-lateral border of the frontal horn, but later we can affirm that the XI nucleus has disappeared entirely from the corner indicated, although in this and even in regions lying much more caudally the nervus accessorius may arise and in that case its nucleus must still be present; in other words, this nucleus may have sunk away in the midst of genuine frontal horn cells and the derivatives of the dorsal motor vagus nucleus may finally disappear in the middle of the motor elements of the grey matter of the neck. There is therefore the possibility that the bundles described by BOLK contain accessorius fibres after all, I will add, however, immediately that I am willing to admit the possibility of a simultaneous rise of XI and frontal horn roots, in the first place because a priori the coincidence of viscero-motor and somatomotor fibres must not be considered as impossible in view of the fact that everywhere motory, sensory, and autonomic fibres combine, and in the second place because of the fact that in Camelidae XI fibres must necessarily originate together with cervical nerves. These animals have a musculus trapezius, a nucleus accessori spinalis and no nervus accessorius spinalis. (This observation of **Lesbre**'s has been confirmed by Professor **Wingate Todd** of Cleveland in a letter directed to Dr. C. U. **Ariëns Kappers**).

A more difficult question is presented in this respect by the dorsal motor vagus nucleus itself. In the lower vertebrates numbers of cells leave the spinal portion of the nucleus out of the connection into a more ventral level; in the Alligator a part of the dorsal motor vagus nucleus is even attached to the frontal horn grey matter, and in birds to the tongue nucleus, which here forms the direct continuation of this grey matter (**Kappers**). In mammals the rise of the vagus and hypoglossus cells in the hypoglossus region between the two nuclei is a common phenomenon, which undeniably is as clearly seen in the giraffe as anywhere. Spinally from the nucleus XII,, however, it was apparent in many sections in the giraffe series, that these ventral cells form one whole with a series of frontal horn cells of small type, often an arched series of cells were even noticeable, which began deep in the frontal horn and ended dorsally from the central canal; the same was frequently observed in the first cervical segment, i. e. spinally from the dorsal motor vagus nucleus. My interest in this circumstance increased when I met the same phenomenon, though in a much stronger degree, in my series of the calf foetus, where these ventral cells of the said vagus nucleus, reaching deep into the motor horn, are of much larger type. This phenomenon was to be seen in this series, for instance, in these sections where there was a connection between this vagus nucleus and the XI nucleus (fig. 21). Thus in this respect also there are very primitive conditions in the giraffe as in the tongue nucleus, which I am unable to explain, the more so as I know nothing of the rise of the nervus vagus in this animal.

CONCLUSIONS.

1. The nervus accessorius spinalis occurs in the 1st and 2nd cervical segment in the giraffe as in the other mammals, with the exception of Camelidae.

2. Spinally from the nucleus XII. the dorsal motor vagus nucleus of the giraffe appears to be at five consecutive places in direct connection with nucleus XI.

3. In the most spinal portion the dorsal motor vagus nucleus of the giraffe does not occur constantly; in front of its frontal pole, there is still a small, quite separate, portion of this nucleus.

4. Frontally from the unions of Nucl. mot. X. dorsalis and

nucleus XI in the giraffe, a commissural motor vagus nucleus occurs which is not continued.

5. In the first cervical segment it is repeatedly observable that medial and central anterior horn cells of small type rise upwards like an arch to above the central canal at exactly the place where frontally from the nucleus mot. X dorsalis will appear; in the most spinal portion of the vagus nucleus numbers of vagus cells leave the connection for a more ventral level, and in a large portion of the hypoglossus region this is so often the case that the vagus and tongue nuclei are completely joined.

6. The ambiguus is strongly developed in a large part of that portion of the nucleus which lies in the closed portion of the oblongata, and occurs here often in forms which are not to be met with in other animals; the frontal growth of the ambiguus is very strongly developed and reaches the facialis region, somewhat cranially from the frontal pole of nucleus X dorsalis.

7. In the giraffe the simultaneous presence of nucl. mot. dorsalis vagi, nucleus access., and nucleus ambiguus is repeatedly to be met with.

8. In the spinal end of the oblongata the main group of the nucleus accessorii in the giraffe lies on the border of anterior and posterior horns; this nucleus, however, repeatedly radiates both in a medial and in a lateral direction. In the latter case the nucleus frequently consists of 2 groups, the medial one being at the usual place between the anterior and posterior horns, while the lateral one lies in the substantia reticularis. Spinally from this we see the direct connection of the nucleus with the cells lying on the latero-dorsal border of the frontal horn, and further spinally the nucleus does not occur again on the border of the anterior and posterior horns; behind the first cervical segment thus it shifts in a latero-ventral direction.

9. The tongue nucleus in the giraffe is, in comparison with the vagus nucleus, short but unusually strongly developed; frontal from the commissural motor vagus nucleus a commissural tongue nucleus occurs, which like the one mentioned above, is not continuous, but ends close to the calamus. In the same region the tongue nucleus has an irregular quadrilateral shape, more frontally it splits into a dorsal and a ventral portion.

10. The oliva inferior is strongly developed; there is a small connecting olive; the nucleus reticularis inferior is poorly developed.

Physics. — *"A difference between the action of light and of X-rays on the photographic plate".* By Prof. I. K. A. WERTHEIM SALOMONSON.

(Communicated in the meeting of September 25, 1915).

In a series of experiments on the quantitative action of *X*-rays and light on photographic plates, I found a characteristic difference between the two kinds of rays.

In these experiments so-called exposure-scales were made by exposing one half of a plate to regularly increasing light-quantities and the other half in the same way to Röntgen-rays. Both halves were developed at the same time in one developing tray and also fixed simultaneously in one tray.

On each of the negatives we find a series of small fields, which have been exposed to the action of light or of *x*-rays of intensities increasing in the ratio of 1, 2, 4, 8, 16 etc., and which show an increasing density. On the half exposed to the X-rays the time of exposure and the hardness of the rays are also recorded. The transparency of each of the small fields is photometrically measured. The reciproques of the figures obtained in this way give the *absorption-factor*, the logarithm of which is the optical *density*. From the figures for the density curves are drawn, the densities being plotted as ordinates to the logarithms of the exposures as ordinates, In this way we get the "characteristic curves" of the plates as used by HURTER and DRIFFIELD, EDER and others.

The different precautions taken in these experiments need not be described: sufficient be it that the exposures, once started, were automatically carried out, and that any irregularities in the intensity of the light and the X-radiation either could bear no influence on the result or could be immediately detected.

Curves like these always show a curvature convex to the X-axis corresponding to the underexposed part. The "correct exposures" give a straight line. This part generally commences at a density of roughly 0.5. The straight line prolonged to the axis of abscissae meets it in the "point of inertia" (Beharrungspunkt) which is used by HURTER and DRIFFIELD to indicate the "speed" of the plate. It is almost entirely independent of the time of development, the kind of developer used and its temperature, which influence only the slope of the curve in the straight part. We also know that the quantity of silver in a negative increases proportionally to the logarithm of the exposure.

TABLE 1.

I	*φ*	2 *log ctg φ*	*R*	*φ'*	2 *log ctg φ'*
Negative 5 A and 5 B.					
1	43°24′	0.049	1	38°19′30″	0.204
2	39.55 30″	0.155	2	33.34 30	0.356
4	33.45	0.350	4	26.24	0.615
8	23.12	0.736	8	17.37 30	0.996
16	14.30	1.175	16	10.52 30	1.433
32	8.0	1.704			
64	4.16 30	2.253			
Negative 6 A and 6 B.					
1	43°42′	0.039	1	40°49′30″	0.127
2	40. 4 30″	0.150	2	36.12	0.271
4	35.15	0.301	4	29.31 30	0.494
8	24.54	0.667	8	22. 6	0.783
16	16.13 30	1.072	16	15.27	1.117
32	10. 1 30	1.505			
64	8. 4 30	1.696			
Negative 7 A and 7 B.					
1	43°51′	0.035	1	41° 6′30″	0.118
2	42. 3	0.090	2	38.18	0.205
4	37.51	0.219	4	33.25 30	0.361
8	30.13 30″	0.469	8	26.19 30	0.611
16	20.12	0.868	16	18.19 30	0.960
32	12	1.355			
64	7. 9	1.803			
Negative 8 A and 8 B.					
1	44°	0.030	1	39°45′	0.160
2	40.48′	0.128	2	34.33	0.324
4	33.16 30″	0.366	4	26.43 30″	0.596
8	22.12	0.778	8	18.13 30	0.965
16	13.22 30	1.248	16	11.18	1.399
32	8. 7 30	1.691			
64	4.22 30	2.236			

In the next table I give the result of the measurement of 4 pair of negatives. (See p. 672)

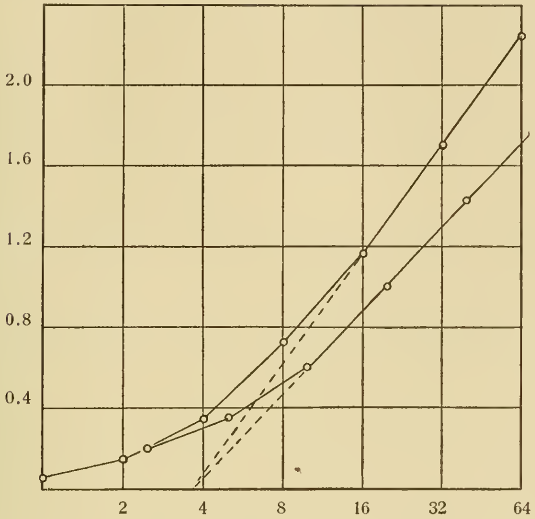


Fig. 1.

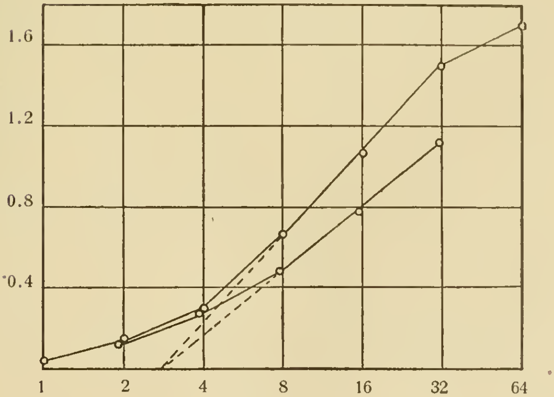


Fig. 2.

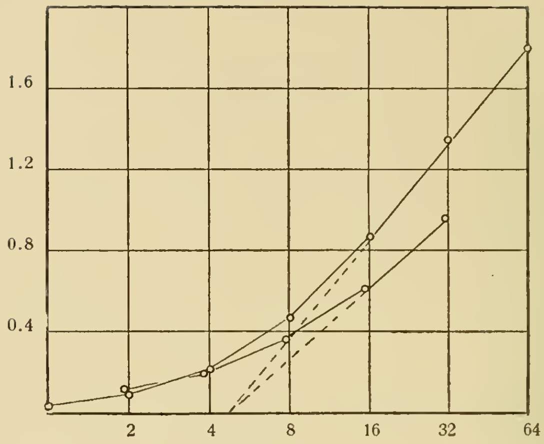


Fig. 3.

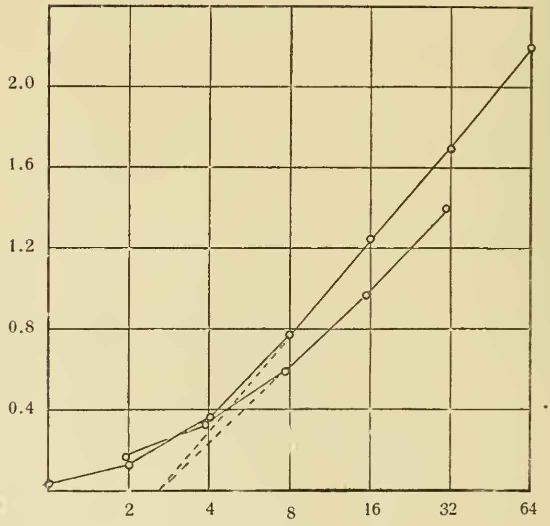


Fig. 4.

The fact to which I wish to draw attention is, that for every pair of negatives the characteristic curve for light slopes considerably more than the one for X-rays. This is clearly shown in fig. 1—4. Each of them contains two curves, the upper one showing the action of light, the lower one the X-ray curve. The slope of these curves always proved to be different in the manner indicated and to be independent of the development if only both halves of the plate were developed in the same tray for the same length of time without undue restriction of the time. Changes in the development merely caused changes in the slope of both curves at the same time and in the same way.

We may expect a physical difference in the action of light and of X-rays on the photographic plate. The sensitive layer strongly absorbs light, whereas X-rays are only slightly absorbed. As we know that the action of both kinds of rays increases with the intensity, we may in the case of light look for a strong action at the surface of the sensitive layer and for a markedly diminished action in the lower strata of the emulsion. In the case of X-rays which are not notably weakened after passing through the silver-bromide-emulsion we may reasonably expect that the action in the deeper layers is not less than the action on the surface. After development the reduced silver should be nearly equally deposited in every part of the gelatine layer if the negative had been obtained with X-rays. In light-negatives the silver would probably be accumulated on the surface and only a slight amount would be present in the deeper strata. Any one who has developed many light- and X-ray-negatives knows, that with the former only the parts exposed to the strongest lights are visible at the back after development but before fixing, whereas properly developed unfixed RÖNTGEN-negatives present nearly the same appearance at the back as on the front surface.

We may ask if this difference might be responsible for the difference in the slope of the characteristic curves. It seems to me that this is possible and even quite probable, if we consider the question in the following way.

Let us first consider how the reduced silver is deposited in light- and RÖNTGEN-negatives. After this we shall see how this effects their transparency.

We may represent the absorption of light and RÖNTGEN-rays in the gelatinobromide-emulsion by the well-known formula

$$I_l = I_0 \varepsilon^{-\mu l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which I_l is the intensity of the radiation after passing a layer of thickness l, I_0 being the intensity of the radiation at the surface, μ the absorption coefficient of the absorbing medium for the incident rays.

By multiplication by t, the time, and equating $I_l\, t = Q_l$ and $I_0\, t = Q_0$ we get;

$$Q_l = Q_0\, \varepsilon^{-\mu l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

a formula for the quantity of radiating energy at a distance of l below the surface. Differentiating 2 gives:

$$-\, d\, Q_l = Q_0\, \mu \varepsilon^{-\mu l}\, dl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

an expression for the light absorbed in a stratum of thickness dl at a distance l below the surface. As the quantity of silver reduced by development in this stratum is proportional to $-dQ_l$ we may put:

$$d\, Ag = k\, Q_0\, \mu\, \varepsilon^{-\mu l}\, dl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which integrated gives:

$$Ag = KQ_0\, (1 - \varepsilon^{-\mu l}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

as a formula for the total quantity of reduced silver between the surface and a layer at a distance l below it.

From (5) we deduce:

$$\frac{dAg}{dQ} = K\, (1 - \varepsilon^{-\mu l}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

i.e. the increase of silver caused by an increase of exposure depends on the absorptioncoefficient μ. If μ is large the differentialquotient is also large.

In order to calculate the density of the negative, we suppose that the absorption in an infinitely thin layer is proportional to the amount of silver in it and also with the intensity of the light falling on it. Using (4) for the quantity of silver we get the equation:

$$-\, d\, I_l = c\, I_l\ .\ K\, Q\, \mu\, \varepsilon^{-\mu l}\, dl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or after integration

$$D = log\, \frac{I_0}{I_l} = cK\, Q\, (1 - \varepsilon^{-\mu l}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in which D is the density, I_0 the intensity of the light before, and I_l the same after passing through the negative.

From (8) we find:

$$\frac{dD}{dl} = c\, K\, (1 - \varepsilon^{-\mu l}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This last equation shows that the increase of density also depends on the absorption coefficient μ of the rays used in producing the negative.

These formulae are only available in cases of underexposure. For correct exposure we can get an expression by applying the empirical formula given by HURTER and DRIFFIELD. This formula (10) "represents the necessary relation between the density and the exposure which must be fulfilled if photography is true to nature" (HURTER).

This formula slightly modified is:

$$D = log \frac{I_0}{I_t} = a + b\, Ag = a_1 + b_1\, log\, Q \, . \quad . \quad . \quad . \quad (10)$$

in which a, a_1, b and b_1 are numerical constants, Ag the total quantity of reduced silver, Q the total energy of the light. If we use the expression for Ag from (5) in this formula we get:

$$D = log \frac{I_0}{I_t} = a + b\, Ag\,(1 - \varepsilon^{-\mu l}) = a_1 + b_1\, log\, Q\,(1 - \varepsilon^{-\mu l}) \; . \; (11)$$

in which we have also corrected the value for Q by using (8) and putting in it only that part of Q which really has been absorbed.

If the results of this discussion represent the facts with sufficient accuracy, we may draw the conclusion, that between light- and Röntgen-negatives still another point of difference should exist.

We may expect that in cases of the same density a light-negative contains considerably less silver than a Röntgen-negative; in cases of light- and Röntgen-negatives containing the same quantity of reduced silver, the transparency of the latter will invariably be greater.

In order to test the truth of these conclusions I asked my assistant Dr. KATZ to make a careful quantitative analysis of the amount of silver in a set of larger plates forming together an exposure-scale. The 10 plates measuring nearly 10 × 15 cm. were cut from one plate 30 × 40 cm. Five of them were used for the lightscale, the other 5 for the Röntgen-exposure scale. The results of all the measurements are given in table II. (See p. 678),

The vertical columns contain: Under Plate 42 the number of each plate; under Q the relative quantities of light; under φ we find the reading of the polarisation photometer; under 2 $log\, ctg\, \varphi$ the measured density, whereas the next column contains the most probable value for the calculated density, supposing a linear relation between $log\, I$ and $log\, ctg\, \varphi$. The following vertical columns contain: the measured quantity of silver on the whole surface of each plate, the exact measured surface, the quantity of silver per square centimeter. In the last column the most probable quantity of silver is given, calculated on the supposition of a linear relation between $log\, Q$ and

TABLE II.

Plate 42	Q	φ	$2\log \mathrm{ctg}\,\varphi$ meas.	$2\log \mathrm{ctg}\,\varphi$ calc.	mgr. silver	Surface	Ag p. cm^2 meas.	Ag p. cm^2 calc.
L_1	1	25°0′	0.663	0.6654	19.4	96.7	0.201	0.1954
L_2	2	14.34½	1.170	1.1590	28.6	93.7	0.306	0.3202
L_3	4	8.50½	1.617	1.6526	39.9	88.4	0.452	0.4451
L_4	8	4.34½	2.194	2.1462	57.7	99.7	0.578	0.5700
L_5	16	2.48½	2.619	2.6398	69.1	100.7	0.689	0.6948
R_1	1	37°33′	0.228		15.1	93.6	0.161	0.1582
R_2	2	32.21	0.397		21.0	97.3	0.216	..2190
R_3	4	26.3	0.622	0.6272	26.4	94.6	0.279	0.2798
R_4	8	17.0	1.029	1.0187	32.4	96.1	0.338	0.3406
R_5	16	11.13½	1.405	1.4102	39.9	98.6	0.405	0.4014

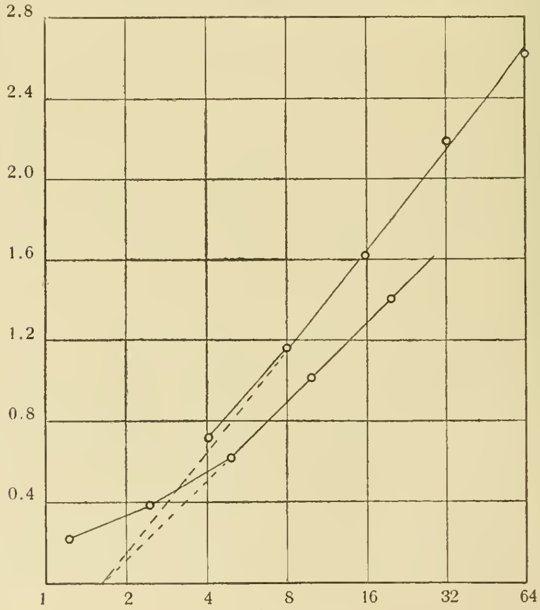


Fig. 5.

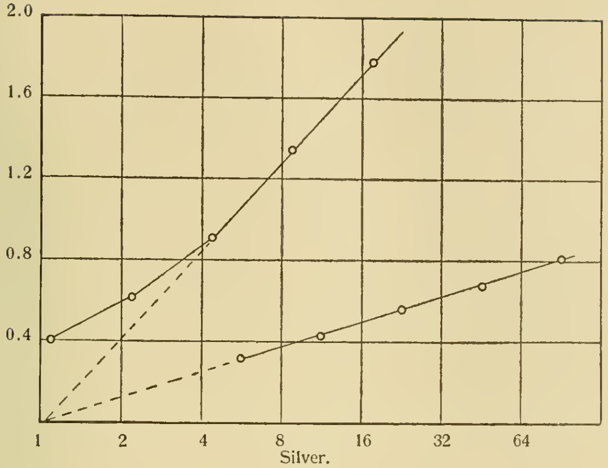


Fig. 6.

the quantity of silver per unit surface. The formulae used for the calculation of the figures on the 5th column were

$D_l = 0.1708 + 0.4138 \, log_{(2)} Q \; Q$ and $D_R = 0.5473 + 0.3915 \, log_{(2)} Q$.

The second formula was calculated from 3 figures only.

For the last column I used the formulae:

$100 \, Ag_l = 7.055 + 12.485 \, log_{(2)} Q$ and $100 \, Ag_R = 9.74 + 6.08 \, log_{(2)} Q$

We see immediately from the table, that the conclusion as to the difference in the amount of silver contained in the film after exposure to light and to X-rays seems to be true. We find that L_1 and R_3 show only a slight difference in density viz. 0.663 and 0.622, the Röntgennegative being the more transparent one. Yet this contains 0.279 mgr. of silver per unit whereas the denser light negative contains only 0,201 mgr. The same thing is found for L_2 and R_4.

If two negatives with nearly the same quantity of silver be compared, for instance L_1 and R_2. containing 0,201 and 0,216 mgr. of silver, we find the light-negative about 50 percent denser than the Röntgennegative, which, however, contains more silver.

I must advance still another argument in favour of my theoretical deductions. If these be true we ought also to expect differences in the slope of the characteristic curves when ordinary light waves of different length are used, the absorption-coefficients of which in bromide-silver-gelatine is different. In Eder's Handbook of Photography, Part III, we find on plate II a series of characteristic curves pertaining to light of different wavelength between 4100 and 5100. The curve for 4600 shows maximal action and also maximal slope. Experiments by **Eder** on orthochromatic plates, the curves of which are given on other plates, also prove the fact that stronger absorption or a large value for μ concurs with stronger slope in the curve.

Another fact mentioned by **Eder** (l.c. p. 223) is the greater density of collodion negatives as compared with gelatine-negatives containing the same amount of silver. As the former are notably thinner than gelatinefilms this is equivalent to a larger absorption in the thinner films. If, finally, the thickness of a layer containing a certain amount of silver is so far reduced that the conditions, present in a silver-mirror are approached, **Eder** finds that only 0,039 mgr. of silver per

TABLE III.

Number	$\frac{dS}{dL}$	$\frac{dS}{dR}$	Quotient	Hardness	Quotient calc.
5 *A* and *B*	.505	.409	1.232	7.2 BENOIST	1.250
6 *A* and *B*	.419	.311	1.349	6.1 „	1.336
7 *A* and *B*	.445	.300	1.482	4.2 „	1.483
8 *A* and *B*	.468	.401	1.167	8.4 „	1.157
42	.489	.391	1.250		

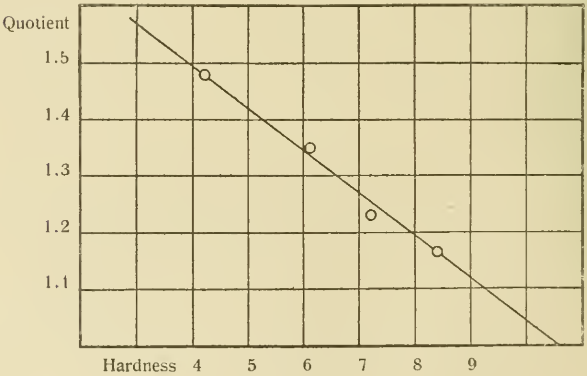


Fig. 7.

square centimeter is sufficient to produce a density of 1.5 and 0.052 mgr. of silver a density of 2.0.

On the other hand I found in my experiments one fact that at first sight did not agree with my deductions. If from the different series of experiments given in table I and II we calculate the increase of density with the increase of the action of the light and of the Röntgenrays, we find the figures given in table III, graphically represented in fig. 7. (See p. 680).

The first column gives the number of the experiment, the second one the increase of density when the action of light is doubled; the third one the increase of density on doubling the action of the Röntgenrays.

In the fourth column the quotient of the figures in the former columns is given. The 5th column contains the penetrating power of the X-rays expressed in degrees Benoist.

The figures in the 4th column are useful to indicate the amount of difference in slope of the characteristic curves. If these be compared with those for the hardness of the rays, we find the remarkable fact, that the difference in slope is less for penetrating rays than for rays from a lower-vacuum tube. This is best seen in the curve of fig. 7 which shows an absolutely unexpected linear relation between the quotient and the penetrating power. The figures in the last column of table III are calculated with the linear equation:

Quot.: = 1.809 — 0.0776 Degrees Benoist.

Though this seemingly anomalous behaviour of the harder rays might be caused in different ways, we cannot reasonably suspect a secondary radiation originated in the gelatine bromide layer itself, as this would occur in every part of the layer. We can only suppose that the more penetrating rays are mixed with an exceedingly absorbable radiation which is present to a far less extent in the radiation of medium hardness. Perhaps a very absorbable radiation might be generated by the harder X-rays by impact on the glass support after their passage through the sensitive layer. If the primary rays already contain a certain amount of soft rays, these may be derived from the anticathode (as a soft characteristic platinum or tungsten-radiation) or from the glass-bulb, or perhaps from the envelope in which the plate was exposed to the rays. Between the first and the last of these possibilities we must have the difference, that in the first case the deepest parts of the gelatine layer contain more silver than the surface, whereas in other cases the surface of the gelatine will be richest in silver. In order to decide in this question I asked Dr. Klessens to make a few microscopic slides from transverse sections of the gelatine layer of different negatives.

Microphotographs of these, enlarged about 500 times show immediately that the theoretical deductions in my paper are confirmed. In fig. 8 a transverse section through a light-negative shows a strong deposit of silver in the upper part of the gelatinelayer and hardly any silverparticles in the deeper strata. A section through a Röntgen-film made with soft rays (3° Benoist) is shown in fig. 9. The silverparticles are almost equally distributed in the layer. From a negative with hard X-rays (8° Benoist) I got the photograph shown in fig. 10,

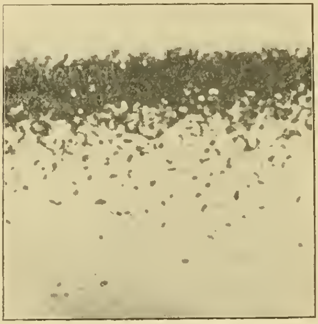


Fig. 8.

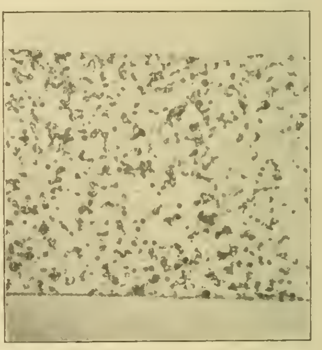


Fig. 9.

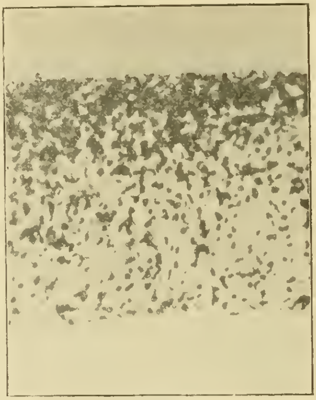


Fig. 10.

in which the surface of the gelatine contains more silverparticles than the deeper strata. With rays of medium hardness I found a more even distribution of the silver particles, showing that these rays contained only a limited amount of extremely soft rays.

Astronomy. — *"On the influence exercised by the systematic connection between the parallax of the stars and their apparent distance from the galactic plane upon the determination of the precessional constant and of the systematic proper motions of the stars."* By Prof. E. F. VAN DE SANDE BAKHUYZEN and C. DE JONG.

(Communicated in the meeting of Sept. 25, 1915.)

Since the researches made by KAPTEYN, it may be regarded as an established fact, that stars of a given magnitude are at a greater mean distance from us, in proportion as they are nearer to the galactic plane. At the galactic poles the mean parallax is found to be about one and a half times as great as in the galactic plane itself. As in the researches so far undertaken concerning the precessional constant and the systematic proper motions of the stars this connection had not been taken into consideration, it is obvious that the determination of these quantities may be affected by systematic errors.

For some time it had been the intention of one of us to institute a nearer investigation of this matter, all the more because it might throw light upon a difference, found by NEWCOMB, between the values of the precession-constant, as deduced on the one hand from Right Ascension- and on the other one from Declination-observations. Later on it was noticed, that NEWCOMB himself had indicated the possibility of such an explanation of the difference, (*Prec. Const.* p. 67 and 73) and also that EDDINGTON in his well known monograph published last year, "*Stellar movements and the structure of the universe*", in pointing out the desirability of taking the differences of distance into consideration, had already made a beginning in this direction. At the same time, he only deals with the influence of the inequality of the distance upon the determination of the apex of the Parallactic motion (p. 81—83), and only develops it in the case of the investigation being based upon stars which are evenly distributed over the entire celestial sphere.

A new research, therefore, embracing the whole question, was by no means superfluous. We have undertaken it, and in the following paper we communicate our results. The term "*Systematic proper motions*" is here taken in a somewhat limited sense; it includes only those motions which are functions of the spherical place of the star, although the coefficients may still be dependent upon their distance from us, and perhaps also upon the spectral type, (we leave that here out of account). Systematic movements which are the consequence of star-streams, or may be ascribed to an equivalent non-spherical distribution of the individual motions, which we might call *systematic proper motions of the second kind* [1]), are excluded from our investigation.

In the first place, then, the dependence of the parallax upon the galactic latitude must be expressed in a simple formula; for the derivation of this we have used the table given by KAPTEYN and WEERSMA in their paper *Publ. Groningen* **24**, 15 In that table values for the mean parallax are given for the magnitudes 3.0 to 11.0, and for galactic latitudes: between — 20° and + 20°, between ± 20° and ± 40° and between ± 40° and ± 90°. For all magnitudes the same ratio is assumed: between π_β and π_0 and with sufficient accuracy for our purpose — the table is given as "quite provisional" — we could put: $\pi_\beta = \pi_0\,(1 + c\,sin^2\,\beta)$.

The three columns of KAPTEYN and WEERSMA's table were assumed to apply to gal. latitudes of ± 10°, ± 30° and ± 60°, and it appeared that the coefficient c must be given a value between 0.60 and 0.70 We assumed therefore

$$\pi_\beta = \pi_0\,(1 + 0.65\,sin^2\,\beta)$$

or

$$R_\beta = \frac{R_0}{1 + 0.65\,sin^2\,\beta}$$

The relation assumed by EDDINGTON is equivalent to a formula of the same form with $c = 0.60$.

Our value for R must now be substituted in the equations for the systematic proper motion, whereby, for the present, we confined ourselves to the terms dependent upon a precession-correction and upon the parallactic motion.

The usual equations are

$$\mu_\alpha\,cos\,\delta = \angle\,m\,cos\,\delta + \angle\,n\,sin\,\delta\,sin\,\alpha + \frac{X}{R}\,sin\,\alpha - \frac{Y}{R}\,cos\,\alpha$$

$$\mu_\delta = -\frac{Z}{R}\,cos\,\delta + \angle\,n\,cos\,\alpha + \frac{X}{R}\,sin\,\delta\,cos\,\alpha + \frac{Y}{R}\,sin\,\delta\,sin\,\alpha$$

Substituting in these the value of R, expressed in R_0, and afterwards, according to the formula

$$sin\,\beta = sin\,\delta\,cos\,i \quad cos\,\delta\,sin\,(\alpha - \theta)\,sin\,i$$

---

[1]) The frequency-surface may be more general than the ellipsoid, but must, according to our definition, have a centre, as the part of the movement that depends upon the spherical place (Systematic Prop. mot. 1st kind) is subtracted from the total movement.

in which θ and i represent the node and inclination of the galactic plane in respect to the equator, expressing everything in equatorial coordinates, we get, after the expansion of the powers and products of the goniometrical functions of α, leaving the value of θ, i and c for the present undetermined:

$$\mu_\alpha \cos\delta = \Delta m \cos\delta + \tfrac{1}{4} c \sin 2i \cos\theta \frac{X}{R_0} \sin 2\delta - \tfrac{1}{4} c \sin 2i \sin\theta \frac{Y}{R_0} \sin 2\delta$$

$$+ \Big[\Delta n \sin\delta + \frac{X}{R_0} + \tfrac{1}{4} c \sin^2 i \,(2 + \cos 2\theta) \frac{X}{R_0} \cos^2\delta +$$

$$+ c \cos^2 i \frac{X}{R_0} \sin^3\delta + \tfrac{1}{4} c \sin^2 i \sin 2\theta \frac{Y}{R_0} \cos^2\delta \Big] \sin\alpha$$

$$- \Big[\frac{Y}{R_0} + \tfrac{1}{4} c \sin^2 i \sin 2\theta \frac{X}{R_0} \cos^2\delta +$$

$$+ \tfrac{1}{4} c \sin^2 i \,(2 - \cos 2\theta) \frac{Y}{R_0} \cos^2\delta + c \cos^3 i \frac{Y}{R_0} \sin^2\delta \Big] \cos\alpha$$

$$+ \Big[\tfrac{1}{4} c \sin 2i \sin\theta \frac{X}{R_0} \sin 2\delta + \tfrac{1}{4} c \sin 2i \cos\theta \frac{Y}{R_0} \sin 2\delta \Big] \sin 2\alpha$$

$$+ \Big[\tfrac{1}{4} c \sin 2i \cos\theta \frac{X}{R_0} \sin 2\delta - \tfrac{1}{4} c \sin 2i \sin\theta \frac{Y}{R_0} \sin 2\delta \Big] \cos 2\alpha$$

$$- \Big[\tfrac{1}{4} c \sin^2 i \cos 2\theta \frac{X}{R_0} \cos^2\delta - \tfrac{1}{4} c \sin^2 i \sin 2\theta \frac{Y}{R_0} \cos^2\delta \Big] \sin 3\alpha$$

$$+ \Big[\tfrac{1}{4} c \sin^2 i \sin 2\theta \frac{X}{R_0} \cos^3\delta + \tfrac{1}{4} c \sin^2 i \cos 2\theta \frac{Y}{R_0} \cos^2\delta \Big] \cos 3\alpha$$

$$\mu_\delta = - \frac{Z}{R_0} \cos\delta + \tfrac{1}{2} c \sin 2i \sin\theta \frac{X}{R_0} \cos\delta \sin^2\delta -$$

$$- \tfrac{1}{2} c \sin 2i \cos\theta \frac{Y}{R_0} \cos\delta \sin^2\delta - \tfrac{1}{2} c \sin^2 i \frac{Z}{R_0} \cos^3\delta - c \cos^2 i \frac{Z}{R_0} \cos\delta \sin^2\delta$$

$$+ \Big[\frac{Y}{R_0} \sin\delta - \tfrac{1}{4} c \sin^2 i \sin 2\theta \frac{X}{R_0} \cos^2\delta \sin\delta + \tfrac{1}{4} c \sin^2 i \,(2 + \cos 2\theta) \frac{Y}{R_0} \cos^2\delta \sin\delta$$

$$+ c \cos^2 i \frac{Y}{R_0} \sin^3\delta + c \sin 2i \cos\theta \frac{Z}{R_0} \cos^2\delta \sin\delta \Big] \sin\alpha$$

$$\Big[\Delta n + \frac{X}{R_0} \sin\delta + \tfrac{1}{4} c \sin^2 i \,(2 - \cos 2\theta) \frac{X}{R_0} \cos^2\delta \sin\delta +$$

$$+ c \cos^2 i \frac{X}{R_0} \sin^3\delta - \tfrac{1}{4} c \sin^2 i \sin 2\theta \frac{Y}{R_0} \cos^2\delta \sin\delta - c \sin 2i \sin\theta \frac{Z}{R_0} \cos^2\delta \sin\delta \Big] \cos\alpha$$

$$- \Big[\tfrac{1}{2} c \sin 2i \cos\theta \frac{X}{R_0} \cos\delta \sin^2\delta - \tfrac{1}{2} c \sin 2i \sin\theta \frac{Y}{R_0} \cos\delta \sin^2\delta -$$

$$
\begin{aligned}
&- \tfrac{1}{2}\, c \sin^2 i \sin 2\,\theta\, \frac{Z}{R_0} \cos^3 \delta \Big] \sin 2\,\alpha \\
&+ \Big[\tfrac{1}{2}\, c \sin 2\, i \sin \theta\, \frac{X}{R_0} \cos \delta \sin^2 \delta + \tfrac{1}{2}\, c \sin 2\, i \cos \theta\, \frac{Y}{R_0} \cos \delta \sin^2 \delta \\
&+ \tfrac{1}{2}\, c \sin^2 i \cos 2\,\theta\, \frac{Z}{R_0} \cos^3 \delta \Big] \cos 2\,\alpha \\
&- \Big[\tfrac{1}{4}\, c \sin^2 i \sin 2\,\theta\, \frac{\Lambda}{R_0} \cos^2 \delta \sin \delta + \tfrac{1}{4}\, c \sin^2 i \cos 2\,\theta\, \frac{Y}{R_0} \cos^2 \delta \sin \delta \Big] \sin 3\alpha \\
&- \Big[\tfrac{1}{4}\, c \sin^2 i \cos 2\,\theta\, \frac{X}{R_0} \cos^2 \delta \sin \delta - \tfrac{1}{4}\, c \sin^2 i \sin 2\,\theta\, \frac{Y}{R_0} \cos^2 \delta \sin \delta \Big] \cos 3\alpha
\end{aligned}
$$

If in these general formulae we substitute:

$$\theta = 18^{\mathrm{u}}45^{\mathrm{m}} = 281^\circ$$

$$i = 63^\circ$$

$$c = 0.65.$$

we get :

$$
\begin{aligned}
\mu_\alpha \cos \delta = {} & \triangle\, m \cos \delta - 0.02\, \frac{X}{R_0} \sin 2\,\delta + 0.13\, \frac{Y}{R_0} \sin 2\,\delta \\
&+ \Big[\triangle\, n \sin \delta + \frac{X}{R_0} + 0.13\, \frac{X}{R_0} \sin^2 \delta + 0.14\, \frac{X}{R_0} \cos^2 \delta - 0.05\, \frac{Y}{R_0} \cos^2 \delta \Big] \sin \alpha \\
&- \Big[\frac{Y}{R_0} - 0.05\, \frac{X}{R_0} \cos^2 \delta + 0.38\, \frac{Y}{R_0} \cos^2 \delta + 0.13\, \frac{Y}{R_0} \sin^2 \delta \Big] \cos \alpha \\
&- \Big[0.13\, \frac{X}{R_0} \sin 2\,\delta - 0.02\, \frac{Y}{R_0} \sin 2\,\delta \Big] \sin 2\,\alpha \\
&+ \Big[0.02\, \frac{X}{R_0} \sin 2\,\delta + 0.13\, \frac{Y}{R_0} \sin 2\,\delta \Big] \cos 2\,\alpha \\
&+ \Big[0.12\, \frac{X}{R_0} \cos^2 \delta - 0.05\, \frac{Y}{R_0} \cos^2 \delta \Big] \sin 3\,\alpha \\
&- \Big[0.05\, \frac{X}{R_0} \cos^2 \delta + 0.12\, \frac{Y}{R_0} \cos^2 \delta \Big] \cos 3\,\alpha
\end{aligned}
$$

$$
\begin{aligned}
\mu_\delta = {} & - \frac{Z}{R_0} \cos \delta - 0.26\, \frac{X}{R_0} \cos \delta \sin^2 \delta - 0.04\, \frac{Y}{R_0} \cos \delta \sin^2 \delta - \\
&- 0.26\, \frac{Z}{R_0} \cos^3 \delta - 0.13\, \frac{Z}{R_0} \cos \delta \sin^2 \delta \\
&+ \Big[\frac{Y}{R_0} \sin \delta + 0.05\, \frac{X}{R_0} \cos^2 \delta \sin \delta + 0.14\, \frac{Y}{R_0} \cos^2 \delta \sin \delta + 0.13\, \frac{Y}{R_0} \sin^3 \delta + \\
&+ 0.10\, \frac{Z}{R_0} \cos^2 \delta \sin \delta \Big] \sin \alpha
\end{aligned}
$$

$$+\left[\Delta n + \frac{X}{R_0}\sin\delta + 0.38\frac{X}{R_0}\cos^2\delta\sin\delta + 0.13\frac{X}{R_0}\sin^3\delta + \right.$$

$$\left. + 0.05\frac{Y}{R_0}\cos^2\delta\sin\delta + 0.52\frac{Z}{R_0}\cos^2\delta\sin\delta\right]\cos\alpha$$

$$-\left[0.04\frac{X}{R_0}\cos\delta\sin^2\delta + 0.26\frac{Y}{R_0}\cos\delta\sin^2\delta + 0.10\frac{Z}{R_0}\cos^3\delta\right]\sin 2\alpha$$

$$-\left[0.26\frac{X}{R_0}\cos\delta\sin^2\delta - 0.04\frac{Y}{R_0}\cos\delta\sin^2\delta + 0.24\frac{Z}{R_0}\cos^3\delta\right]\cos 2\alpha$$

$$+\left[0.05\frac{X}{R_0}\cos^2\delta\sin\delta + 0.12\frac{Y}{R_0}\cos^2\delta\sin\delta\right]\sin 3\alpha$$

$$+\left[0.12\frac{X}{R_0}\cos^2\delta\sin\delta - 0.05\frac{Y}{R_0}\cos^2\delta\sin\delta\right]\cos 3\alpha$$

In many cases it is convenient to modify the formulae so that in place of R_0 they contain the mean distance R_m corresponding to the magnitude or the mean magnitude under consideration. We will define this mean distance as the reciprocal value of the mean parallax, and therefore put:

$$R_m = \frac{R_0}{1 + 0.65 \times \text{mean value } \sin^2\beta}$$

We must then integrate $\sin^2\beta$ over the whole surface of the sphere, and in this way we find: mean value of $\sin^2\beta = \frac{1}{3}$, so that $R_0 = 1.22\ R_m$, and this relation must be substituted in all the terms which are dependent upon the parallactic motion.

To save space, we give below only the values of the numerical coefficients in the new formulae containing R_m.

Coefficients in the formulae containing R_m.

$$\mu_\alpha \cos\delta =$$

$$\begin{array}{lllllll}
 & +1.00 & -0.02 & +0.11 & & & \\
+[& +1.00 & +0.82 & +0.11 & +0.11 & -0.04] & \sin\alpha \\
-[& +0.82 & -0.04 & +0.31 & +0.11 &] & \cos\alpha \\
-[& +0.11 & -0.02 & & &] & \sin 2\alpha \\
+[& +0.02 & +0.11 & & &] & \cos 2\alpha \\
+[& +0.10 & -0.04 & & &] & \sin 3\alpha \\
-[& +0.04 & +0.10 & & &] & \cos 3\alpha
\end{array}$$

$$\mu_0 =$$

$$\begin{array}{llllllll}
 & -0.82 & -0.21 & -0.03 & -0.21 & -0.11 & & \\
+\,[& +0.82 & +0.04 & +0.11 & +0.11 & +0.08 & &]\; \sin\alpha \\
+\,[& +1.00 & +0.82 & +0.31 & +0.11 & +0.04 & +0.43 &]\; \cos\alpha \\
-\,[& +0.03 & +0.21 & +0.08 & & & &]\; \sin 2\alpha \\
-\,[& +0.21 & -0.03 & +0.20 & & & &]\; \cos 2\alpha \\
+\,[& +0.04 & +0.10 & & & & &]\; \sin 3\alpha \\
+\,[& +0.10 & -0.04 & & & & &]\; \cos 3\alpha
\end{array}$$

Using these formulae we can now trace the influence which the systematic difference in the distance of the stars of the same magnitude will have upon the derivation of the precessional constant and of the elements of the parallactic movement, and thus deduce the corrections, which must be applied to results in the derivation of which the differences of distance were not taken into account. When we consider this question more closely, however, we soon see that a sharp determination of the corrections, which would hold for all the determinations of these constants hitherto made, is hardly possible.

Even if we assume that the same law of mean variation of distance with the gal. latitude holds for all individual magnitudes, which is perhaps still doubtful for the brightest classes [1], it does not follow that it will also hold for the mean magnitude of a material which extends over several classes, as the distribution of the separate magnitudes may be different for the different regions of the heavens. The working of the simple law may also be disturbed, when, as is often done, and frequently quite rightly, proper motions above certain limits are excluded from the discussion.

Further, it is evident that the correct value of the necessary corrections will be influenced by the manner, followed in each particular case, of establishing and solving the equations. Where the separate determination of the various unknown quantities is just possible, we may try to do so, or by preference take those which would be determined with the least weight from other investigations. There is, moreover, ample room for differences of opinion as to the attribution of the weights, and often in different instances different distributions of weights will recommend themselves. If there is reason to believe that a group of stars belong together physically, this may determine us to attribute to it the weight of only one star, and in general, the discussion may be based upon the individual stars, or

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[1] NEWCOMB in his *Precessional constant* Section XIV p. 43–46, points out the difficulties which the answering of this question presents.

upon larger or smaller trapezia in which the celestial sphere is divided.

Some investigators have made use of different methods and have discussed and combined the respective results; Newcomb, in particular, has done this in an admirable manner. It is therefore often difficult, even for the results of one investigator, to fix the exact value of the corrections to be applied to them, and whereas an *accurate* knowledge of the foundation of our investigation, namely the exact mean variation of the distances, is not yet attained, it would certainly not be worth while to make elaborate calculations concerning the influence of this variation. We shall therefore only trace this influence in a few simple suppositions concerning the method of calculation followed. For this we use the formulae expressed in R_m, as it can be seen at once that the values previously obtained for the components of the parallactic motion will agree most nearly with the corrected results for that distance.

In the first place we will consider the influence of the assumed law of distances, upon the results for the precessional constant.

a. Determination of the Precession from Right Ascensions. In this deduction we may either determine the correction of the total luni-solar precession Δp by expressing Δm and Δn in it, or, eliminating Δn by attributing equal weights to the results from groups formed according to the A. R., confine ourselves to the determination of Δm; the influence of Δn disappears of course, when the material used is symmetrically distributed over north and south declinations. If we allow for the influence of Δn, the correction terms which contain $\sin \alpha$ must be taken into consideration, and we must investigate how the influence of these terms will be divided between the term in Δn which contains $\sin \delta$ and that in $\frac{X}{R_m}$, which is constant for all declinations. Now owing to the approximate equality of two coefficients the whole coefficient of $\sin \alpha$ is reduced to $\Delta n \sin \delta + 0.93 \frac{X}{R_m} - 0.04 \frac{Y}{R_m} \cos^2 \delta$ and, even without the rigorous formation of the normal equations, it is clear that, for not too high declinations, the term with $\cos^2 \delta$ will principally influence the parallactic motion.

So it follows that, even if we take the influence of Δn into account, provided our stars are distributed over all R.A. and we do not attribute too great differences of weight to the different groups, we may practically only pay attention to the correction terms which do not depend upon α. Calling the value of Δm (variation in 100 years) which is found, if the correction terms are left out of consideration, $[\Delta m]$, then

$$[\Delta m] = \Delta m - 0.04 \frac{X}{R_m} \sin\delta + 0.21 \frac{Y}{R_m} \sin\delta.$$

If we accept for the mean distance of the Bradley-stars (mean magn. 5.5) according to Newcomb's results: $X = +0''.20$, $Y = -2''.60$ and according to his table on p. 39, as a mean value $\sin\delta = +0.20$, we get $\Delta m = [\Delta m] + 0''.11$ or

$$\text{corr. } dp \text{ Newc.} = +0''.12.$$

A separate correction of Newcomb's 7 zones (p. 39) gives the result corr. $dp = +0''.11$.

In the second place we compute the correction which must be applied to the value of Δm, deduced by Dyson and Thackeray from the comparison of Groombridges catalogue with the second 10 year catalogue. Taking 7.0 as the mean magnitude of the Groombridge-stars, and accordingly (see Newc. p. 34) adopting for X a small value, putting $Y = -\frac{10}{13} . 2''.60 = -2''.00$, and accepting (*Monthly Not.* **65**, 440) as mean declination of the stars $+52°$, we find for the correction to be applied to $[\Delta m]$: $+0''.42 \sin 52° = +0''.33$.

In general, if the difference of distances is disregarded, the precessional constant deduced from the right ascensions will be too small if we had used stars of *north declination* and *too large* if the stars had *south declination.*

b. Determination of the precession from the Declinations. To trace the errors made in this case, by the assumption of equal distances, we must consider the terms containing $\cos\alpha$. We have two principal terms of this form: $\Delta n \cos\alpha$ and $\frac{X}{R_m} \sin\delta \cos\alpha$. Almost always, and unless the mean decl. of the stars in question is large, it will be preferable to determine the sum of Δn and the influence of X and then to substitute the value of X derived from the R. A. This is also Newcomb's method, and we shall accordingly assume that this has been done and put:

$$\text{coeff. of } \cos\alpha - \frac{X}{R_m} \sin\delta = [\Delta n]$$

then, after an easy transformation:

$$[\Delta n] = \Delta n - (0.07 - 0.20 \cos^2\delta) \sin\delta \frac{X}{R_m} + 0.04 \cos^2\delta \sin\delta \frac{Y}{R_m} + $$
$$+ 0.43 \cos^2\delta \sin\delta \frac{Z}{R_m}.$$

For NEWCOMB's result from the BRADLEY-stars we find, taking according to NEWCOMB $\frac{Z}{R_m} = +1''50$:

$$\Delta n = [\Delta n] - 0''.00 + 0''.02 - 0''.13 = [\Delta n] - 0''.11$$

so that

$$\text{corr. } \delta p \text{ Newc.} = -0''.29.$$

As the first correction term is always small and the three others have as factor $\cos^2 \delta \sin \delta$, while the sum $-0.20 \frac{X}{R_m} - 0.04 \frac{Y}{R_m} - 0.43 \frac{Z}{R_m}$ has a considerable negative value, *the precessional constant from declinations* will be found *too large* for stars with a *north declination*, or when in the compared catalogues stars with a *north declination* are preponderant, while stars with a *south declination* will yield *too small* a *value*.

We have therefore arrived at the remarkable result that, in deriving the precessional constant in the ordinary way, in which no attention is paid to the dependence of the distances upon the galactic latitude, from catalogues with preponderating north declinations the lunisolar precession p is found *larger* from the *declinations* than from the *R.A.*, while the true value must lie between these two, and nearer to the result from the R.A., and thus, to some extent at least, the discrepancy found by NEWCOMB is accounted for. The values finally assumed by NEWCOMB for δp and those corrected according to our investigation are as follows:

	NEWCOMB	Corrected
δp from R.A.	$+0''.36$	$+0''.48$
,, Decl.	$+1\ .12$	$+0\ .83$

The difference found by NEWCOMB is thus reduced to half, and no longer presents a serious difficulty.

It should be mentioned once more, that, after the completion of our calculations, the explanation found here appeared to have been suggested by NEWCOMB himself as a possible cause of the discrepancy; so far his remarks upon this subject do not appear to have received sufficient attention.

Distinguishing by the names of "vernal region" and "autumnal region" the regions between R.A. $19^h.5$ and $5^h.5$ and between $7^h.5$ and $17^h.5$, he says on p. 67: "A very little consideration "will show that if the stars of a given apparent magnitude are "farther away within the vernal region than within the autumnal "region, then the smaller parallactic motions in the former region "will tend to diminish the precession found from the right ascensions "and increase that found from the declinations", while later on p. 71 in drawing up his final conclusions he says: "I have already "remarked that a possible cause for the discrepancy . . . . .". As a matter of fact the galaxy, for the northern heaven is in the vernal region, and for the southern in the autumnal one.

As NEWCOMB further, according to observations of the sun and of Mercury, considered as probable a correction of the assumed centennial motion of the equinox in the system N_1 by $+0''.30$, he finally assumed $\delta p = +0''.82$. With this correction, our results become

$$\begin{array}{lr} \delta p \text{ from A.R.} & +0''.78 \\ \text{from Decl.} & +0\ .83 \\ \hline \delta p \text{ mean} & +0''.80 \end{array}$$

so that the discrepancy would then vanish entirely. If we do not accept the latter correction, our final result is

$$\delta p \text{ mean } \ +0''.66.$$

There is a striking agreement between the mean of the results from α and δ, as they are found by us, with that which NEWCOMB found by eliminating the parallactic motion from the motions of the individual stars, by a method corresponding in principle to one given before by KAPTEYN (use of the proper-motion-component τ). NEWCOMB found in this way:

$$\delta p = +0''.64$$

or, if he accepted the corrected motion of the equinox, by estimation, $+0''.84$.

From this we get a strong impression that the principal uncertainty which still remains in the *precessional constant according to the* BRADLEY-*stars*, is not due to the method of treatment, but to possible errors in the catalogues compared and particularly on the one hand to an error in the equinox and on the other hand to periodic errors in the declinations, the $\Delta\delta_\alpha$.

The precession in R.A. (the value for m) deduced from the GROOMBRIDGE-stars by DYSON and THACKERAY, was already much larger than the m according to NEWCOMB, and the discrepancy becomes still greater by applying our corrections. Beside this result they deduced a value for Δn from the R.A. and Decl.-observations together, which is grounded upon the principle that from large and from small proper motions the same R.A. of the apex must be found. It cannot be seen at once, how the difference in distance of the stars will affect the results by this method. This investigation gave $\Delta p_{\text{Newc.}} = +0''.43$, while the R.A. after applying our correction gave $\Delta p_{\text{Newc.}} = +0''.76 + 0''.33 = +1''.09$. In these results too, catalogue-errors probably play a considerable part.

Finally we must draw attention to the terms which we found, depending upon 2α and 3α, amongst which there are some which may attain values which can certainly not be neglected.

We have in R.A. the terms:

$$+0.11 \sin 2\delta \frac{Y}{R_m} \cos 2\alpha - 0.10 \cos^2 \delta \frac{Y}{R_m} \cos 3\alpha$$

that is for stars of the magnitude $5^m.5$:

$$-0''.29 \sin 2\delta \cos 2\alpha + 0''.26 \cos^2 \delta \cos 3\alpha$$

and in Decl., to confine ourselves to the terms in 2α,

$$-0.08 \cos^3 \delta \frac{Z}{R_m} \sin 2\alpha - 0.20 \cos^3 \delta \frac{Z}{R_m} \cos 2\alpha$$

that is for stars $5^m.5$

$$-0''.12 \cos^3 \delta \sin 2\alpha - 0''.30 \cos^3 \delta \cos 2\alpha .$$

These terms will, when we do not take account of them in our calculations, be added to the corresponding ones arising from periodic catalogue-errors, and show all the more clearly, that no conclusions can be easily drawn from limited areas of R.A., and that it is advisable in investigations of this kind as far as possible to give equal weights to the different R.A.-groups.

In the second place we investigate the influence of the assumed law of distances upon the determination of the parallactic motion.

We assume here that the X and Y-components are deduced from the *R.A.* only, that is, from the terms which depend respectively upon $\sin \alpha$ and $\cos \alpha$, and that for the determination of X a value of Δn is introduced, which is deduced from other terms (m in α, n in δ). If we then indicate by $\left[\frac{X}{R_m}\right]$ the value which is found when we regard the distance as only dependent upon the magnitude, and act in the same way with regard to the two other components, and if we further apply a few simple transformations, as was already partially done above, we get

$$\left[\frac{X}{R_m}\right] = 0.93 \frac{X}{R_m} - 0.04 \cos^2 \delta \frac{Y}{R_m}$$

$$\left[\frac{Y}{R_m}\right] = 0.93 \frac{Y}{R_m} - 0.04 \cos^2 \delta \frac{X}{R_m} + 0.20 \cos^2 \delta \frac{Y}{R_m}$$

$$\left[\frac{Z}{R_m}\right] = 0\ 93\,\frac{Z}{R_m} + 0.21\,sin^2\,\delta\,\frac{X}{R_m} + 0.03\,sin^2\,\delta\,\frac{Y}{R_m} + 0.10\,cos^2\,\delta\,\frac{Z}{R_m}$$

These equations contain in the correction-terms only $cos^2\,\delta$ and $sin^2\,\delta$, so that they do not disappear even by integration over the whole sphere. We see thus, that, even when the stars used are spread evenly over the whole sphere, 1st the velocity-components for the mean distance, corresponding to $sin^2\,\beta = \frac{1}{3}$, are not equal to those which are found in the assumption of equal distances, and 2nd that the changes which X, Y, and Z undergo are not proportional to the quantities themselves, so that the place deduced for the apex also undergoes a change. As we have: mean value of $cos^2\,\delta = \frac{2}{3}$, m. v. of $sin^2\,\delta = \frac{1}{3}$, we find for the entire sky:

$$\left[\frac{X}{R_m}\right] = 0.93\,\frac{X}{R_m} - 0.03\,\frac{Y}{R_m}$$

$$\left[\frac{Y}{R_m}\right] = 1.06\,\frac{Y}{R_m} - 0.03\,\frac{X}{R_m}$$

$$\left[\frac{Z}{R_m}\right] = 1.00\,\frac{Z}{R_m} + 0.07\,\frac{X}{R_m} + 0.01\,\frac{Y}{R_m}.$$

Starting from the same values of the three components for the BRADLEY-stars, as were accepted before, the corrected values for the mean distance are as follows:

	Original	Corrected	Correction
X	+ 0″.20	+ 0″.14	— 0″.06
Y	— 2 .60	— 2 .43	+ 0 .17
Z	+ 1 .50	+ 1 .51	+ 0 .01

and the R.A. and Decl. of the apex become:

	Original	Corrected	Correction
A	274° 24′	273° 20′	—1° 4′
D	+ 30 0	+ 31 48	+1 48

As we said at the beginning of this paper, this particular problem appeared to have been already treated by EDDINGTON in his *Stellar movements* p. 81—83. He found, starting from practically the same data, but by an entirely different method, that A in particular will need a correction, viz. of about —2.°4. The two results for A agree tolerably well, and ours is also not accurate to a few minutes. We find also an appreciable value for the correction of D, although the Z-component remains almost unchanged.

The result found for the whole sky is equal to that for $\delta = \pm\ 35°15'$. As a second example we will calculate the corrections for $\delta = 0$.

$$\left[\frac{X}{R_m}\right] = 0.93\,\frac{X}{R_m} - 0.04\,\frac{Y}{R_m}$$

$$\left[\frac{Y}{R_m}\right] = 1.13\,\frac{Y}{R_m} - 0.04\,\frac{X}{R_m}$$

$$\left[\frac{Z}{R_m}\right] = 1.03\,\frac{Z}{R_m}$$

and herewith we find, starting from the same original values as above,

	Original	Corrected	Correction
X	$+0''.20$	$+0''.11$	$-0''.09$
Y	$-2\ .60$	$-2\ .29$	$+0\ .31$
Z	$+1\ .50$	$+1\ .46$	$-0\ .04$
A	274°24′	272°45′	$-$ 1°39′
D	$+30\ 0$	$+32\ 32$	$+2\ 32$

The corrections to be applied differ not much, therefore, from those in the first case.

As the components of the parallactic motion are thus found to require appreciable corrections, those found above for the precession are no longer quite correct, but their errors are of the same order as other unavoidable inaccuracies in the calculation.

The result of our research is thus to show that in researches concerning precession and systematic proper motions it is necessary to take into account the dependence of the mean distance upon the galactic latitude: its influence upon both the precessional constant, and the parallactic prop. motion cannot be neglected.

By taking this influence into account it is possible to bring into fair agreement NEWCOMB's results for the precessional constant found from observations of R.A. and from those of Decl. For the present, therefore, it is not necessary to follow HOUGH and HALM, who proceed from a new definition of the precession, by which this is not to be determined with reference to the whole of the stars, but with reference to the mean of the two star streams regarded as of different strength in different parts of the sky: a method which, moreover, as it would appear, involves great difficulties.

This, of course, does not mean that we can now rely upon the precession, determined relatively to a large complex of stars, giving us the true *mechanical precession*. To throw more light upon this subject many more extensive researches will be necessary, in which attention must also be paid to general rotations possibly occurring in our system of stars, as first proposed by SCHÖNFELD. It seemed premature to include terms of this kind in our present calculations.

Physics. — "*Experimental proof of the existence of Ampère's molecular currents.*" By Prof. A. Einstein and Dr. W. J. de Haas. (Communicated by Prof. H. A. Lorentz).

(Communicated in the meeting of April 23, 1915).

When it had been discovered by Oersted that magnetic actions are exerted not only by permanent magnets, but also by electric currents, there seemed to be two entirely different ways in which a magnetic field can be produced. This conception, however, could hardly be considered as satisfactory and physicists soon tried to refer the two actions to one and the same cause. Ampère succeeded in doing so by his celebrated hypothesis of currents circulating around the molecules without encountering any resistance.

The same assumption is made in the theory of electrons in the form e.g. in which it has been developed by H. A. Lorentz, the only difference being that, like electric currents in general, the molecular currents are now regarded as a circulation of elementary charges or electrons.

It cannot be denied that these views call forth some objections. One of these is even more serious than it was in Ampère's days; it is difficult to conceive a circulation of electricity free from all resistance and therefore continuing for ever. Indeed, according to Maxwell's equations circulating electrons must lose their energy by radiation; the molecules of a magnetic body would therefore gradually lose their magnetic moment. Nothing of the kind having ever been observed, the hypothesis seems irreconcilable with a general validity of the fundamental laws of electromagnetism.

Again, the law of Curie-Langevin requires that the magnetic moment of a molecule shall be independent of the temperature, and shall still exist at the absolute zero. The energy of the revolving electrons would therefore be a true zero point energy. In the opinion of many physicists however, the existence of an energy of this kind is very improbable.

It appears by these remarks that after all as much may be said in favour of Ampère's hypothesis as against it and that the question concerns important physical principles. We have therefore made the experiments here to be described, by which we have been able to show that the magnetic moment of an iron molecule is really due to a circulation of electrons.

The possibility of an experimental proof lies in the fact that every negative electron circulating in a closed path has a moment of momentum in a direction opposite to the vector that represents its magnetic moment, the ratio between the two moments having a definite value which is independent of the geometric dimensions and of the time of circulation. The magnetic molecule behaves as a gyroscope whose axis coincides wich the direction of the magnetisation. Every change of magnetic state involves an alteration of the orientation of the gyroscopes and of the moment of momentum of the magnetic elements. In virtue of the law of conservation of moment of momentum the change of "magnetic" moment of momentum must be compensated by an equal and opposite one in the moment of momentum of ponderable matter. The magnetisation of a body must therefore give rise to a couple, which makes the body rotate. [1])

§ 1. *Magnetic moment and moment of momentum of the molecule.*

The magnetic moment of a current of intensity i flowing along a circle of area F is given by the formula

$$\mathfrak{m} = iF,$$

or if the current consists in an electron circulating n times per second by

$$\mathfrak{m} = neF \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It may be represented by a vector perpendicular to the plane of the circle, the positive direction of this vector corresponding in the well-known way to the positive direction of the current.

The moment of momentum is

$$\mathfrak{M} = 2mnF, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

if we let coincide its positive direction with that of the magnetic moment.

Hence:

$$\mathfrak{M} = \frac{2m}{e}\,\mathfrak{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For a body in which a certain number of electrons are circulating, this becomes

$$\Sigma\mathfrak{M} = \frac{2m}{e}\,\Sigma\mathfrak{m},$$

or if we denote the magnetisation $\Sigma\mathfrak{m}$ by I

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[1]) This paper had gone to press when we learned that O. W. RICHARDSON (Phys. Rev. Vol. 26, 1908 p. 248) had sought already for the effect in question, without however obtaining a positive result.

$$\Sigma\mathfrak{M} = \frac{2m}{e} I. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

§ 2. *Consequence of the existence of a magnetic moment of momentum.*

Any change of the moment of momentum $\Sigma\mathfrak{M}$ of a magnetized body gives rise to a couple θ determined by the vector equation

$$\theta = - \Sigma \frac{d\mathfrak{M}}{dt} = 1{,}13.10^{-7} \frac{dI}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the numerical coefficient has been deduced from the known value of $\frac{e}{m}$ for negative electrons.

It has been our aim to verify the relation expressed by (5). We shall show in the first place that the calculated effect is not too small to be observed. Let the body be an iron cylinder with radius R, which can rotate about its vertical axis. We shall deduce from (5) the angular velocity ω the cylinder acquires by the reversal of a longitudinal magnetisation, which we suppose to have the saturation value I_s. Denoting by Q the moment of inertia of the cylinder, and writing λ for the above coefficient $1{,}13 \,.\, 10^{-7}$, we find

$$Q\omega = \int \theta dt = 2\lambda I_s \,.$$

Now, if the saturation value of the magnetisation per cm^3 is 1000, which is not a high estimate, we have $I_s = \frac{M}{7{,}8} \,.\, 1000$. The moment of inertia is $Q = \frac{1}{2} MR^2$, and we find for $R = 0{,}1$ cm

$$\omega = 0{,}6 \,.\, 10^{-2},$$

an angular velocity that can easily be observed.

§ 3. *Description of the method.*

At first sight it seems that equation (5) may be tested in the following way. A soft iron cylinder C is suspended by a thin wire D coinciding with the axis of the cylinder prolonged, the period of the torsional oscillations being a few seconds. Let the cylinder C be surrounded by a coil K whose axis coincides with that of C. Then, on reversing a current in K, a rotation of C ought to be observed. In reality, however, this simple method cannot be thought of. As the field of the coil will not be uniform the cylinder would probably show highly irregular motions completely masking the effect that is sought for.

Better results are obtained if the effect is magnified by resonance. For this purpose an alternating current having the same or nearly the same frequency as the oscillations of C about the wire D is made to flow through the coil.

For the oscillations of C about the vertical axis under the influence of the couple θ we have the equation

$$\theta = Q\ddot{\alpha} + \Theta\alpha + P\dot{\alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which the angle α, the deviation from the position of equilibrium is reckoned positive in the same direction as the current in the windings. Q is the moment of inertia, Θ the torsion constant of the wire and P a small coefficient of friction. Instead of Θ and P we shall introduce two new constants

$$\omega_0 = \sqrt{\frac{\Theta}{Q}}, \quad \varkappa = \frac{P}{2Q} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

the first of which is 2π times the free frequency, as it would be in the absence of friction, whereas $\varkappa$ is the constant of damping. Indeed the free oscillations (the equation for which is deduced from (6) by putting $\theta = 0$) are given by

$$\alpha = Ce^{-\varkappa t} \cos\left(\sqrt{\omega_0^2 - \varkappa^2}\, t + p\right).$$

The differential equation (6) is easily solved if we develop θ as a function of t in a Fourier series. Now according to (5) θ has the same phase as $\frac{dI}{dt}$. Hence, if the magnetisation were proportional to the current we could directly represent θ as a harmonic function whose phase would be $\frac{1}{4}\pi$ in advance of that of the current i in the coil. The proportionality will, however, hold for small intensities only. If the amplitude of i is made to increase so that the magnetisation approaches saturation, the magnetisation curve takes a different form. Finally, for very large amplitudes of i, the magnetisation will suddenly pass from one saturation value into the opposite one, simultaneously (except for a small difference of phase) with the change of direction of the current. For this limiting case the calculation will now be made.

The couple acting on the cylinder may be represented by fig. 1, in which the sinusoid refers to the current i [1]).

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[1]) The curve with the sharp peaks represents the value of $\frac{dI}{dt}$, to which the couple θ is proportional. It was obtained in the following way. The iron cylinder, which had its right position along the axis of the coil K, was surrounded by a narrow glass tube covered with windings and immediately beside this tube a similar one, equal to it and covered in the same way, was placed. The windings of the two

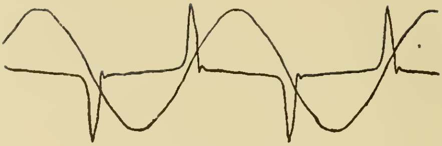

Fig. 1.

Each sharp peak corresponds to a reversal of the magnetisation and we have for each of them

$$\int \theta \, dt = \pm 2\lambda I_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Let the origin $t = 0$ coincide with a point in Fig. 1, where the current passes from the negative to the positive direction. Then we may write

$$i = A \sin \omega t, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and θ may be developed in a series

$$\theta = \sum_{n=1}^{n=\infty} B \cos n \, \omega \, t \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Of this series the first term only need be considered here, as the effect corresponding to it is the only one that is multiplied by resonance, so that the other terms have no sensible influence on the motion of the cylinder. Now, multiplying (10) by $\cos \omega t$ and integrating over a full period $T = \frac{2\pi}{\omega}$ we find

$$\int_{-\frac{\pi}{2\omega}}^{+\frac{3\pi}{2\omega}} \theta \cos \omega t \, dt = \frac{\pi}{\omega} B_1 .$$

On the left hand side θ is different from 0 only in the very small intervals at $t = 0$ and $t = \frac{\pi}{\omega}$. For the first of these we may put

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tubes were connected in such a way, that a current passing through them flowed round the tubes in opposite directions.

Under these circumstances, the current induced in the windings is exactly proportional to $\frac{dI}{dt}$, the demagnetizing action of the poles of the iron bar being eliminated, as well as the induction due to the field of the coil K. The graph for the induced current, and therefore for $\frac{dI}{dt}$ or θ was obtained by means of an oscillograph of SIEMENS and HALSKE. The alternations of the current i, represented by the sinusoid, were registered in the same way.

$\cos\omega t = 1$ and for the second $\cos\omega t = -1$ so that we find, using (8)

$$B_1 = \frac{4\lambda\omega}{\pi} I_s . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{11}$$

Instead of (6) we now get the equation

$$B_1 \cos\omega t = Q\ddot{\alpha} + \Theta\dot{\alpha} + P\alpha , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{12}$$

the periodic solution of which is

$$\alpha = \frac{B_1}{u} \cos(\omega t - v), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{13}$$

if the constants u and v are determined by

$$\left.\begin{aligned} u \cos v &= (\omega_0{}^2 - \omega^2)\, Q \\ u \sin v &= 2\, \varkappa\, \omega\, Q \end{aligned}\right\} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{14}$$

Here the quantity u, to which we shall give the positive sign, determines the amplitude whereas the phase of the oscillations is given by the angle v. For the amplitude, which we shall denote by $|\alpha|$, we find

$$|\alpha| = \frac{B_1}{u} = \frac{4\lambda\, I_s}{\pi Q \sqrt{\dfrac{(\omega_0{}^2 - \omega^2)^2}{\omega^2} + 4\varkappa^2}} \quad . \quad . \quad . \quad . \tag{15}$$

For $\omega = \omega_0$ it becomes a maximum $|\alpha|_m$, viz.

$$|\alpha|_m = \frac{2\lambda\, I_s}{\pi\, Q\, \varkappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{16}$$

As to the phase, we first remark that according to (14) $v = \frac{\pi}{2}$ for $\omega = \omega_0$. If the frequency of the alternating current is higher than that of the cylinder, we have $v > \frac{\pi}{2}$ and in the opposite case $v < \frac{\pi}{2}$. When ω is made to differ more and more from ω_0, the phase v approaches the value π in the first case and 0 in the second. If the constant of damping $\varkappa$ is small we may say that these limiting values will be reached at rather small distances from ω_0 already. In our experiments this was really the case and we may therefore say, excepting only values of ω in the immediate neighbourhood of ω_0 that $v = \pi$ for $\omega > \omega_0$ and $v = 0$ for $\omega < \omega_0$. Taking into account what has been said about the positive direction one will easily see that, if the current i and the deviation α had the same phase, the cylinder would at every moment be deviated in the direction the current in the coil has just then. In reality the phase of the oscillations of the cylinder is behind that of the current by an amount $v - \frac{\pi}{2}$; this follows from (9) and (13). Remembering further that in the deduction of (11) it has been assumed that the circulating electrons are negative and that if they were positive ones, the sign of B_1 and the phase of the effect would be reversed we are led to the following conclusion:

Negative electrons.

$\omega > \omega_0$. The phase of the oscillations of the cylinder is a quarter of a period behind that of the current.
$\omega < \omega_0$. It is a quarter of a period in advance.
$\omega = \omega_0$. The vibration has the same phase as the current.

Positive electrons.

$\omega > \omega_0$. The phase of the oscillations of the cylinder is a quarter of a period in advance of that of the current.
$\omega < \omega_0$. It is a quarter of a period behind that of the current.
$\omega = \omega_0$. The vibration of the cylinder and the current have opposite phases.

It is important to notice that there is a quarter of a period difference of phase between the active couple $B_1 \cos \omega t$ and the current $i = A \sin \omega t$ and likewise between the active couple and the alternating magnetisation. This is always so, independently of the relative values of ω and ω_0 and of the sign of the circulating electrons.

§ 4. *Short description of the apparatus.*

The alternating field which has been mentioned several times already was excited by two coils placed with their axes along the same vertical line and with a distance of about 1 cm between them. They were mounted on a brass foot to which three foot screws could give different inclinations. The coils were connected in series and gave a field of about 50 Gauss. The iron cylinder was suspended along their axis. This cylinder, 1.7 mm thick and in the first experiments 7 cm long, was carefully turned of soft iron. Centrally in its top there was bored a narrow hole of diameter 0.3 mm in which a fitting glass wire was sealed. At its middle the cylinder wore a very light mirror made from a silvered microscope covering glass. The light of a single wire lamp was thrown on the mirror through the space between the two coils. The reflected rays formed an image on a scale placed at a distance of 45 cm When the cylinder was set vibrating this image was broadened into a band, the width of which determined the double deviation.

In order to obtain resonance, it must of course be possible to regulate the length of the glass wire. For this purpose we used a clamping arrangement by which the glass wire could be tightly held at different points of its length.

The clamp and the suspending wire with the cylinder could rotate together about a vertical axis in a fixed column. The effective current was read on a precision instrument. Finally, the whole apparatus was surrounded by an arrangement by which the terrestrial magnetic field could be compensated. We shall revert to it further on.

§ 5. *The experiments.*

Let us now examine the principal disturbing causes.

1. At the ends of the cylinder alternating poles are induced. Acting on these the horizontal component of the terrestrial field can give rise to a couple alternating with the same frequency as the current and tending to rotate the cylinder about a horizontal axis. (Effect I).

Rotations of this kind have not, however, been observed by us.

2. According to the views of WEISS the ferromagnetic crystals are lying irregularly in all directions. It may therefore happen that some of them are directed in such a way that their magnetism is not reversed by the alternating field. In this case there will be a permanent horizontal component of the magnetisation, which, acted upon by the alternating horizontal component of the magnetic field in the coil, will give rise to an alternating couple around the vertical axis with the same frequency and phase as the alternating field (Effect II).

3. The axis about which the cylinder rotates will not coincide accurately with its magnetic axis.

A permanent horizontal magnetic force such as that of terrestrial magnetism, will therefore produce torsional oscillations of the cylinder. The couple which excites these oscillations has the same phase as the magnetisation and (in the case of strong currents) as the alternating current itself.

4. It is easily seen that the FOUCAULT currents which are induced

in the cylinder cannot have any influence in our experiment, their sole effect being a slight retardation of the magnetic reversals. So far as we can see, the above effects are the only ones that have the same frequency as the current in the coil and are therefore magnified by resonance. When now the coil was connected to the main alternating current conductors the image on the scale remained perfectly at rest so long as the length of the suspending wire was not such as to make the frequency of a free vibration of the cylinder coincide very nearly with that of the alternating field. The resonance appeared and disappeared again by a change of length of the wire by 1 mm, the whole length being 8 cm.

In order to find the length required for resonance and to make sure that the suspended apparatus did not vibrate in one of its higher modes, we used the following method by which we could also determine the moment of inertia of the cylinder.

At the lower end of the iron cylinder we sealed a short copper cross bar whose moment of inertia was 10,7.

For the moment of inertia of the cylinder calculation had given 0,0045.

It follows from this that the period of oscillation of the cylinder becomes $\sqrt{\frac{10,7}{0,0045}} = 48,8$ times greater by adding the small cross bar. If therefore we chose the length of the wire so as to have a frequency 1 [1]) with the cross-bar, the frequency without it would be about 48,8. This is nearly equal to the frequency of the alternating current.

We were sure by this that the suspended system would vibrate in its fundamental mode. In order to determine the moment of inertia more accurately however, the cylinder was now placed within the coil and the length of the wire was increased until the resonance was at its maximum. Then the frequency of the free vibrations might be supposed to be equal to that of the alternating current which was found to be 46,2. After this the arrangement was removed from the coil and the cross bar fixed to it. We then found the frequency 1,14. From these numbers we deduce

$$Q = 10,7 \left(\frac{1,14}{46,2}\right)^2 = 0,0065.$$

After these preparations it was found that Effect II, i. e. the oscillation caused by permanent poles in the cylinder, was of no

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[1]) By frequency we always mean the number of complete oscillations in a second.

importance. The double deviation remained unchanged when the position of the axis of the coil with respect to a vertical line was changed by means of the foot screws, a change which gave rise to horizontal alternating fields.

Effect III, however, which was caused by the action which stationary magnetic fields can exert on the alternating poles on account of their excentric position could easily be observed. The double deviation changed immediately when a permanent magnet was brought near the coil. The influence of the terrestrial magnetism was also apparent. When it was not compensated we got, in the case of resonance, a broadening of the image on the scale up to 3 cm for a scale distance of 45 cm. In all further experiments the terrestrial field has therefore been compensated, the measurements required for this being made with an earth inductor and a ballistic galvanometer. The horizontal and vertical components of the terrestrial field were compensated separately by means of hoops of about 1 m. diameter on which copper wire was wound. The current was taken from storage cells, and precision Ampèremeters of SIEMENS and HALSKE served for continually controlling its strength.

Whether the compensation was obtained could be tested by turning the upper end of the suspending wire. The amplitude of the oscillations changed by this so long as the terrestrial magnetism was still acting on the iron magnetized by the alternating current. After compensation however this azimuthal sensibility of the effect had disappeared. After all there remained a well marked double deviation of 4,5 mm.

We now had to make sure that this was really the effect we sought for. For this purpose we first availed ourselves of the circumstance that the acting couple must differ a quarter of a period in phase from the current and the magnetisation. We brought a permanent magnet near the coil, thereby calling forth effect III and adding to the couple $B_1 \cos \omega t$, with which we are concerned, a new one, which has the same or the opposite phase as the magnetisation and therefore differs a quarter of a period in phase from $B_1 \cos \omega t$. Whatever be the sign of this additional couple, the amplitude of the resulting one must become larger than B_1. We found indeed that the broadening of the image always increased when we brought a magnet near the coil.

Further the theory requires that the magnitude of the effect depends on the intensity of the alternating field in the same way as the magnetisation itself. This was likewise confirmed by experiment.

Finally we shall compare the observed magnitude of the effect with the theoretical one. If we take 1200 for the magnetisation reached by the iron, we get (the volume of the cylinder being 0,16 cm^3) $I_s = 192$. By direct observation of the oscillations in the alternating field we found

$$K = 0{,}533.$$

As
$$Q = 0{,}0065,$$
it follows from (16) that
$$|\alpha| = 0{,}0036.$$

For a scale distance of 45 cm this gives for the double deviation $4|\alpha| \,.\, 45 = 0{,}65$; as has been said already, we have found 0,45 by our experiments.

As to this difference we must observe that the theoretical value is an upper limit, as the magnetism does not change its sign instantaneously.

On account of the demagnetising influence of the free poles the field in the coil must be rather strong if on its reversal the magnetisation is to take immediately a constant value in the new direction.

§ 6. *Determination of the phase.*

We have seen that the active couple differs a quarter of a period in phase from the alternating magnetisation. Further it follows from § 3 that by comparing the phase of the effect (P_1) with that of the alternating current (P_2) we shall be able to decide, whether the electrons circulating round the iron molecules are really *negative* ones. We have tried to effect this by proceeding in the following way.

The single wire lamp used for the scale reading was connected with the main alternating current conductors in parallel with the coil that contained the iron cylinder. If then we brought a permanent magnet near the lamp, the incandescent wire was set into motion by alternating electromagnetic forces, so that, besides the oscillations due to the vibrations of the mirror, the image also performed those that were caused by the motion of the wire.

By observing whether the addition of this last vibration increased or decreased the amplitude of the image, we could compare the phase P_1 with that of the new vibrations. Now this latter is determined by the phase of the glowing wire and this in its turn depends on the phase of the current in it, whereas the difference between this phase and P_2 is determined by the self-induction of the coil. It would therefore be possible to compare the phases P_1 and P_2.

Unfortunately, when our experiments had been brought to a conclusion and one of us had left Berlin it came out that a mistake had been made in the application of the method, so that we must consider as a failure this part of our investigation. The negative sign of the circulating electrons is however made very probable by the agreement between the magnitude of the observed effect and the value we have deduced for it from that of the ratio $\frac{e}{m}$ for negative electrons.

§ 7. *More accurate measurements.*

The measurements thus far described furnished a satisfactory confirmation of the theory, but were much lacking in precision. The field in the coil was too weak practically to cause the sudden reversals of the magnetisation assumed in the theory. Further the coefficient of damping $\varkappa$ could not be determined with any accuracy. Even the question may arise whether the influence of the damping is represented rightly by the term $P\dot{\alpha}$ in equation (6).

For these reasons we have somewhat modified our apparatus. In order to quicken the reversals of the magnetisation we used instead of the former short coil one of 62 cm length (about 100 windings to a cm) the amplitude of whose field, for an effective strength of 1,45 Ampère was 260 Gauss in its central part and therefore 130 Gauss at the ends. In order to diminish the demagnetizing influence of the poles we further used a cylinder of 16 cm length and 0,17 cm diameter. The mirror was now suspended by a thin walled tube that was sealed to the lower end of the iron cylinder. It just projected beneath the lower end of the coil. In order to avoid a determination of the coefficient of damping and assumptions about the law of damping a series of experiments were made in which, for a definite length of the wire, the amplitude $|\alpha|$ was determined for different frequencies of the alternating current, so that a "resonance curve" could be drawn.

The alternating current was furnished by a generator placed in the cellar of the building and moved by the current of a battery of storage cells. The apparatus in the working room comprised a variable resistance connected in parallel to the windings of the field magnets. By varying this resistance we could change within certain limits the exciting current in the motor and therefore the number of its revolutions and the frequency of the induced alternating current. The current which passed through the variable resistance was controlled by an ampèremeter. When all other things were kept constant the frequency of the alternating current was a function of the strength of the current in the variable resistance. Besides we used a resonance frequency meter of Hartmann and Braun, with which we could accurately determine definite frequencies (45 ; 45,5; 46 up to 55). The intermediate frequencies were interpolated by means of the ampèremeter. The amplitude of the vibrations of the cylinder was measured in the same way as in the former experiments. However, in order to increase the precision we now took a scale distance of 145 cm.

In fig. 2 the results have been plotted graphically. The numbers

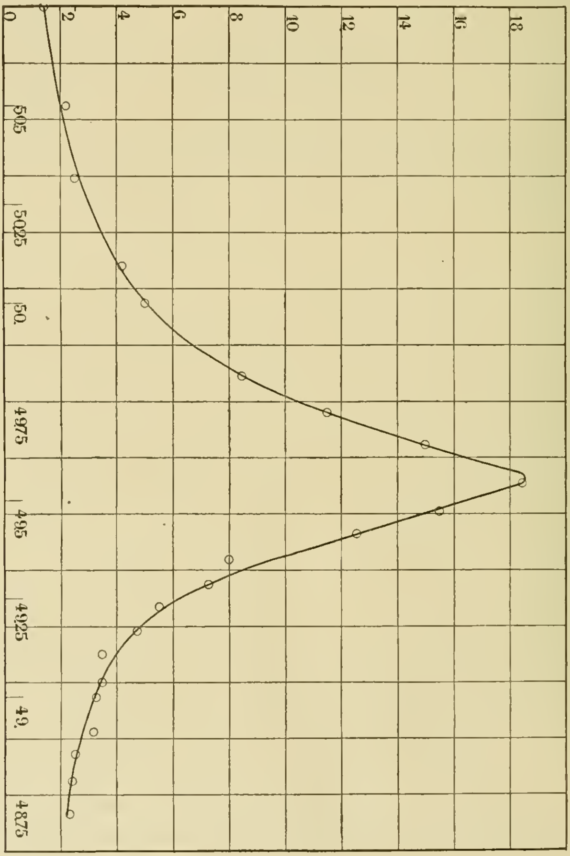

Fig. 2.

on the horizontal [1]) axis give the frequencies of the alternating current, those on the vertical axis 10 times the double deviation in centimeters.

For the calculation we each time used two points at the same height combined with the ordinate of the highest point of the curve. If for shortness' sake we put

$$\frac{4\lambda I_s}{\pi Q} = \mu,$$

it follows from (15) that

$$\frac{\mu}{|\alpha|} = \sqrt{\frac{(\omega^2-\omega_0^2)^2}{\omega^2} + 4\varkappa^2}.$$

Now, if $\omega_1 (> \omega_0)$ and $\omega_2 (< \omega_0)$ are the two values of ω corresponding to the same amplitude $|\alpha|$ we have the equations

$$\frac{\mu}{|\alpha|} = \sqrt{\frac{(\omega_1^2-\omega_0^2)^2}{\omega_1^2} + 4\varkappa^2} \text{ and } \frac{\mu}{|\alpha|} = \sqrt{\frac{(\omega_0^2-\omega_2^2)^2}{\omega_2^2} + 4\varkappa^2}.$$

By elimination of ω_0 and $\varkappa$ from these and from

$$\frac{\mu}{|\alpha|_m} = 2\varkappa$$

we find

$$\frac{\mu^2}{|\alpha|^2} - \frac{\mu^2}{|\alpha|^2_m} = (\omega_1-\omega_2)^2.$$

Let r be the difference in frequency of the two chosen points, so that $\omega_1 - \omega_2 = 4\pi r$ and let us put

$$\frac{|\alpha|}{|\alpha|_m} = b.$$

Then we find, after introducing the value of μ

$$\lambda = \pi^2 \frac{Q}{I_s} |\alpha|_m \cdot r \sqrt{\frac{b^2}{1-b^2}}. \quad \ldots \ldots \quad (17)$$

When the resonance curve has been drawn, (17) gives a value of λ for each ordinate $|\alpha|$. If this value or what amounts to the same $r\sqrt{\frac{b^2}{1-b^2}}$ is constant, this proves that the influence of the damping can really be represented by a linear term in the equation of motion.

The following table contains the values of r and b, taken from the diagram and those of $r\sqrt{\frac{b^2}{1-b^2}}$ we have deduced from them.

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[1]) If the figure is brought into the right position by a rotation of 90°.

Ordinates	ν	b	$\sqrt{\frac{b^2}{1-b^2}}$	$\nu\sqrt{\frac{b^2}{1-b^2}}$
15	0,0911	0,812	1,32	0,120
12	0,152	0,649	0,853	0,130
9	0,221	0,488	0,560	0,124
7	0,293	0,380	0,413	0,121
5	0,403	0,271	0,280	0,114
4	0,489	0,217	0,222	0,108
3	0,618	0,163	0,165	0,0957

The last column shows that for the greater deviations, not less than 7 mm, the curve agrees satisfactorily with theory, $\nu\sqrt{\frac{b^2}{1-b^2}}$ being sufficiently constant. If we pass on to smaller ordinates this quantity seems to decrease very rapidly. It must be remarked however that the small ordinates cannot be measured with sufficient precision. We shall therefore use the first four ordinates only. The mean of the numbers deduced from them is

$$\nu\sqrt{\frac{b^2}{1-b^2}} = 0,124.$$

Further it follows from the curve that

$$|\alpha|_m = \frac{1,85}{145,4} = 0,320 \, . \, 10^{-2}.$$

The moment of inertia of the vibrating system was determined by measuring the change of frequency produced by the addition of a small moment of inertia, which is accurately known.

We found ¹) for it

$$Q = 0,0126$$

If now we take 1300 for the magnetization (calculated from the hysteresis curve of the material and the constants of the coil) we find for the magnetic moment of the cylinder

$$I_s = 470.$$

With these numbers equation (17) leads to the value

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¹) It may be mentioned here that, assuming a pure cylindrical form, we calculated for the moment of inertia of the cylinder without the glass tube and the little mirror $Q = 0,0102$.

$$\lambda = 1{,}1 \,.\, 10^{-7},$$

which agrees very well with the theoretical one $1{,}13.\ 10^{-7}$.

We must observe, however, that we cannot assign to our measurements a greater precision than of $10\,^0/_0$.

It seems to us that within these limits the theoretical conclusions have been fairly confirmed by our observations..

The experiments have been carried out in the "Physikalisch-Technische Reichsanstalt". We want to express our thanks for the apparatus kindly placed at our disposition.

Physics. — "*On a possible influence of the* FRESNEL-*coefficient on solar phenomena*". By Prof. P. ZEEMAN.

(Communicated in the meeting of September 25, 1915).

We shall prove here, that the presence of the term $-\frac{\lambda}{\mu}\frac{d\mu}{d\lambda}$ of LORENTZ in the expression for the FRESNEL coefficient (cf. also my paper Vol. **18**, p. 398 of these Proceedings) may give rise to a change in the propagation of lightwaves if in a moving, refracting medium a change of velocity occurs. I suppose the medium to have everywhere the same density and to be flowing with a velocity v parallel to the axis of X in a system of coordinates that is at rest with respect to the observer. In the direction of the Z axis a velocity gradient exists in such a way, that the velocity decreases with the distance to the X axis and becomes zero at the distance $z = \Delta$. If now the incident lightbeam (with a plane wave front) is parallel to the axis of X, the parts of the wave fronts which are near this axis will be more carried with the medium than those at a greater distance. The wave front will thus be rotated.

If the velocity decreases linearly in the direction of the Z axis the wavefront will remain plane. In a time t the angle of rotation, (supposed to be small) will be $\alpha = \frac{\varepsilon . v . t.}{\Delta}$, where ε is the FRESNEL coefficient and where v and Δ have the above mentioned meaning. More in general we may consider an element of the wave front and then write $\frac{dv}{dz}$ for $\frac{v}{\Delta}$. Moreover t may be expressed as a function of the velocity of light and the path through which the rays have travelled, so that we find

$$\alpha = \frac{\varepsilon l}{c/\mu}\frac{dv}{dz} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In general this angle is infinitesimal, but it will take higher values if $-\frac{d\mu}{d\lambda}$ becomes very large. In the expression $\varepsilon_L = 1 - \frac{1}{\mu^2} - \frac{\lambda}{\mu}\frac{d\mu}{d\lambda}$ we only need to keep the last term, so that (1) becomes

$$\alpha = -\frac{\lambda}{\mu}\frac{d\mu}{d\lambda}\cdot\frac{l}{c/\mu}\cdot\frac{dv}{dz} = -\lambda\frac{d\mu}{d\lambda}\frac{l}{c}\frac{dv}{dz} \quad . \; . \; . \; . \; . \quad (2)$$

If the normal of the wave fronts forms an angle i with the direction in which the gradient of the velocity changes most, we find

$$\alpha = -\lambda\frac{d\mu}{d\lambda}\frac{l}{c}\frac{dv}{dz}\sin i \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

This equation makes it possible to construct the path of the light ray starting from a given point in a given direction.

In order to show how great the influence of the dispersion term may become in different cases I give here some tables referring to water, carbonic disulphide and sodium vapour.

For water and carbonic disulphide we have calculated with the data from well known tables the values of μ for some values of λ (in Å.U.) In the third column the values of $-\frac{d\mu}{d\lambda}$ (λ in cm.) are given, while in the fourth the Fresnel coefficient ε_L is found. The last column gives the value of the dispersion term separately.

For sodium I take the value of λ and $\mu_{obs.}$ from Wood's 1) observations, made at 644° C.; now ε_L reduces to the dispersion term. The values of ε_L and of $-\frac{d\mu}{d\lambda}$ are only of interest as to the order of magnitude.

Water.

λ *in* Å.U.	μ	$-\frac{d\mu}{d\lambda}$	ε_L	$-\frac{\lambda}{\mu}\frac{d\mu}{d\lambda}$
4500	1.3393	650	0.464	0.021
4580	1.3388	615	0.463	0.021
5461	1.3346	390	0.454	0.015
6440	1.3314	270	0.449	0.013
6870	1.3308	216	0.447	0.012

Carbonic disulphide.

4358	1.6750	5000	0.774	0.130
5461	1.6370	1900	0.690	0.063
6870	1.6160	1200	0.668	0.051

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1) Physical optics. p. 427. 1911

Sodium vapour.

λ in $\overset{\circ}{A}.U.$	$\mu_{obs.}$	$-\frac{d\mu}{d\lambda}$	$-\frac{\lambda}{\mu}\frac{d\mu}{d\lambda}=\varepsilon_L.$
5882	0,9908		
		$1,3.10^5$	7,8
5885	0,9870		
		$8,1.10^5$	48
5886,6	0,9740		
		$17.\ 10^5$	102
5888,4	0,9443		
		$280.\ 10^5$	2100
5889,6	0,614		

In the application we are going to make of equation (2) α is supposed small, so that we need not integrate over the path of the ray. We suppose in the sun a radially rising, selectively absorbing gas mass, in which a velocity gradient exists perpendicular to the radius. Even without the density gradients, which are necessary in the theory of JULIUS, there must be here a deflection of the light waves, especially for the wavelengths in the neighbourhood of the absorption lines.

If we try to work out quantitatively the idea, on which rests equation (2) we directly meet with the difficulty, that the necessary data are failing. Still we may derive a conclusion from (2), be it with little evidence, viz. that also with extremely small density of the considered vapour there may exist an observable influence of the FRESNEL coefficient on the light waves.

Let the radially ascending gas mass be found in the centre of the visible solar disc and suppose that an objective of e. g. 30 cm. diameter be used for observation. The light cone proceeding from the considered point of the sun has then (the distance of the earth to the sun being $1,5.10^{13}$ cm.), a value of $\frac{30}{1,5 \times 10^{13}} = 2.10^{-12}$ in radials. A ray deviating with half this amount from the line that connects the centre of the sun with the objective does not fall in the telescope. A ray to the rim of the objective however needs a deviation of the whole amount to fall beside the telescope.

For l we may take the depth of the "reversing layer", viz. a number of the order of 1000 k.m.

As to $\frac{d\mu}{d\lambda}$, according to the above mentioned observations of WOOD, this is in the neighbourhood of the sodium line and at 644° C. of the order 10^6. The density of sodium vapour is at 644° C. of the order 10^{-5}. This follows from a calculation, which Mr. C. M. HOOGENBOOM, assistent at the Physical Laboratory, made at my request, using the observations of Hackspill [1]).

As to the density of the metal vapours on the sun, which give rise to the finest lines in the solar spectrum, we may treat these according to Lorentz [2]) as being very small. If p is the pressure in mm. mercury of the metal vapour, l the length of the layer that is traversed by the rays, Lorentz finds at $T = 6000^{\circ}$ $pl < 0{,}0015$ or $pl < 15000$ depending on the suppositions made. For $l = 10^{8}$ c.m. would follow $p < 0{,}00015$ mm. mercury in the latter case and $p < 0{,}00015 \times 10^{-7}$ mm. mercury in the former one. To the mentioned pressures correspond the densities 9.10^{-12} and 9.10^{-19}.

Let $-\frac{d\mu}{d\lambda}$ be proportional to the density, then we should find for a density 9.10^{-19} $-\frac{d\mu}{d\lambda} = \frac{10^{6}.\, 9.10^{-19}}{10^{-5}} = 10^{-7}$ at 644° C. We shall suppose this number to be still valid at 6000°.

For $\alpha = 10^{-12}$ and $\lambda = 6.10^{-5}$ c.m. we then roughly find from equation (2) $\frac{dv}{dz} = 50$. This number and therefore the velocity gradient becomes 10^{7} times smaller, if we take 10^{-11} for the density of the metallic vapour and still smaller, if we assign a higher value to $-\frac{d\mu}{d\lambda}$ than we did above.

A few objections can be made to the application of the above given discussion to the explanation of solar phenomena. I shall mention these shortly.

Even if we confine ourselves to rays proceeding from one point of the sun, there seems to be a difficulty in the fact, that while rays of a definite wave length and definite direction are deflected away from the objective, there are other rays of the same wavelength and originally another direction, which are deflected towards the objective. This difficulty may be avoided by assuming a partition of velocities symmetrical with respect to the line connecting sun and objective. Then all rays that must be taken into consideration are deflected. If now we had to consider the light from one point of the sun only, we might directly conclude, that for the mentioned small velocity gradients the deflection of the light rays must give rise to observable phenomena. One of these phenomena would be the occurrence of complicated changes closely connected with the

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[1]) Hackspill. Ann. de Chim. et de Phys. (8) **28**, 676 and 661. 1913.

[2]) H. A. Lorentz. On the width of spectral lines. These proceedings, **23**, 470. 1914.

dispersion bands of Julius, in the neighbourhood of the simple absorption line that would be observed in a gas mass at rest. If however instead of one point of the photosphere we consider a part of observable apparent area we only get a mean effect, which will be small.

Only a very special partition of the velocity may then give rise to a strong action.

Large velocity gradients will occur in the neighbourhood of surfaces of discontinuity; then $l\frac{dv}{dz}$ may become very large and α even of another order of magnitude. Ascending and descending currents may be found in neighbouring parts of space. Currents in these two directions may deflect the light, so that finally the light from a finite part of the photosphere may be deflected.

The aim of this communication is only to call the attention of astrophysicists to the fact, that under favourable circumstances the *simultaneous* existence of *velocity gradients* and *anomalous dispersion* in gases that are extremely rare and without density gradients, may give rise to a *deflection* of light.

Anatomy. — "*On the Relation between the Dentition of Marsupials and that of Reptiles and Monodelphians.*" (*First Communication*). By Prof. L. Bolk.

(Communicated in the Meeting of May 29. 1915).

On the morphological significance of the dentition of Marsupials opinions have varied greatly in the course of time. The special characteristic of this dentition, the almost entire absence of a teeth-change, naturally gave rise to the question: with which of the two sets of teeth of the Monodelphian mammals does that of the Marsupials correspond, with the deciduous or with the permanent set? Older authors, more particularly led by comparative anatomical investigations, were generally of opinion that it must be considered as identical with the permanent set of the Monodelphian mammals. This was e.g. the opinion of Owen, Flower, Oldfield Thomas. With the Marsupials the milk-dentition would, according to them, remain undeveloped with the exception of a single tooth, namely the one immediately preceding the first molar. In fact with most Marsupials an existing tooth is here sooner or later expelled and replaced by a successor, in the same way as happens in the Monodelphian mammals with all the milk-teeth.

The opinion that the dentition of Marsupials corresponds with the second set of teeth of the Monodelphians was generally held until about 1890, when in a comparatively short time it gave way to a different view. It was namely at that period that ontogenetical researches came more to the fore and led not only to a change in the conception about the Marsupial dentition, but also introduced new ideas into odontology, which were the starting-point for so much capriciousness in the interpretation of the phenomena and caused so much diversity of opinion that in the casuistic literature on the ontogenesis of the Marsupialian dentition one finds the different authors continually at variance; as soon as detailed questions are dealt with there is hardly any agreement. This period in the history of odontology begins with the papers Kükenthal, Leche and Röse. Especially the researches and views of the first of these authors were of paramount importance for the new course.

However much these authors might differ in other respects, they agreed on the point that the functionating dentition of the Marsupials must be considered to correspond to the milk-dentition of the Monodelphians. And as to the tooth which precedes the first molar and is replaced, it should be looked upon as a milk-tooth which is replaced by the only developed tooth of the permanent dentition. In short, while in the opinion of the older anatomists Marsupials only possess the second set of teeth and of the first only temporarily a single tooth, this opinion is reversed after 1890: Marsupials possess only the milk-set and of the second one only a single tooth develops. For Kükenthal and Röse this tooth was the remnant of the lost dentition, for Leche on the other hand it was the first element of a new series of teeth, attaining full development in the Monodelphians.

When investigating the development of the dentition of a Marsupial, preferably of a Polyprotodont, without being biased by existing theories, one cannot help wondering a little at the weakness of the grounds on which Kükenthal based his theory, the more so since on a premise against which many objections might be raised he wanted to introduce an entirely new conception into mammalian odontology, a conception which made its confusing influence felt over the whole range of this department of science. This conception is the so-called prelacteal dentition. As such this author distinguishes a dental series which would precede the milk-teeth series. Hence we should have to distinguish in mammals at least three dentitions: the prelacteal, the lacteal and the permanent one. Of these three the lacteal would be the functionating dentition with Marsupials, of the permanent one only a single tooth (the last premolar) would develop and of the prelacteal one small teeth would be evolved but never reach full development and always be reduced.

How did the investigators between 1890 and 1900 arrive at this view? Embryological investigation of the development of the Marsupialian dentition showed that also with this group of vertebrates two dental series were undoubtedly evolved. And the topographical relation of the tooth-germs of either series was exactly similar to that which is found in the Anlage of the dentition of the Monodelphian mammals, viz. the germs of one series lie buccally of those of the other series and alternate with them. Now it appeared, however, that otherwise than with the Monodelphian mammals, the teeth of the buccal or outer set become rudimentary, while the germs of the inner set develop into the functionating dentition. At first sight this would seem to confirm the view of the older anatomists that the functionating dentition of the Marsupials corresponds with the second or permanent set of the Monodelphians, for also this latter develops from the inner series of tooth-germs. If Kükenthal had only given this obvious interpretation to his observations, as e.g. Wilson and Hill [1]) did in 1897, much confusion and contradiction in odontological literature would have been avoided. But Kükenthal was led astray by a histological phenomenon to which he attributed a paramount and in my opinion erroneous significance. He saw namely that the free border of the dental lamina, after the germs of the inner series had evolved, became slightly thickened. This phenomenon drew his particular attention and he attributed so great a significance to it that it became the basis for his theory. He saw namely in this thickening the indication of still another dental series, so that three sets of teeth would evolve with Marsupials, an outer one, of which the teeth show a rudimentary development and are afterwards reduced, a middle one, the teeth of which form the functionating dentition, and an inner one which however only appears as a thickening of the free border of the dental lamina and of which only a single tooth would develop — the only successional tooth of Marsupials. I wish to point out at once, however, that no investigator has ever observed in this slightly thickened free border of the dental lamina anything that points to even a beginning of dental development. Now this should raise our doubt whether in this thickening we may see a phenomenon, actually pointing to a dental series which the

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[1]) Development and succession of teeth in Perameles. Quat. Journ. of microsc· Sc. Vol. XXXIX. 1897.

Marsupials would have lost in their latest phylogenetical evolution.

Leche, who also assigned a definite significance to the free border of the dental lamina, therefore gave another explanation which from this point of view was more plausible, namely that it should not be considered as the last trace of a lost dental series but as the first indication of a new one. Leche's opinion found no adherents and so the free border of the dental lamina was assumed by a group of investigators, following Kükenthal, to prove that the Marsupials must have lost a dental series. And once arrived at this point of view these authors were now obliged to identify this series, being the most inwardly situated, with the permanent set of teeth of the Monodelphian mammals and the middle series, which in Marsupials develops into the functionating dentition, could then only be identified with the milk-dentition of the higher mammals.[1])

Now the difficulty arose how to explain the outer row of small teeth which in Marsupialian embryos evolve and partially develop, but are afterwards reduced. This led Kükenthal to introduce into literature the conception of a prelacteal dental series, a dentition which would precede the milk-teeth.

The reason why Kükenthal attached so much importance to the thickened border of the dental lamina is not very evident, the less so as it created such a fundamental difference in the dental evolution between Didelphian and Monodelphian mammals. In both groups the Anlage of two series of tooth-germs is found, an outer and an inner one. But instead of identifying these two, the inner row of the Didelphian mammals is identified by him with the outer row of the Monodelphians, while the inner row of these latter is met with in Marsupials as a simple thickening of the border of the dental lamina in which never a trace of real dental evolution has been observed, and the outer row is referred to a hypothetical dental series which is supposed to have functionated in the hypothetical ancestors of the mammals. Now this interpretation seems rather strained and moreover it must a priori be highly improbable that the dental series which in the Monodelphian mammals has such a preponderating significance as a permanent dentition would have disappeared in the more primitive Didelphian mammals without leaving a trace, even in the embryo. Placing ourselves for a moment on Kükenthal's viewpoint that there have originally been three

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[1]) The opinion that from this thickened edge of the dental lamina the only tooth having a predecessor (P_4) would originate, is wrong. This particular tooth belongs to the series of the other functionating teeth and its Anlage is exactly the same but only starts a little later than the other teeth.

series of teeth, we should expect that where the so-called prelacteal dental series is still visible as a number of small but fully developed teeth, also something would be seen of that inner row, since it is this latter which develops so powerfully in the Monodelphian mammals. And especially since according to KÜKENTHAL one of the teeth of this inner row does not become rudimentary, but develops fully.[1]) So while one element of this inner row attains its full development, the development of all the other would always have been completely checked. This is exactly opposite to what is observed in the outer one of the supposed three rows, which also does not produce fully developed teeth, but the elements of which do often appear as well-shaped little teeth that are reduced after having formed.

This difference in development between the outer and inner row with Didelphian mammals could in my opinion only be explained by assuming that the inner row were checked in its development long before the outer one. But in this case the ancestral forms of Marsupials would have possessed not three but only two dental series, which would however not have agreed with the two series of the Monodelphian mammals.

The preponderant and absolutely unjustified significance assigned by KÜKENTHAL, RÖSE and DEPENDORF to the thickening of the border of the dental lamina of Marsupials has complicated the problems of dentition in no small measure. WILSON and HILL already showed this in 1897 by pointing out in particular that in this thickened lamina not the least traces of local thickening can be observed which would indicate a commencing Anlage of any tooth. According to them the free border of the dental lamina simply originates by emancipation of the tooth-germs of the teethband.

So KÜKENTHAL postulated already three dental series for the Marsupials: a prelacteal, a lacteal and a permanent one. But the complications of this problem of dentition were not at an end yet. For also at the lingual side of the Anlage of the molars the so-called free teethband border was observed.

Now KÜKENTHAL and other authors are of opinion that the molars originate by fusion of the Anlage of teeth of both series, namely of elements of the lacteal and of the permanent dentition. By this hypothesis one was obliged to assign to the free teethband border lingually of the molars a different meaning from that lingually of the more frontally situated teeth.

With these latter it was an indication of the lost series of per-

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[1]) It has been remarked above that this opinion is erroneous.

manent teeth, but since these would with the Marsupials have also been incorporated in the formation of the molars, the free teethband border lingually of the Marsupialian molars could only have the meaning of still a fourth series of teeth. In this way the idea of a series of post-permanent teeth was introduced into odontological literature.

Thus we see that only on account of the significance assigned to the free teethband border the conceptions of prelacteal and post permanent teeth were successively introduced into odontology and that besides the identification of Didelphian and Monodelphian mammals became different from that given by the older anatomists. Not to mention more substantial objections which will be presently explained, the general question is justified whether it was admissible to build up such a far-reaching theory on such a feeble base and to make morphological deductions of paramount importance from such a weak starting-point to the reality of which objections might moreover be raised. And if no other arguments had led me to reject Kükenthal's theory as erroneous, it would already have appeared to me little plausible by its general internal weakness.

Still this theory has found several adherents because no argument could be adduced by which it could a priori be declared to be false; besides the theory seemingly linked the phenomena of tooth-changing in Reptiles and Monodelphian mammals. One of the characteristics of the reptilian dentition is so-called polyphyodontism; during life the process of tooth-changing is an unlimited one and a number of dental series evolve in succession. With mammals on the other hand tooth-changing occurs only once, they only develop two dental series, are diphyodontic. Exceptionally also monophyodontism is found, no tooth-change taking place. The indeed obvious view was now generally held that the diphyodontism of Mammals had developed out of the polyphyodontism of Reptiles, the number of tooth-changes having gradually diminished to one and hence that of the dental series to two. And on account of this view the idea that with Marsupials indications of four dental series would be found, namely a prelacteal, lacteal, permanent and postpermanent one, had nothing objectionable. On the contrary this interpretation of phenomena supported the apparently so logical deduction of diphyodontism from polyphyodontism. So factors were certainly present which secured a favourable reception for Kükenthal's theory.

Considerations of a more general kind would, as was stated above, have already made this theory less acceptable for me. But my object in this paper is not to point out the weak side of this theory and so to arrive at the conclusion that it cannot be right. I propose in what follows to investigate the morphological significance of the Marsupialian dentition, starting from quite different viewpoints.

A few years ago the Proceedings of this Academy contained a paper by myself on the relation between the mammalian and reptilian dentition. In particular the question was dealt with whether the diphyodontism of Mammals might be derived from the polyphyodontism of Reptiles by diminishing the number of tooth-changes. In such a derivation it is tacitly assumed that the tooth-changing process in Reptiles and in Mammals are identical phenomena. In the paper mentioned and in later more extensive papers it has been shown that this supposition is not correct. The tooth-changing process of Reptiles and that of Mammals are two phenomena different in principle. Hence we may not derive the diphyodontism of the latter from the polyphyodontism of the former. And in order to prevent confusion that might be caused by the meaning of these words in which the older conception is reflected, it is desirable to drop these terms and to indicate by other terms what is essential in the mammalian and reptilian dentition. These terms will be given presently.

In my investigation on the morphological significance of the Marsupialian dentition I have from the outset started from another point of view than preceding authors. For them the question was in what relation the dentition of the Didelphian mammals stands to that of the Monodelphians, what could be found in Marsupials with their absence of a tooth-change of the two dental series of the Monodelphians. For me the principal question was: to what extent do we still find in Marsupials during the Anlage of the dentition phenomena that are characteristic for the dentition of Reptiles? For a right understanding of the answer to this question a short account must precede of the chief evolutionary phenomena of the reptilian dentition as compared with that of Mammals.

In the mentioned paper it has been shown that the reptilian dentition originates from tooth-germs, evolving in two rows on the teethband, one row on the buccal side close below the epithelium of the cavity of the mouth and a second row on the free border of the teethband. Both rows consequently lie as an outer and an inner one with respect to one another, for which reason they are distinguished as Exostichos and Endostichos. And since the first Anlage of the dentition is double-rowed it may be indicated as "distichical".

Another characteristic is that the tooth-germs of both rows alternate with each other. First the tooth-germs of the exostichical row become visible and the teeth so evolved remain also in their development a little in advance of those of the endostichical row In Mammals the same structural principle is met with. Here also the Anlage of the dentition is in a buccal — exostichos — and in a lingual row or endostichos and the elements of the two rows alternate as with the Reptiles. Hence the dentition of both groups of vertebrates is distichical in Anlage. In the course of its further development however essential differences arise between the dentitions of Reptiles and Monodelphian Mammals.

With the Reptiles the endostichical teeth are regularly intercalated between the exostichical, so that in the functionating dentition the two rows are fixed on or in the jaw in a single row. So it is characteristic of the morphology of the reptilian dentition that in it the two rows of teeth functionate simultaneously. I should like to express this fact by calling the reptilian dentition "hamastichical". And since at any rate in the beginning between every two exostichical teeth an endostichical one is inserted and takes part in the construction of the dentition, the mixing of the rows being thus a regular one, also this fact might find expression in the characterisation of the reptilian dentition. Hence the functionating dentition of the Reptiles should be described as an "isocrasic hamastichical" one.

In regard to this characteristic a fundamental difference is now met with between Reptiles and Monodelphian Mammals. Although also with these latter the two dental rows evolve shortly after each other, still the inner one or endostichos generally develops much more slowly and its elements do not push themselves between those ot the exostichos. This latter forms a compact dentition of which the teeth pierce with a certain regularity and functionate during some time, while the teeth of the endostichos remain below the surface, developing slowly. When they have reached a certain degree of development they gradually expel the teeth of the endostichos, i. e. the milk-set, fill up their places and form the second or permanent set. The typical difference between the reptilian and mammalian dentition consequently is that the functionating dentition of the former consists of elements of both rows, while on the other hand with the mammals the two rows functionate one after another. Hence I distinguish the dentition of the Monodelphian mammals as *chorisstichical* as compared with the hamastichical one of the Reptiles. It should be pointed out however that according to the investigations of Leche the functionating dentition of Erinacidae also consists of a mixture of elements of the rows. Probably this expresses the very primitive character of this animal group.

In what precedes the chief characteristic of the nature of the tooth-change in mammals has also been indicated: the endostichical row expels the exostichical, in other words the two rows succeed one another, there is a change of series. This form of tooth-change will therefore be distinguished as "stichobolism". With Reptiles the change must have an entirely different character, as here the two rows constitute simultaneously the functionating dentition, so that there can be no question of substitution of one series by another. So with Reptiles the change is of a much more elementary character. In this group the productivity of the teeth-band does not stop with the Anlage of a single exo- and endostichical dental series. On the contrary, after the endostichical series has been evolved, a third series appears which must be considered as the substituting series of the first evolved exostichos. After this a fourth appears which will replace the first endostichos and so on. The elements of these subsequent series are formed by the matrices from which the first two series came forth, in this way that a matrix first produces an element for the first exostichos, then for the second exostichos and so on. The second product of a matrix is destined to expel and replace the first and is in its turn expelled by the third product. All the products of the same matrix may be distinguished as a dental family. With Reptiles every tooth is therefore to be considered as a generation that will be replaced by a following younger generation, produced by the same matrix. So an exostichical tooth will always be expelled by an exostichical one. Consequently there are as many matrices in the teeth-band as the dentition has functionating teeth. These matrices go on producing continuously. With some Reptiles the time between the formation of two dental generations is longer, with others shorter, but there is no question of a change of series, as the series functionate simultaneously. Here the change has the characteristic that the members of a family, successively produced by a matrix, replace each other. In contradistinction to the stichobolism of the Monodelphian mammals I propose to distinguish this process as "merobolism".

What is now the relation between the mammalian dentition in which only once an exo- and endostichical series is evolved and the reptilian dentition in which a number of exo- and endostichical series succeed each other like as many generations? The simplest conception is that with Reptiles the dental matrix extends its productivity over the whole life of the individual, giving birth each time to an elementary tooth, while on the other hand with Mammals the whole productivity of a dental matrix is exhausted in the formation of a single product, containing potentially a larger number of elementary teeth, a number of dental generations. A whole dental family of the Reptiles has as it were been condensed in a mammalian tooth. This dental Anlage will therefore be distinguished as "symphyomeric".

So the mammalian tooth is not identical with a reptilian one, but represents all the generations which come forth from one matrix of the teeth-band, i. e. a reptilian dental family. In most cases two, sometimes three such generations can be recognised on the relief of the mammalian teeth, they are according to their structure dimeric or trimeric.

The reptilian teeth on the other hand are always *monomeric*, each tooth corresponds to a single generation only, these generations succeeding each other sometimes more sometimes less rapidly. In contradistinction to the symphyomeric dental Anlage of Mammals the dentition of Reptiles must therefore be indicated as *stoicheomeric*.

Summarising the main points of the above comparison between the dentitions of Reptiles and Monodelphian mammals, we have what follows. The Anlage of the dentition is in both groups distichical, the Anlage of the teeth with Monodelphian mammals symphyomeric, with Reptiles stoicheomeric, the shape of the teeth with the Mammals dimeric, seldom tri- or polymeric, with the Reptiles monomeric, the functionating dentition with the Monodelphian mammals chorisstichical, with the Reptiles isocrasic hamastichical, the tooth-change with the Mammals stichobolic, with the Reptiles merobolic. Comparing this characterisation of the dentitions of the vertebrate groups with the generally accepted one, that the dentition of Reptiles is polyphyodontical, the teeth simple, with the Mammals the dentition diphyodontical and the teeth partly composite, it would appear as if I had made the difference between the two forms of dentition larger. But this is not so much the case as it seems. The essential difference is that by me the relation between the so-called polyphyodontism of the Reptiles and the diphyodontism of the Mammals is rejected in principle, since the tooth-change is an entirely different phenomenon in these two groups. Directly related to this is the difference in structure of the functionating dentition on which I have laid stress.

The differences described above are schematically represented in fig. 1. Scheme A refers to the Reptiles, the exostichical teeth are dotted, the arrows show the mechanism of the tooth-change. Scheme B refers to the Monodelphian mammals. The dots and arrows have the same meaning as in A.

Basing ourselves on what precedes we may answer the question what place the dentition of the Didelphian mammals occupies in the

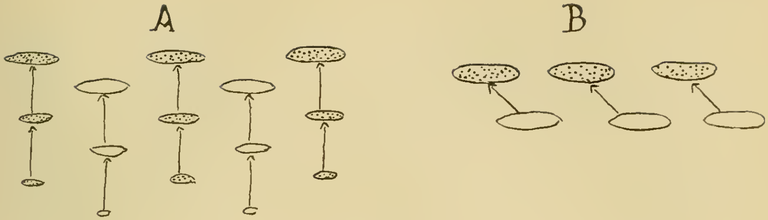

Fig. 1.

system. It is easily perceived that for each of the above described points of difference between the reptilian and monodelphian dentitions this question must be put and answered separately. Now there are three possibilities: *a*. it behaves like the reptilian dentition, *b*. like that of the Monodelphian mammals, and *c*. it occupies an intermediate position and has points in common with both, so that it is no longer a reptilian dentition but not yet in every respect that of a Monodelphian mammal. The answer, based on an investigation of a fair number of young ones of several marsupial groups is given as succinctly as possible in the following table.

	Anlage of the dentition	Anlage of the teeth	Shape of the teeth	Form of the dentition	Tooth-change
Reptiles	Distichical	stoicheomeric	monomeric	hamastichical (isocrasic)	merobolic
Monodelphian mammals	Distichical	symphyomer.	dimeric or trimeric	chorisstichical	stichobolic (complete)
Marsupials	Distichical	symphyomer. or stoicheom.	monomeric or dimeric	hamastichical (anisocrasic)	stichobolic (very incomp.

This table shows that according to my investigations the Marsupials agree with the Reptiles and the remaining mammals only in regard to the Anlage of their dentition, since also with them it is evolved in two rows: an exostichal and an endostichical one, but that for the rest the Marsupials form in every respect a transition between Reptiles and Monodelphian mammals.

This will be shown successively for each of the ontogenetical and morphological properties of the dentition and the teeth. In this first communication only the dentition as a whole will be dealt with, in a following one the teeth as elements of the dentition will be studied more closely.

Concerning the dentition it will therefore be attempted to show that its Anlage is distichical, i.e. that the Anlage has two rows, while its final structure is hamastichical, i.e. that elements of both rows contribute to the construction. As to the distichical nature of the marsupialian dentition, this can of course be shown best with the dentition of polyprotodontic Marsupials.

The further discussion will be based on the partially developed dentition of a pouch-young of Perameles obesula, starting with the lower jaw. In fig. 2 this Anlage has been sketched. In agreement

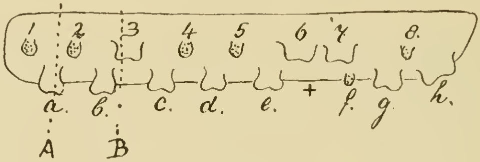

Fig. 2.

with other authors I found here a number of evolved but not further developing small teeth. These have been dotted in fig. 2.

The scheme in which the teeth are shown in their mutual topographical situation, represents the dental Anlage when the teeth-band is viewed from the buccal side. It is evident that the tooth-germs lie in two rows, one nearer the surface epithelium and one along the lower margin of the teeth-band. There are eight teeth in the exostichical row, numbered 1—8, the endostichical row also contains eight teeth, indicated by *a—h*. The teeth of the two rows are clearly seen to alternate. The object studied by me, from which fig. 2 has been drawn, was at about the same stage of development of the dentition as the object described as stage IV by Wilson and Hill in their monograph on the evolution of the dentition of Perameles. Of the eight exostichical teeth only three attain further development, namely the third, sixth and seventh in the row, the other are reduced.

The exostichical teeth are evolved from the lateral margin of the teeth-band, as with the Reptiles. This is also the case with the Monodelphian mammals, but still the Marsupials agree in this respect much more with the Reptiles than with these mammals. How great in young stages of development the agreement is between the Anlage of the teeth of Marsupials and Reptiles, may be seen by comparing figs. 3 and 4. In fig. 3 the teeth-band with the Anlage of an exostichical and endostichical tooth of a young Lacerta is sketched, the exostichical tooth lies parietally close below the epithelium of the cavity of the mouth, the endostichical Anlage lies terminally. Fig. 4 is a reproduction of Wilson and Hill's fig. 37 and refers to the Anlage of

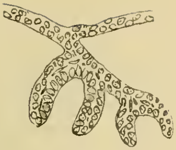

Fig. 3.

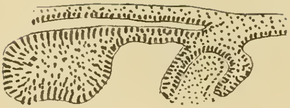

Fig 4.

teeth 3 and 4 in the scheme of fig. 2, at a stage of development somewhat younger than was at my disposal. The agreement is so striking that only the more powerful development of the primitive pulp-cells in fig. 4 proves that it is not a teeth-band with dental

Fig. 5.

Anlage of a Reptile. Already LECHE pointed out this agreement of the teeth-band apparatus with the tooth-germs between Marsupials and Reptiles for Myrmecobius (Morph. Jahrb. XX p. 118). This author says in the place referred to: "dasz die erhaltenen Bilder in Bezug auf die Beziehungen der Schmelzleiste des rudimentären Zahns zur Leiste der persistierenden eben so sehr von den bei allen übrigen Säugethieren vorkommenden Befunden abweichen, wie sie an Zustände bei manchen Reptilien erinnern" (that the obtained pictures in regard to the relations of the border of the teethband of the rudimentary tooth to the teethband of the permanent teeth differ as much from what is found with mammals as they remind us of the conditions with many Reptiles).

As will be seen from fig. 3, of the exostichical teeth only three develop, namely those numbered 3, 6, and 7. Especially the meaning of tooth 3 and 7 is important for our further discussion and therefore it is necessary that its exostichical nature is definitely proved. So in fig. 5 some fifteen successive sections are given through the region of the teeth-band, enclosed in fig. 2 between the lines *A* and *B*.

In this region lies also the posterior end of the endostichical tooth *a*, visible in the sections *a*, *b*, and *c* as a terminal thickening of the dental lamina. Then follows the exostichical tooth 2, already furnished with a dentine cap, but otherwise rudimentary, sketched in sections *b-f*. That this tooth is formed from the teeth-band not terminally but parietally is clearly seen. Next comes the endostichical tooth *b*, the Anlage of which may be followed in the sections *f-p* as the already terminally invaginated thickening of the dental lamina. But before this Anlage is completed that of the exostichical tooth 3 appears. That also this tooth is connected with the teeth-band not terminally but parietally like the tooth 2 and consequently belongs to the exostichos, is proved beyond doubt by the pictures. As an additional proof the Anlage of tooth *b* and tooth 3 at a younger stage of development is given in fig. 6. This is a reproduction of WILSON and HILL's fig. 34. In my opinion there can be no doubt as to the exostichical nature of tooth 3 in Perameles. That so much stress is

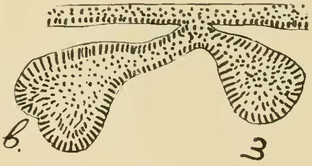

Fig. 6.

laid on this point is on account of the circumstance that while teeth *a* and *b* will later develop into the first and second incisors, tooth 3 produces the third incisor. Now it follows from what precedes that with Perameles the functionating incisors do not all originate from a single dental series, but partly from the endostichos (= permanent set of the Monodelphian mammals), partly from the exostichos (= milk-set of the same mammalian group).

As to the dental Anlage of tooth 6, this will produce the last premolar, the only tooth which, as we know, is replaced in the marsupialian dentition and which in all respects behaves as a milk-tooth. To this I shall return later. As to the manner of Anlage and the relation between the tooth germ and the teeth-band there is not the slightest difference between tooth 3 and 6. This is acknowledged as well by WILSON and HILL as by DEPENDORF, although this latter without any reason and quite erroneously simply considers this as a secondary state. This view was forced upon the author since otherwise he would according to his system necessarily have arrived at the conclusion that tooth 3 and 6 belonged to the so-called prelacteal dental series, while a complete development of teeth of this series may not be assumed by adherents of a prelacteal dental series. This is a very striking instance how strongly the idea of a "prelacteal dentition" spoils objectivity in judging the facts. WILSON and HILL, who like myself consider the row 1—8 in fig. 2 as the row of the milk-set, accordingly state expressly that tooth 6 at its first appearance is evolved from the buccal wall of the teeth-band and not terminally. Curiously enough however they do not state this for tooth 3 and 7, although their drawings clearly show such an Anlage at any rate for tooth 3, as will appear from figure 6, here reproduced. Very peculiar is DEPENDORF's reasoning concerning the remarkable situation of tooth 3. "Würde der Kiefer", he says on p. 255, "später nicht an Länge zunehmen, so hätten wir im Bereiche der Incisivi von Perameles ebenfalls einen Zahnwechsel zu erwarten, in der Art, wie er wirklich bei den Diprotodontiern in der Prämolarenreihe vor sich geht" (If the jaw did not later increase in length we should have to expect in the region of the incisors of Perameles a tooth-change as it actually occurs with the Diprotodontians in the premolar series). So he grants indirectly that the Anlage of the developing tooth 3 in regard to that of tooth *b* and *c* agrees entirely with the relation of a tooth-germ of the milk-set to that of the permanent teeth.

For the genetical significance of the teeth constituting the dentition of Perameles it is important emphatically to point out that the teeth

3 and 6 which develop fully, belong to the same series and are entirely equivalent to the rudimentary little teeth 1, 2, 4, 5, and 8. Tooth 7 will presently be separately dealt with. Bearing in mind that by the adherents of Kükenthal's theory these rudimentary little teeth are adduced as a proof for the assumed prelacteal dentition, the importance of the mentioned fact becomes evident. If we accept Kükenthal's theory teeth 3 and 6 must be considered as prelacteal teeth reaching development. This consequence however no adherent of this theory has until now had the courage to accept. The viewpoint of this paper is much simpler and more natural, the teeth 1—8 are exostichical (milk-teeth of the Monodelphians) and among these 3 and 6 attain development and push themselves in between the elements of the endostichical teeth, as with the reptilianlike ancestral forms also the remaining teeth of this series would have done.

The point of view of this paper leads in its consequences to somewhat radical conclusions as to the relation of the incisors of the Marsupials to those of the Monodelphian mammals. For if the functionating incisors of the Marsupials are derived from the two dental series and so form a hamastichical row, they must not be identified with the incisors of either set of teeth of the Monodelphians, but with both. In other words the incisors of a polyprotodontian Marsupial are identical with the incisors of both the milk-set and the permanent set of the Monodelphians. By this conclusion it seems to me that an existing difficulty in the comparison of the incisors of Monodelphian and Didelphian mammals is solved in a simple manner. The largest number of incisors of the Monodelphian mammals is three, in the permanent and milk-set together six. With the Marsupials five develop at the utmost, although the Anlage of six is present. As well in the permanent as in the milk-dentition at least three would accordingly be lost with the Didelphians. But no trace of them has ever been detected. And so there always remained an unbridged gap between the two groups of mammals. In my opinion this gap does not exist. The highest number of incisors, evolved with Marsupials, was stated to be six.[1]) Woodward has found this number in Petrogale. Of these six only three develop with Petrogale, namely 2, 4 and 6, while 1, 3 and 5 become rudimentary. It is clear that here we have development of the incisors of the endostichical series only, while the exostichical teeth do not develop. The three teeth that become rudimentary must be identified with the three milk-

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1) The total number of rudimentary and developing teeth may occasionally be larger than six in the domain of the incisors, e. g with Dasyurus, but this is the result of a complication which will be explained in the following communication.

incisors of a Monodelphian mammal, the three that develop with the three incisors of the permanent dentition. In this way a natural connection is established between the number of incisors of the two groups. Here I shall restrict myself to a simple mentioning of this view, remarking in passing that e.g. of the five incisors developing with Didelphis three will belong to one series, two to the other. So the hamastichical character of the dentition is still very strongly expressed there.

It has been shown above that also the series of incisors in the lower jaw of Perameles is hamastichical, the first and second incisor being endostichical, the third exostichical. For the upper jaw this is not so easily proved, since there the incisors are evolved more directly and individually from the buccal epithelium. Five incisors develop here in all. As many are evolved in the lower jaw and phenomena, observed in older specimens, rendered it probable that also these five would be evolved in two rows. To prove this more fully would take up too much space here. That the five incisors in the upper jaw correspond with the five, evolved in the lower jaw, follows still from the fact that rudimentary incisors do not occur in the upper jaw.

I need not enlarge here on the exostichical character of tooth 6. From this tooth-germ the premolar is formed which undergoes substitution. Now in the domain of tooth 6 and 7 an irregularity in the constitution of the dentition is met with. As far as tooth 6 the elements of the two series alternate regularly and so after the exostichical tooth 6 an endostichical one would have to follow. But this tooth is still lacking at the stage of fig. 2. Still at the spot marked by a cross the free border of the dental lamina is already slightly thickened and with further development the endostichical tooth will here be formed which is destined to replace the exostichical tooth 3 (the third premolar). Wilson and Hill have described these stages more fully. It should be particularly pointed out here that this substituting tooth is formed in the same way from the free border of the dental lamina as the teeth *a*, *b*, *c* etc., for these also are formed terminally. So the substituting tooth is isostichical with the teeth *a*, *b* etc., the strong development of tooth six however seems to be the cause of its later Anlage.

After tooth 6 now follows tooth 7 and concerning this one I disagree with Wilson and Hill in this respect that according to my view also this dental Anlage, from which the first molar will develop, belongs to the exostichos. If this view is right, this would mean that with Perameles also the first molar belongs to the exostichical dentition, i.e. the milk-dentition of the Monodelphians. It may be stated at once that the same holds for the first molar of the upper jaw set of Perameles.

It is easier to prove the correctness of this view for the lower than for the upper jaw. Following up the Anlage of the tooth-germ of the first molar in the lower jaw, it is clear that it does not evolve from the free border of the dental lamina, but from the labial wall, contrary to the second molar which is formed indeed as an endostichical tooth from the free border of the dental lamina. But in the lower jaw a more definite proof may be given, namely: Following up the Anlage of M1 — i.e. tooth 7 — in the lower jaw, one finds that very shortly before the posterior edge of this Anlage the free end of the teeth-band produces a rudimentary tooth-Anlage. This is indicated in fig. 2 by *f*, and in fig. 7 sections of it on the right and left side of the jaw are drawn. The Anlage of these rudimentary germs puts the exostichical nature of the first molar beyond doubt. If these germs developed further also tooth 7 would be expelled, as is in reality the case with tooth 6.

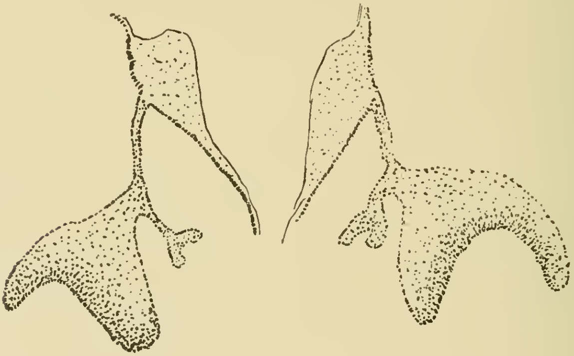

Fig. 7.

The first molar in the upper jaw has been said to belong also to the exostichos. Here however I have found no trace of the corresponding endostichical tooth. And the proof can here only be given by a comparison of the topographical relation of the germs of the first and second molar in regard to the dental lamina. Therefore in fig. 58 thirteen sections are given of the Anlage of the first molar and in fig. 9 of the second molar of the upper jaw. Especially for those who are acquainted with the evolution of the reptilian dentition

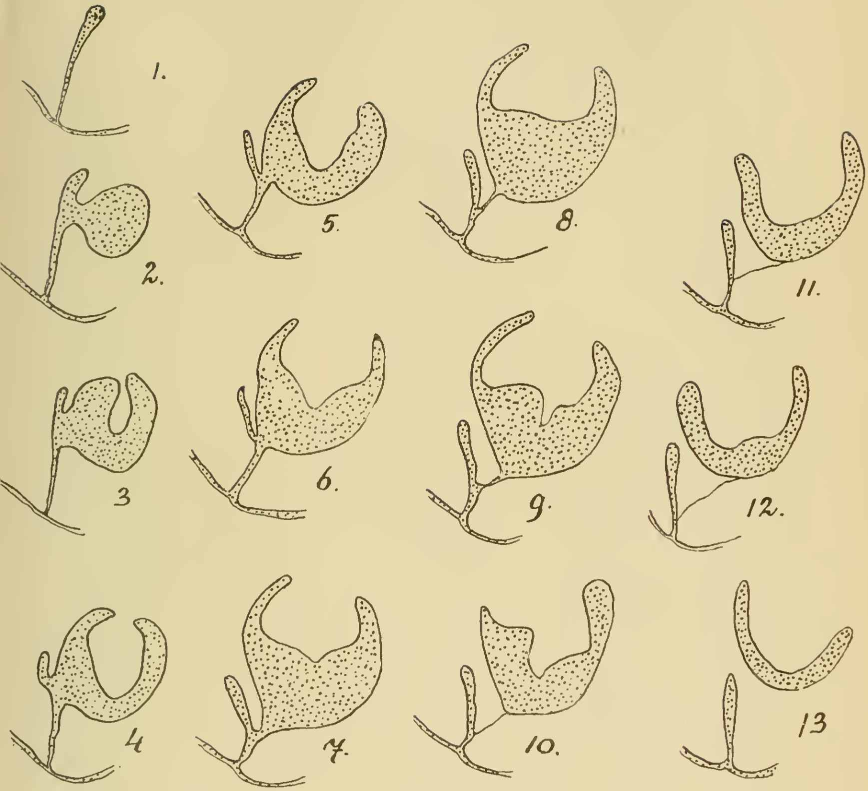

Fig. 8.

it will be clear that in fig. 8 we have a so-called parietal dental Anlage and in Fig. 9 a terminal one. For over the whole length of the Anlage in fig. 8 the lamina ends in a free border and the place where in the posterior part of the enamelling organ the connecting strand between this organ and the dental lamina is attached to this latter, furnishes a certain proof that this Anlage has been evolved from the dental lamina shortly below the buccal epithelium. The tooth-germ of the second molar, on the other hand, sketched in fig. 9, begins as a thickening of the upper edge of the dental lamina and retains this character over its whole Anlage. In the sections 9, 10, 11, and 12 the tooth is visible which is indicated in fig. 2 as tooth

8 and belongs to the exostichical series. This little tooth starts at the same spot on the dental lamina as the connecting strand of the enamelling organ and the first molar in fig. 8.

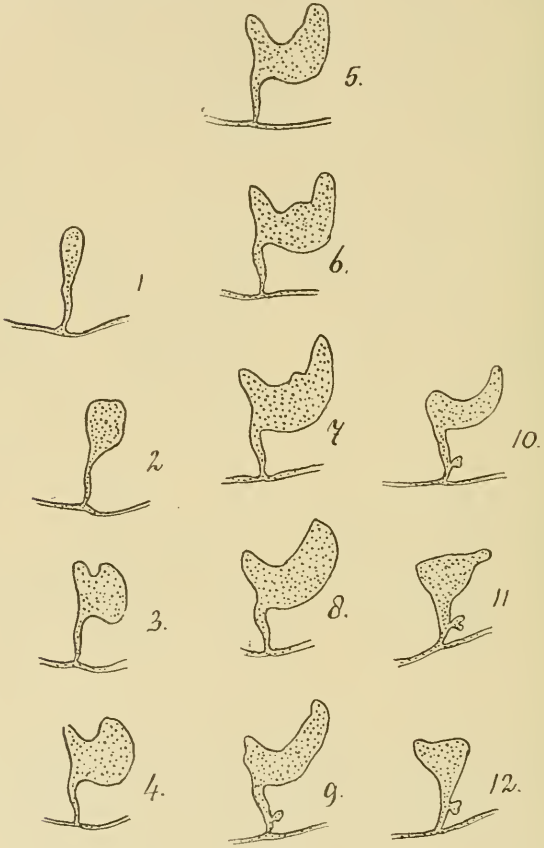

Fig. 9.

These brief indications may suffice here to prove that the first so-called molar of Perameles is exostichical, i.e. a milk-tooth. From what has been said here it becomes probable that the second molar of Perameles is identical with the first molar of the Monodelphians. For the first molar of Perameles is nothing else but the fourth milk-molar which is not expelled and replaced like the third. The first and second milk-molar are formed in Anlage (tooth 4 and 5 in the scheme of fig. 2) but do not develop.

In what precedes it has in my opinion been definitely proved that in its constitution the marsupialian dentition has an essential characteristic in common with the reptilian dentition, namely hamastichism. For the dentition of Perameles chiefly consists of endostichical teeth (these are the so-called permanent teeth of the Monodelphians), but of the exostichical series the third incisor and first molar functionate permanently, the third milk-molar temporarily together with these endostichical teeth. In the upper jaw with its five incisors the hamastichical character is still more clearly perceived since of these five incisors three belong to the exostichical and two to the endostichical series.

It is remarkable that in literature one repeatedly comes across remarks, presented in the shape of possibilities or surmises, which fit in perfectly with the here briefly framed theory of the marsupialian dentition. If these investigators had not always been influenced by the opinion that the diphyodontism of Mammals and the polyphyodontism of Reptiles were identical, only quantitatively different phenomena, a more correct conception of the marsupialian dentition would in my opinion have sooner prevailed. But in this erroneous premise the conceptions of prelacteal and postpermanent dentitions were rooted and it was these which blocked the road for a right understanding of 'the marsupialian dentition. So e.g. Röse says in his investigation of the dental evolution of Marsupials: "Es scheint mir sehr wahrscheinlich dasz auch bei Phalangista nicht allein der letzte Prämolar, sondern auch der dritte Incisivus des Oberkiefers aus der zweiten Zahnreihe entsteht." (To me it seems very likely that also with Phalangista not only the last premolar but also the third incisor of the upper jaw is formed from the second dental series). This statement of Röse is similar to that of Dependorf, quoted above, who also, in this case for Perameles, expresses the possibility that the incisors originate from the two dental series. [1]). The significance of this fact for the identification of the incisors of Marsupials and Monodelphian Mammals has been explained above.

A very remarkable discussion as to the manner in which with the Monodelphians the four milk-molars and their substituting teeth have originated, is found in Woodward's: "Development of the

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[1]) In this respect Bensley's statement is remarkable that with Didelphis the incisors of the lower jaw do not stand in a single row, the second stands more inwardly between the first and the third. (On the evolution of the Australian Marsupialia. Transact. Linn. Soc. London. Vol. IX, p. 187)

Teeth of the Macropodidae" (Proc. Zool. Soc. 1893). The author points out that with Amphilestes "there are 12 or 13 cheek-teeth present, and no evidence of the presence of two sets of teeth. May not the five posterior ones", the author continues, "represent the five molars (Bettongia) while the first 8 might be supposed to give rise to the 8 premolars, (4 milk and 4 permanent) and by the retardation of each alternate one the condition in the Placentalia might be brought about, the 2nd, 4th, 6th and 8th being retarded and displaced to form a second or replacing set, while the 1st, 3d, 5th and 7th develop early and are replaced by the former" (loc. cit. p. 470). So here the tooth-change is explained as a possible shifting into two rows of a larger number of teeth in the most primitive mammals.

If Woodward had known that two-rowedness is an essential characteristic of the dentition of Reptiles and certainly also of the Marsupials, he would have explained the relation between the dentition of Amphilestes and the Marsupials with four premolars in the opposite direction and then in my opinion correctly. It seems to me that with Amphilestes hamasthichism is still fully expressed, i. e. the four teeth of the endostichical row push themselves between the four teeth of the exostichical row as with the Reptiles. In the now living Marsupials this hamastichism has for the greater part been lost by a number of exostichical teeth becoming rudimentary, with the Placentalia it has been entirely lost exactly on account of the more complete development of the exostichical teeth, by which the endostichical ones were retarded and the foundation was laid for a system of tooth-change, in which the exostichical teeth were replaced by the endostichical.

Now this process deviates in its essential points entirely from that of the Reptiles. But for a correct insight into these relations the knowledge of the structural principle of the distichism of the reptilian dentition was required. And in this communication it has been proved in principle that this distichism leads with Reptiles to a hamastichically built dentition, with the Monodelphian Mammals to a chorisstichically built one, while the Marsupials form a transition between them, as their dentition is still partly hamastichical, one element being with many forms replaced in the same manner as with the Monodelphian mammals, so that also the phenomenon of chorisstichism is already present in principle. But it should be clearly pointed out that the question to what extent the marsupialian dentition is still hamastichical will have to be solved for each form separately.

A view, entirely agreeing with the principle developed in this paper, has already been held by Winge in regard to the large number of molars of Myrmecobius. This author is namely of opinion that this large number must be explained by the non-expulsion of milk-teeth. So also for this author the dentition of Myrmecobius at any rate consists of a mixture of milk-teeth — exostichical teeth in my nomenclature — and "permanent" i. e. endostichical teeth. Also according to Winge the dentition of the mentioned Marsupial is consequently hamastichical.

Finally in this relation the results may be mentioned of Leche's investigation of the dentition of Erinaceus which consists of elements of the milk-set and of the permanent set. Whether this hamastichism is a secondary acquisition or the direct continuation of the original phylogenetic condition does not matter. However, this phenomenon is certainly remarkable in a form which has remained so primitive as Erinaceus. That besides hamastichism, be it to a limited extent, may also re-appear in other Monodelphian mammals, is proved by the dentition of the catarrhine Primates, in which the first molar is an element of the milk-set, become permanent.

If we now return once more to our starting-point and compare the here developed theory of the constitution of the marsupialian dentition with the two existing theories, it appears to stand between these two. While according to the older investigators the functionating dentition of the Marsupials corresponds with the permanent dentition of the Monodelphians, according to the more recent workers with the milk-dentition, it is in my opinion built up of elements of both, although in a very disproportional mixture. It is an anisocrasic, hamastichical dentition, betraying by its hamastichism its nearer relation to the dentition of the Reptiles and certainly also of the most primitive Mammals, and by its anisocrasy its progressive character as compared with that of the Reptiles.

In this communication I have endeavoured to prove that the Marsupialian dentition in its evolution and constitution still shows relationship to that of the Reptiles, in a following one it will be shown that also in the development and structure of the Marsupialian tooth there exist points of agreement with the Reptilian teeth.

Physiology. — "*Further researches on pure pepsin.*" By Dr. W. E. Ringer. (Communicated by Prof. C. A. Pekelharing.)

(Communicated in the meeting of September 26, 1915).

Some years ago Pekelharing and myself[1]) found that pure pepsin has not a so-called iso-electric point, that is to say, not with any concentration of hydrogen-ions has it a minimal electric charge with opposite charges on either side of this H-concentration. Pepsin always appeared to be electro-negative and ever to move towards the anode in the electric field. This result conflicted with the experience of Michaelis and Davidsohn[2], who found in their pepsin an iso-electric point at a concentration $C_H = 5.5 \times 10^{-5}$ ($p_H = 4.26$). We found, however, that when we add protein or albumoses to our pepsin, the enzyme behaves as in the experiments of Michaelis and Davidsohn. It then educes an iso-electric point, more or less distinct according to the amount of protein added. This may also happen when the enzyme has been prepared under unfavourable circumstances. Michaelis and Davidsohn made their experiments with Grübler's pepsin, an impure commercial preparation. The impurities of their pepsin are obviously responsible for their results.

In the meantime Michaelis and Mendelssohn[3]) have brought forward another publication, in which they assert that pepsin is an enzyme, obeying the laws of dissociation and of which the free cations act proteolitically. We know now, especially after the important experiments by Sörensen, that the H-ion-concentration is of great importance for the action of hydrolitic enzymes. A number of enzymes have been examined in this respect; it appeared that there is a maximum action at a definite reaction; on either side of this optimal H-ion-concentration the action decreases at first slowly, then rapidly. Sörensen had already observed this phenomenon in his researches on pepsin and had already determined the optimum. He cautiously avoids accounting for this phenomenon and only states that the location of the optimal reaction depends to some extent on circumstances; it shifts towards greater C_H in prolonged digestion experiments, which Sörensen ascribes to the fact that pepsin is rendered inactive in solutions with small H-ion-concentrations. The longer the period of digestion, the greater the effect of this lack of activity.

Michaelis and his co-workers, however, have endeavoured to

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[1]) Zeitschr. f. physiol. Chem. Bnd. 75, S. 282 (1911),

[2]) Biochem. Zeitschr. Bnd. 28, S. 1 (1910).

[3]) Biochem. Zeitschr. Bnd. 65, S. 1 (1914).

account for the influence of the reaction on the enzymic activity. They suppose this activity to have something to do with the electric charge; they consider pepsin to be a so-called amphoteric substance, which combines on either side of the iso-electric point with bases or acids, so that compounds are formed, which are in some measure to be compared with salts.

According to them the compound containing acid becomes active; when in solution it is, like salt, partly dissociated, and the pepsin-ions are considered to be the active constituents. From this it seems to follow that with a greater amount of acid the activity must increase beyond the iso-electric point. As to a decrease with a still greater amount of acid, MICHAELIS supposes that perhaps in that case bivalent pepsin-ions may be formed without activity. He tries to substantiate this view on the basis of experiments, just as he does with other enzymes. He supposes the activity to vary in proportion to the amount of pepsin-ions present in the solution. Now it should be observed that the curve representing the activity of enzymes, such as pepsin, as a function of the H-ion-concentration is comparatively only slightly typical and has, in still stronger acid solutions, a rather abrupt rise up to the optimum and a less sudden fall. All sorts of conjectures may induce one to suggest an approximate interpretation of such a curve, and it seems to me to be a bold one to explain the phenomena in this case by supposing pepsin, of which we really are still much in the dark, to form a salt when combined with acids, and the electrically charged pepsin-ions to be active in this process, and moreover by supposing bivalent-ions to be educed when a second basic group of pepsin unites with acids, and assuming these bivalent-ions to be inactive in contradistinction to univalent-ions. This conjecture appears to be all the more hazardous, as we had already denied the existence of the iso-electric point. MICHAELIS also asserts that the question of identity or non-identity of pepsin and chymosin may be solved in such a sense, that pepsin combined with bases (consequently beyond the iso-electric point) acts as chymosin, in which case the pepsin-anions are supposed to be inactive[1]) as such.

With a view to further researches on the action of pepsin and the nature of the action, it seemed to me to be of prime importance to settle the question whether or not there is an iso-electric point in pepsin, once for all. Should our previous results be confirmed, it would be incumbent upon me to study the peculiar action of

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[1]) Cf. "Die Wasserstoffionenkonzentration." By L. MICHAELIS, (1914).

pepsin more closely, because then MICHAELIS' way of solving the problem would appear to be erroneous. I, therefore, made two sets of experiments; in the first I watched the behaviour of pepsin in the electric field as accurately as possible; in the second I tried to study in a different way from MICHAELIS the bearing of the H-ion-concentration on the enzymic action.

Above all I wanted an adequate quantity of pure pepsin. According to PEKELHARING this is best obtained from the pure gastric juice of a dog, provided with a PAWLOW fistula in the stomach and in the esophagus. Such a dog was at my disposal. It had been operated upon by Prof. LAMERIS and produced 300—500 c.c. of gastric juice after being given a fictitious meal two or three times a week.

The enzyme was prepared after PEKELHARING. The gastric juice was dialyzed and subsequently centrifugalized. The precipitate obtained was washed and dried (pepsin 1). The centrifuged fluid mixed with its own volume of a saturated solution of ammonium-sulfate, yields another precipitate that was filtered off, dialyzed, dissolved in hydrochloric acid of about 0.05 n. at 37°, and dialyzed again. The greater part of it is then thrown out of solution again (pepsin 2). By a prolonged dialyzation of pepsin, precipitated by ammonium sulfate, and by dissolving it in oxalic acid and dialyzing it again for a very long time, I have succeeded in obtaining a chlorin-free pepsin. So we know now that pure pepsin is free from phosphorus (PEKELHARING) and from chlorine as well, and that the amount of chlorine in common pepsin is to be ascribed to hydrochloric acid, either held back or combined or adsorbed. The chlorine-free pepsin (3) I employed for a good many experiments; its activity was equal to that of the chlorine-containing pepsin 1 or 2.

First set. The behaviour of pure pepsin in the electric field.

In order to avoid as many disturbances in my experiments as possible, I improved upon my previous method. First of all I raised the capacity of the non-polarisable electrodes. I then placed the whole apparatus in a thermostat at 25°, and finally, at least in the conclusive largest set of tests, I raised the specific gravity of the pepsin solution by an indifferent, neutral substance with no affinity for acids, viz. cane-sugar. The increased specific gravity, which I had also applied in similar experiments with ptyalin, precludes convection-streams of the fluids during the passage of the electric current. By proceeding thus no manner of disturbance took place, although the apparatus was an elaborate contrivance and consequently difficult in handling. Still, however indifferent cane-sugar seems to be and most likely will be in these experiments, it may be objected that without this substance the process might have been different. I insist upon saying therefore, that in an initial set of experiments, without any addition, the results were quite the same, except an occasional disturbance in one case. As in this set of experiments the specific gravity of pepsin-solution and of the side-fluid was about the same, the disturbance must have been due to a slight rise of the specific gravity of the latter generated by the current, which necessarily engendered a streaming of the fluids. The results obtained with pepsin-solutions to which sugar had been added, are given in the following table. It will be seen that in every experiment the movement of pepsin was anodal; consequently it was charged negatively. In an earlier publication we have already demonstrated that by the addition of protein or albumoses an iso-electric point was in some sense brought forth. I now repeated these experiments with albumoses, which confirmed my former results, only the addition of the albumoses had to be greater than before, which must be ascribed to the higher degree of purity of the pepsin.

This evidence goes to show that with a sufficient quantity of albumoses the movement is reversed, though it never becomes quite cathodic. It is remarkable that amino-acids do not seem to unite with pepsin, although a combination (or an adsorption) was expected in view of the opposite electrical charge.

We now know for certain, therefore, that pepsin has not an iso-electric point. This being settled, something else requires consideration, which at first sight seems to clash with our experience, viz. the existence of a minimal solubility of the pure pepsin in the neighbourhood of the neutral point ($p_H = 4-5$). However, we need not wonder at this. Pepsin, surely, must not be bracketed with ordinary proteins. It differs from them altogether, for instance by the remarkable property to coagulate in hydrochloric acid solution, when heated rapidly (PEKELHARING). Still, this peculiar behaviour of pepsin (no iso-electric point and none the less a minimal solubility) drew my attention. I have tried to learn more about this. PEKELHARING has already put forward the hypothesis that pepsin might be a combination of the real enzyme and protein[1]). Granting this to be true, the behaviour in the electric field can be accounted for, when the compound is decomposed in acid solution. If it is not decomposed in a very faint acid

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[1]) Archives des Sciences biologiques. Tome XI, p. 37 (1904).

TABLE I. Movement of pepsin in the electric field. To the pepsin-solution $1^0/_0$ cane-sugar is added. 20 mgr. of pepsin to 50 c.c. Estimation of the amount of pepsin after METT.

Nr.	Normality of the pepsin-solution	Normality of the side-fluid	Tension Volts	Duration of the experim. hours	Digestive action of the fluid mm. per 48 hours per tube	
					at the cathode	at the anode
1	phosphate-solution $p_H = 4.1$	phosphate-solution $p_H = 4.1$	100	5	0	5.8
2	0.00155 Hydrochl. acid	0.00136 Hydrochl. acid	120	5	0	4.4
3	0.00369 „	0.00330 „	100	5	0.5	4.5
4	0.00621 „	0.00582 „	100	5	0.14	3.1
5	0.0058 „	0.0058 „	80	5	0	3.8
6	0.0064 „	0.0058 „	80	5	0.48	3.5
7	0.0099 „	0.0103 „	90	5	1.0	4.3
8	0.0101 „	0.0101 „	80	5	0.2	3.4
9	0.0169 „	0.0165 „	100	5	1.4	4.8
10	0.0155 „	0.0165 „	80	5	0	3.0
11	0.0314 „	0.0287 „	95	5	0	2.8
12	0.0287	0.0291	90	5	0	3.1
13	0.0582	0.0582	80	5	0	2.4
14	0.0595	0.0592	80	5	0	2.3
15	0.118	0.118	50	5	0	1.8
16	0.235	0.236	20	5	0	1.0

TABLE II. Movement of pepsin after addition of albumoses or amino-acids; for further details see Table I.

Nr.	mgr. peptone GRÜBLER	mgr. albumoses. Our own preparation	Normality of		Tension Volts	Duration hours	Digestion in 48 hours mm. per tube	
			pepsin-solution	side-fluid			at the cathode	at the anode
1		20	0.0324	0.0310	60	5	0	3.2
2		20	0.0165	0.0155	80	5	0.2	1.6
3	20		0.0301	0.0301	60	5	0	2.1
4		100	0.0314	0.0301	50	5	1.0	1.6
5	100		0.0320	0.0301	50	5	0.2	1.7
6		300	0.0310	0.0303	50	5	2.8	1.4
7	400		0.0349	0.0310	50	5	2.9	1.5
8		100 mgr. glycocoll	0.0330	0.0310	50	5	0	1.4
9		500 „ „	0.0369	0.0301	50	5	0	0.8
10		300 „ leucin	0.0310	0.0310	50	5	0	1.4

solution the minimal solubility would not be a matter of surprise at all. Some of my experimental results lend support to the view that pepsin is indeed a compound. Firstly the movement of the enzyme in the electric field in acid solution appeared to be anodal, that of the greater part of the protein cathodal. The separation, however, is by no means complete, nor can it be expected to be so; perhaps the protein moving towards the cathode consists of nothing else but decomposition products of pepsin. I have not been able to ascertain this because of the incomplete separation and the difficulty to procure larger quantities.

Secondly I have noted the quantities of H- and Cl-ions that are combined with the pepsin in the hydrochloric acid solution. If the pepsin, prepared after Pekelharing, is the enzyme itself, it will unlike protein, not combine chiefly with H-ions, but with Cl-ions, as it is always charged negatively. If, however, pepsin is a compound of protein and the enzyme, the protein-constituent will most likely combine chiefly with H-ions, whereas the enzyme-constituent will unite with Cl-ions only. The enzyme itself may be expected to weigh very little indeed, and to combine with only an inappreciable quantity of Cl-ions. It would follow then that in this case, after all, only small differences between the pepsin and the ordinary protein can be expected, and that at most there would be comparatively only a small majority of combined Cl-ions. This supposition was borne out by determinations, performed with very small electrodes, as the ratios of the combined H-ions and the combined Cl-ions were in a hydrochloric-acid concentration of

0.029 n $^{H}/_{Cl}$ for pepsin 3.00 and for albumoses 3.06
of 0.0597 n ,, ,, ,, 1.34 ,, ,, ,, 1.42
and of 0.116 n ,, ,, ,, 1.01 ,, ,, ,, 1.12

In a still stronger hydrochloric acid, 0.235 n, the ratio was, it is true, somewhat higher for pepsin than for albumoses, but with such a strong acid the estimation is liable to so many errors, that the results cannot be relied on.

The mere fact that the pepsin combines chiefly with H-ions, refutes the hypothesis that all the pepsin, as we prepared it, is the enzyme itself, the latter being invariably charged negatively. I, therefore, maintain that my experiments confirm the supposition, that the pepsin, as we prepared it after Pekelharing, is a compound (or an adsorption compound) of a highly complicated protein and the enzyme, the latter being always charged negatively through combination with anions. This combination of anions with the true enzyme betrays itself by the ratio of the combined ions H/Cl being somewhat smaller for pepsin than for albumoses.

. The researches on the ion-combinations have yielded various other results: inter alia I found a more accurate value for the solubility of mercuric chlorid than the one universally received.

Furthermore the determinations of the Cl-ion-combinations with albumoses have clearly illustrated the dissociation of the protein chlorids, but I cannot discuss this point any further here.

Second Set. Experiments on the conditions under which the action of pepsin takes place.

From what has been said thus far it is evident that MICHAELIS' views as to the action of pepsin are not all correct. I have, therefore, tried to use another method in my researches on this action. For the present the study of the condition of the enzyme offered no prospect, as all we know about it is, that it is charged negatively and probably combined with anions. On the other hand more success might attend an attempt to observe the substratum; all the more so because it had been given very little attention to as yet.

The condition of proteins in solution with regard to the reaction and the presence of salts, has been extensively studied in recent years. We know that proteins are capable of combining with acids and bases; that the compounds, which are in some way similar to salts, can dissociate like the latter, but also that at a more considerable concentration of the acids or the bases, this dissociation is arrested. Furthermore it is highly probable that the protein-ions, liberated at the dissociation, hydrate and swell. The more powerful the electric charge of the protein, the more intense the swelling will be. With continual addition of acid to a protein solution the swelling is made to pass through a maximum; the lessening of the swelling beyond the maximum may be partly due to the reduced dissociation, but at the same time to other causes also.

We also know that salts affect the condition of proteins and that they are capable of exerting influence in various ways. In small concentrations and in acid or alkaline solutions the inhibitory action of salts with regard to the electric charge and the swelling plays the principal part. Various salts act in a different manner according to the ions they throw into solution; definite ions, especially the sulfate-ion, are very powerful in arresting the swelling.

In observing the action of pepsin we, therefore, had to take into account the condition of the protein. In my first set of experiments I could readily do this by employing GRÜTZNER's method to determine the action of pepsin. Here the pepsin solution acts on carmin-stained fibrin. The stain of the fluid varies with the quantity of fibrin dissolved; the intensity of the stain, being an index of the peptic action, is determined colorimetrically.

According to MICHAELIS' observations the action of pepsin depends entirely on the H-ion-concentration, that is to say various acid render the pepsin equally active, provided only that this concentration is the same for every one of them. In trying to ascertain this after GRÜTZNER's method, I arrived at different results. It appeared first and foremost that the action of every acid corresponded to the swelling of the fibrin. The optimum of the digestion lay at that reaction which concurred with a maximum swelling. I found this to be the case for hydrochloric acid, oxalic acid, lactic acid, phosphoric acid, sulfuric acid and citric acid. It is peculiar that in acetic acid the swelling occurs not only in highly aqueous solutions, but also in sparingly aqueous solutions, from which I inferred that in the latter the swelling is brought about by the combination with the acetic acid and not with water. Acetic acid and water are similar in their behaviour also in other respects. Be this as it may, the action of the pepsin corresponded to the swelling in solutions containing much water, not in the sparingly aqueous solutions; probably the enzyme acts only on protein swollen up by water, not by acetic acid.

When comparing the action in the various acid solutions at their optimal H-ion-concentration, this action appeared to differ rather much. On the ground of MICHAELIS' views the optima as well as the activity might be expected to be all alike for all acids. The condition of the pepsin, as determined by the C_H, should, according to MICHAELIS, be most favourable at a definite C_H, no matter by what acid the C_H is evolved. As stated before, my results go against this theory, as is shown by the table on p. 746.

The values of p_H and C_H before the action of the pepsin illustrate best the optimal reactions; after the digestion these values underwent various changes in proportion to the progress of the digestion. With sulfuric acid the reaction has even become alkaline, which is owing to the peculiar action of sulfuric acid. I did not notice it with any of the other acids, whatever the concentration may have been. It seems that sulfuric acid has liberated the ammonia, with which the carmin was still united, and that it was in its turn combined with or adsorbed by the fibrin or the carmin. We see now how much the optima (before the action of the pepsin) differ; with phosphoric acid the C_H is highest, 0.011; and with acetic acid

TABLE III. The action of pepsin in different acid solutions at the optimal reactions. Time: 5 minutes.

Acid and normality	Swelling of the fibrin	Digestion measured calorimetrically	Ratio of the action Hydrochloric acid = 1	Estimation of the H-ions-concentration			
				before the digestion		after the digestion	
				p_H	c_H	p_H	c_H
Hydrochl. acid 0.016	3.1	2.7	1	2.05	0.0088	2.68	0.0021
Oxalic acid 0.030	2.65	2.2	0.8	2.13	0.0075	2.62	0.0024
Lactic acid 0.180	3.54	2.7	1	2.21	0.0062	2.61	0.0025
Phosphor. acid 0.074	3.10	2.5	0.9	1.95	0.0113	2.31	0.0050
Sulfuric acid 0.010	0.58	trace	trace	2.40	0.0040	7.23	5.87×10^{-8}
Acetic acid 0.670	3.16	1.8	0.67	2.55	0.0028	3.18	0.00066
Citric acid 0.267	2.77	2.3	0.85	2.18	0.0067	2.56	0.0028

it is lowest, viz 0.003. It is also obvious how unlike the digestion is with the various acids; also, however, that the swelling corresponds fairly to this digestion, except with acetic acid, the behaviour of which substance has already been discussed. What strikes us most is the very low digestion in the sulfuric acid solution and the concurrence of a minimal swelling. I, therefore, disagree with MICHAELIS and his pupils with regard to their assertion that it is virtually only the C_H which determines the action of the pepsin. Pepsin works best in those solutions in which the proteins swell most. This maximum by no means occurs at the same H-ion-concentration with different acids; when the anion is highly hydrophilous, as is the case with sulfuric acid, the action of this ion prevails even in comparatively slight concentration, the optimum of digestion then lies at low C_H, and the digestion is inappreciable, since the swelling can be but slight.

The relation between digestion and swelling becomes even more manifest, when we study the influence of salts. Salts were known to generally impede the action of pepsin. Even common salt does so very strongly in a concentration as in seawater; the action of sulfates especially is very inhibitory. Up to now nothing was known about the cause of this action of salts. MICHAELIS speaks of a "Salzwirkung" noticeable also in the shifting of the optima to the smaller C_H. When looked upon from my standpoint, the action of the salts is quite easy to explain and we are even enabled to say beforehand which salts arrest the action considerably and which are only slightly inhibitory, since salts markedly affect the swelling of protein in dilute solutions and their influence increases according as their ions are more hydrophilous. The salts of a definite metal (Na) have been arranged in the order of the intensities of their inhibitory influence upon the swelling. This series then shows the ions in the order of their hydrophilous nature. The salts will impede the action of the pepsin in the same order. In order to ascertain this, I have made researches on seven salts of sodium, viz. citrate, acetate, chloride, chlorate, nitrate, rhodanate and sulfate. A difficulty arose in these experiments, viz. special caution was to be exercised to prevent the salt from materially altering the C_H, as a change of the C_H brings about a change of the charge of the protein and consequently of the swelling. I fairly got over this difficulty by taking the weak lactic acid. The measurements demonstrated that the addition of salt caused only a slight change of the C_H. In lactic acid solutions, with an acidity in the neighbourhood of the optimum, the C_H can be allowed to fluctuate considerably before any change in the digestion is noticeable. The changes noted by me must, therefore, be ascribed to the action of the salt-ions. Table IV shows the results of the experiments, in which the salt-concentration was smallest; this enabled us to estimate the results more correctly than with more considerable salt-concentrations, which affect the swelling to such an extent as to render it almost too small for a correct determination.

TABLE IV. Experiments on the influence of salts. The salt-concentration is invariably 0.0067 equivalent. Temperature 15°; concentration of the lactic acid 0.18 n.

N0.	Salt Sodium	Swelling m.m.	Time digestion min.	Digestion colorimeter	Digestion reduced to 5 min.	Determination P_H and c_H			
						Before the action of the pepsin		After the action of the pepsin	
						p_H	c_H	p_H	p_H
1	none	34	5	5.85	5.85	2.646	0.0023	2.248	0.0057
2	citrate	26.8	5	5.3	5.3	2.692	0.0020	2.420	0.0038
3	acetate	26.5	5	5.1	5.1	2.760	0.0017	2.435	0.0037
4	chloride	25.4	5	4.8	4.8	2.592	0.0026	2.257	0.0055
5	chlorate	25.0	5	4.6	4.6	Solutions of chlorates cannot be measured			
6	nitrate	23.8	5	4.8	4.8	2.548	0.0028	2.253	0.0056
7	rhodanate	18.1	9	2.0	1.1	2.513	0.0031	2.246	0.0057
8	sulfate	11.7	20	2.8	0.7	2.713	0.0019	2.288	0.0052

This table clearly shows the inhibitory action of the salts and at the same time their influence upon the swelling. It also appears from these data that this influence and the inhibitory action proceed collaterally. There is a slight deviation only with the nitrate in such a sense, that the digesting action is a little more intense than with the chlorate, which, however, may result from an experimental error, the methods of estimating the swelling and the digestion being comparatively rough.

With greater concentrations of the salts the order was modified a little, but there was again the side-by-side progress just alluded to; in these greater concentrations the C_H changes more considerably, which renders it slightly more difficult to note the influence.

Accordingly the sodium salt experiments yield evidence confirmatory of the supposition that the action of the pepsin is determined by the condition of the substrata.

In the above experiments the method used allowed me only to make a rough estimation of the condition of the protein and of the digestion. I, therefore, deemed it necessary to carry out some experiments affording an opportunity to estimate them as correctly as possible. It is very difficult to thoroughly study the condition of the protein, the size of the molecules in the solution, the taking up of water etc. The preceding tests, however, taught us that the swelling seems to play a principal part, which in fact seemed plausible from the very first.

This swelling can be determined in several ways; when working with protein-solutions we determine it by noting the viscosity. To work with solutions seemed to be the best method to arrive at accurate determinations. Much more difficult it is to correctly estimate the action of the pepsin. Here the formol-titration defeats our purpose. I have employed a method, used also by SÖRENSEN and consisting in the determination of the amount of nitrogen, which after the pepsin has been active for some time, can no more be precipitated by tannin.

In determining the viscosity it should be borne in mind that it quickly recedes in solutions containing a pretty large amount of acid, especially in the first few minutes after the addition. It is impossible to obtain a perfectly correct estimation of the initial viscosity in solutions with differing amounts of acid; the maximum for instance will always be found among the lower amounts of acid. I found that this decrease in the viscosity is very much quickened by pepsin, to such a degree that in a very few minutes the rise of the viscosity by acid is no longer noticeable. From this fact we may conclude, that the action caused by the acid alone may be the same as that, brought about by pepsin in acid solution, though it is slower. Both actions consist in splitting the large protein molecules; the problem is really very complex; the splitting yields new products with other properties, and consequently another situation of the maximum of the swelling. The initial viscosity determined directly after the addition of the acid, can only, if my judgment be correct, be an index of the action, which the pepsin can exert on the protein molecules present at the beginning. Most likely the new products, gradually evolved, reach the maximum swelling at another degree of acidity than the original protein. Unfortunately these products of decomposition seem to have little influence on the viscosity also in their swollen state, so that we cannot observe the swelling with regard to these products with great accuracy. From this it follows that we can hardly speak of *the* maximum of swelling of dissolved protein with a definite amount of acid at which pepsin acts best, but that in reality this maximum must necessarily shift according to the formation of other substances, even though the shifting cannot be extensive, because first of all, the decomposition products are, as far as their properties are concerned, very similar to the original protein, and secondly because with pepsin the decomposition does not advance far. In addition there is the practical difficulty that during the digestion the reaction must necessarily change. We are also aware that pepsin, especially in solutions with a very small amount of acid and also in such as have a large amount of it, gradually loses its activity. Finally, even from the modification of the viscosity in the strong acid solutions, without pepsin, it appears that the action of acid alone must not be ignored.

When recapitulating we can state that:

1. Under the influence of the acid the maximum of the viscosity, as determined by us, has shifted a little towards the small amounts of acid.

2. The location of the maxima of the swelling cannot be expected to be entirely constant, when the protein is split up; as yet we cannot say in what direction the shifting takes place.

3. The activity of pepsin gradually slackens, especially in the weak acid solutions, however also in very strong acid solutions. In consequence of this, it is especially in prolonged experiments that the optimum of the activity of pepsin shifts towards the stronger acid solutions.

4. Also the acid itself occasions a certain digestion, which shows

itself especially in strong acid solutions and is instrumental in shifting the optimum of digestion in pepsin-containing solutions towards the stronger acid solutions.

I have expatiated on this point because the question is rather knotty; also because I wanted to show that we cannot expect to find complete concordance between maximum of swelling and optimum of the action of pepsin. The results of a set of experiments with dialyzed and filtered horse-serum have been tabulated in Table V.

TABLE V. Estimation of the action of pepsin upon dialyzed and filtered horse-serum in 4 hrs. at 37°; estimation of the viscosity in these solutions with inactive pepsin at 18°.
The pepsin-solution contained 50 mgr. of pepsin taken up in 50 c.c. very dilute oxalic acid solution, 5 c.c. was used for every protein-solution. The estimation of the viscosity was made 5 min. after the mixing of the protein and the acid; for these tests the pepsin had been inactivated. The estimations were made at 18°, since at 37° it was quite impossible to obtain at all values representing the initial condition. Of course the viscosimeter, the liquids, the pipettes etc. were heated up beforehand to 18°, so that after the mixing we had not to wait longer than five minutes.

N⁰.	10 c.c. of serum + c.c. of water	Hydro-chloric acid 0.5016 in c.c.	Viscosimeter. Time sec.	Proc. N not precipitated by tannin	Estimation p_H and c_H			
					before the action of pepsin		after the action of pepsin	
					p_H	c_H	p_H	c_H
1	10	0	127.2	1.52	5.383	4.14×10^{-6}	5.462	3.454×10^{-6}
2	9.7	0.3	134.2	6.11	3.893	0.00013	4.407	3.92×10^{-5}
3	9.3	0.7	163.8	13.07	3.141	0.00072	3.834	1.47×10^{-4}
4	9.0	1.0	178.8	18.03	2.695	0.0020	3.525	2.99×10^{-4}
5	8.6	1.4	179.6	23.47	2.257	0.0055	3.246	5.67×10^{-4}
6	8.2	1.8	172.0	25.0	1.973	0.0106	2.809	0.00155
7	7.7	2.3	162.5	25.66	1.744	0.018	2.175	0.0067
8	6.5	3.5	148.0	25.09	1.436	0.0366	1.632	0.0234
9	4.0	6.0	142.2	25.09	1.150	0.0708	1.231	0.0588

When representing the viscosity graphically as a function of p_H, the maximum appears to lie at $p_H = 2.5$. The optimum of the peptic action lies at $p_H = 1.7$. SÖRENSEN's values of the latter are from 1.6—2.26 according to the duration of the digestion. In the light of these very reliable values and the above mentioned causes of the varying maxima of viscosity and swelling I am induced to think that also these experiments are confirmatory of the hypothesis that the action of pepsin is not determined by the H-ion-concentration alone, but principally by the condition of the substratum and in the first place by the swelling.

Of course the experiments with protein-solutions have to be continued and extended to other acids and here also the influence of salts has to be studied.

It is perhaps hardly necessary to add that other enzymes have to be subjected to similar observations. The curve representing the viscosity and consequently also the swelling as a function of p_H is strikingly analogous to the curve representing the action of many hydrolitic enzymes as a function of p_H; as with trypsin and also with ptyalin ¹).
We are, therefore, inclined to believe that with these enzymes also the condition of the substrata plays a prominent part.

Chemistry. — "*The action of sun-light on the cinnamic acids.*" By Dr. A. W. K. de Jong.

(Communicated in the meeting of September 25, 1915).

For the continued research of α- and β-"Storax" cinnamic acid it was necessary to possess a method by which large quantities of the α-acid can be readily converted into the β-acid.

The rapid evaporation of an alcoholic solution spread in a thin layer on glass plates certainly provides the means of preparing the β-acid on a small scale, but in this manner one is obliged to always work with small quantities of solution, as otherwise crystals of the α-acid soon occur beside those of the β-acid.

According to Erlenmeyer Jun. ²) the β-acid is formed in the following ways ³).

α-"Storax" cinnamic acid is dissolved in as little ether as possible and precipitated with petroleum ether. If the ethereal solution is not sufficiently concentrated α-acid only, or else a mixture of the two acids, is formed.

A warm solution of the α-acid in dilute (75%) alcohol deposits on cooling the β-acid.

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¹) Vide Van Trigt and Ringer's publication in the Proceedings of the meeting of Nov. 30, 1912, Vol. XXI. Part. I, p. 858 (1912).

²) Ber. **39**, 1581 et seq. (1906).

³) In what manner Lehmann has prepared the β-acid, I have not been able to trace as the original literature is not obtainable in Java.

As a third method he mentions that on heating the α-acid above its melting point the β-acid is formed[1].

The first two methods, however, do not always give the desired result, according to ERLENMEYER. He writes[2]: "In anderen Fällen gelingt die Umwandlung aus noch unbekannten Gründen selbst bei öfterer Wiederholung nicht."

The third method given by him is not correct. Both the solidified melt and the sublimate gave, on being illuminated, α-truxillic acid only.

After various experiments I observed that the β-acid is most conveniently prepared by pouring an alcoholic solution of α-cinnamic acid, saturated at the ordinary temperature, in a large quantity of water with stirring. On being illuminated this product always yielded β-truxillic acid only.

β-cinnamic acid may be also obtained by allowing warm solutions of cinnamic acid to crystallise. In this case the crystals are mostly visible with the naked eye and the change into the α-acid can also be traced.

If, however, we make a saturated aqueous solution at boiling heat, filter the same rapidly through cottonwool and filter off the crystallisations at intervals, the succeeding fractions appear to be different. The fraction depositing at a high temperature yields α-cinnamic acid, whereas at a lower temperature β-cinnamic acid crystallises (as proved by illuminating).

Benzine and petroleum are very suitable liquids for readily tracing the transformation of the cinnamic acids. If we wish to prepare the β-acid in this manner we must take care that the solution is not too concentrated as otherwise plate-like crystals of α-cinnamic acid will appear. The best thing is to cool locally (for instance the bottom of the flask) a warm and not too strong benzene solution. Splendid needles united in feathers are then formed. On these being left undisturbed the crystals are seen to partly vanish, plate-like crystals are formed and a few of the needles although retaining their original shape are seen to become transformed into a series of adjacent plates which convey the impression that they were tacked with the original needles.

The lower the boiling point of the benzene and the greater the concentration the more rapidly we notice the appearance of the plates in addition to the little feathers.

As to the transformation of the β-"Storax" cinnamic acid into the α-acid, ERLENMEYER also reports the following particulars.

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[1] See also: Bioch. Zeitschr. **34**, 356. (1911).

[2] Ber. **42**, 509. (1909).

In dilute (75 %) alcoholic solution the transformation takes place slowly and spontaneously and only at the end of 14 days has the greater part of the β-acid disappeared[1]).

On repeated recrystallisation from ether or dissolving in absolute alcohol, the β-acid is generally converted into the α-acid. In some cases, however, it will remain unchanged for weeks. "Wie es scheint spielt auch bei diesen Umwandlungen die Belichtung eine wichtige Rolle, die aber noch der Aufklärung bedarf[2])". This last remark looks to me as if he has occasionally mistaken the crystals. Here, where the temperature is generally 10—20° higher, the transformation of β-cinnamic acid in water, benzene or alcohol proceeded very rapidly in a few days.

In a dry state and at the ordinary temperature the α-cinnamic acid keeps unchanged for a very long time. The fine powder obtained by pouring an alcoholic solution of cinnamic acid into water is but very slowly converted even after an addition of β-cinnamic acid. A specimen that had been mixed with 1 % of cinnamic acid after being kept in the dark for over a month gave, on illuminating 0.5 gram during one morning, 0.09 gram of α-acid and 0.10 gram of β-truxillic acid.

On heating, however, the β-cinnamic acid, even without previous fusion, is changed very rapidly into α-cinnamic acid. The higher the temperature, the more rapidly the transformation.

From all these data it thus appears that at the ordinary and also at a higher temperature the α-cinnamic acid is the stable modification and that the β-acid, for this temperature range, is always metastable.

From the ready change of the β-cinnamic acid into the α-acid it may be explained that concentrated solutions, which commence to crystallise at a higher temperature than the dilute ones, give α-cinnamic acid, whereas from dilute solutions which crystallise at a lower temperature, β-crystals are deposited.

We have already stated previously with a few words that — considering it has been generally found in the case of the organic acids that in some solvents (benzene, chloroform etc.) they occur at great concentration, almost exclusively, and at low concentrations still partially, as double molecules — we must also assume that in the solid condition at least double molecules occur.

According to BECKMANN[3]) the formula of the double molecule in a general form would be as follows:

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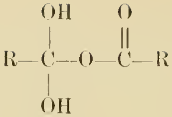
[1]) Ber. 39, 1583. (1906).

[2]) Ber. 42, 509. (1909).

[3]) Z. f. ph. Ch. 6, 469. (1890).

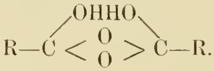


$$R-\underset{OH}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-O-\overset{O}{\overset{\|}{C}}-R$$

An objection to this formula is that two hydroxyl-groups are found at one C-atom which is not possible because water would then be readily split off.

The following formula appears to me to agree better with the data. As is well-known alcohols have the power to form large molecular compounds in the said solvents but only in concentrated solutions, whereas the dilute solution contains single molecules. Hence, we must assume that, in the acids, two causes are at work, which by themselves are not capable of producing the effect, namely the hydroxyl- and the CO-groups.

As the manner in which the OH-groups react on each other cannot be properly represented in the formula as yet, the double molecule might be represented as follows:



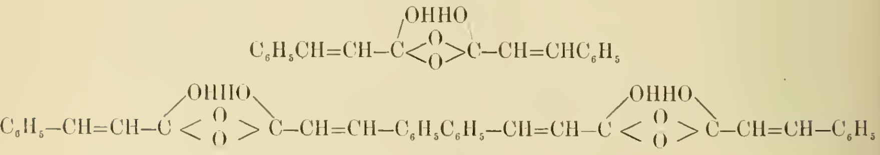
$$R-C\overset{OHHO}{<{}^{O}_{O}>}C-R.$$

For our purpose, however, it is for the moment of less importance what idea one entertains as to the double molecule; it is certain, however, that in the case of acids we generally notice that they combine by means of their carboxyl-groups.

In the case of acids possessing two bonds in their molecule it is very probable that on the transition of the liquid state into the solid one, the attraction of the two bonds may direct the molecules.

Supposing the difference between *α*- and *β*-cinnamic acid to consist solely in a difference of position of the double molecules in the "Raumgitter" we might then arrive to the following schema which elucidates the transformation of the acids into *α*- and *β*-truxillic acid.

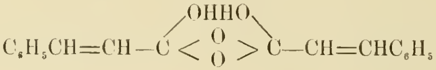
α



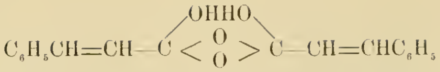
$$C_6H_5CH{=}CH-C\overset{OHHO}{<{}^{O}_{O}>}C-CH{=}CHC_6H_5$$

$$C_6H_5-CH{=}CH-C\overset{OHHO}{<{}^{O}_{O}>}C-CH{=}CH-C_6H_5C_6H_5-CH{=}CH-C\overset{OHHO}{<{}^{O}_{O}>}C-CH{=}CH-C_6H_5$$

β

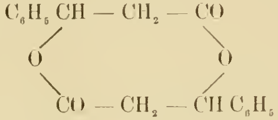


$$C_6H_5CH{=}CH-C\overset{OHHO}{<{}^{O}_{O}>}C-CH{=}CHC_6H_5$$

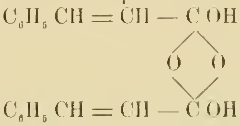


Also when we assume that on solidifying a change in structure of the double molecule takes place and that the formation of the truxillic acids occurs in the double molecule itself and not between two double molecules it is possible to give structural formulae for α- and β-cinnamic acid.

α



β



In the first representation it is not evident why the structure of should make the acid more stable than that of β; in the second representation this is, however, better visible, although a lactide of the formula α will also not possess much stability. Yet there are some facts which lead us to believe that the lactide formula is a very probable one.

An argument in favour of this formula is furnished by the following experiments.

The cinnamates, namely the acid potassium-, the normal potassium-, the calcium- and the barium salt have on exposure to light, in the solid condition always yielded β-truxillic acid only and not in one instance α-truxillic acid, although their preparation had been modified in different ways. The result was the same whether we started from α- or from β-cinnamic acid; the temperature also made no difference. No salts can, therefore, be derived from the α-acid.

If the difference between the α- and the β-cinnamic acid consisted merely in the position of the molecules in the "Raumgitter" it would be rather strange (when the α-arrangement is the more stable one) that this grouping does not occur in the salts. If for the α-cinnamic acid the lactide form is accepted, the non-existence of salts speaks for itself.

We might argue that in the salts no double molecule need occur, or else that these molecules possess a somewhat different structure; for the acid potassium salt, however, this does not do because the acid molecule must, as in the case of the acids, be combined to the potassium salt molecule, as the acid is very strongly combined and cannot be extracted by ether from the solid powdered salt, as has already been stated by ERLENMEYER [1]).

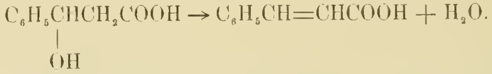
The α-cinnamic acid would then be the lactide of β-phenylhydracrylic acid.

It is known that the α-oxyacids on being heated in a vacuum are converted into lactides; β-oxyacids on heating give unsaturated acids with elimination of water, whereas γ- and δ-oxyacids very readily form lactones.

From this it appears that, as a rule, the substances possessing a carboxyl- and a hydroxyl-group, always have a greater tendency to split off water between these two groups, whether this takes place between the groups of one molecule, or whether the reaction proceeds between two molecules.

Only the β-oxyacids apparently make an exception.

The β-phenylhydracrylic acid, for instance, on being slowly heated breaks up at 180° into cinnamic acid and water according to the equation:



$$C_6H_5\underset{\mid \atop OH}{C}HCH_2COOH \rightarrow C_6H_5CH{=}CHCOOH + H_2O.$$

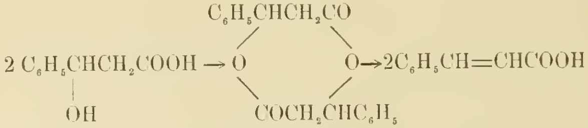
With substances possessing no carboxylgroup this elimination of water does not take place readily, as will appear from the following examples:

$(CH_3)_2\,C_6H_3CH\,(OH)\,CH_2CH_2CH_3$ boils at 270° [2]).

$CH_3CH(OH)C_6H_3\,(CH_3)_3$ boils at 248° [3]).

$C_6H_5CH_2CH\,(OH)\,C_6H_5$ melts at 62° and distils unchanged [4]).

Non-aromatic secondary alcohols also generally boil unchanged [5]). If, however, we assume that from the β-phenylhydracrylic acid a lactide is first formed, this ready elimination of water becomes comprehensible.



The transformation of other β-oxyacids, on heating, may be supposed to take place in a corresponding manner.

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[1]) Ber. 42, 515 (1909).

[2]) BEILSTEIN II, p. 1067.

[3]) Ber. 31, 1008 (1898).

[4]) Ann. 155, 63 (1870).

[5]) C. 1901 I, p. 623.

Chemistry. — "*Nitro-derivatives of alkylbenzidines*". By G. van Romburgh. (Communicated by Prof. P. van Romburgh).

(Communicated in the meeting of October 30, 1915).

Mertens[1]) has obtained in 1877 as a byproduct in the nitration of dimethylaniline an orange-yellow compound soluble with difficulty in alcohol, which he named isodinitrodimethylaniline. From this was obtained on boiling with concentrated nitric acid a product which he again investigated a few years later[2]) and took it for dinitrophenylmethylnitramine. From this was formed on boiling with phenol a splendid red coloured compound which was described as tetranitrodimethylazobenzene. Shortly afterwards P. van Romburgh[3]) showed that these compounds found by Mertens are derivatives of a tetranitrobenzidine without, however, determining the position of the nitro-groups.

I resolved to endeavour to elucidate the structure of these products, and at the same time to study also a number of nitro compounds in the alkylbenzidine series in addition to some reduction products thereof.

The tetranitrotetramethylbenzidine, which in the circumstances, is formed only in small quantity, in the above nitration is obtained in a yield of about 35% of the dimethylaniline employed, when we operate as follows:

30 grams of dimethylaniline are dissolved in 900 c.c. of nitric acid D. 1.11, which are cooled in ice-water to about 5°. After thorough shaking and leaving it for some time in the ice-water it is left at the ordinary temperature. The product that has formed over night is collected, boiled with alcohol and filtered through a hot water-funnel. The substance so obtained is already very pure and, when recrystallised from phenol, it decomposes at 272°.

Aqueous potassium hydroxide is supposed not to act on this compound. I could, however, ascertain that on prolonged boiling some formation of dimethylamine takes place.

The manner in which the product is formed justifies the belief that the nitro-groups occupy the positions 3.3′.5.5′. For in the nitration of dimethylaniline, as shown by Pinnow[4]) there is formed, at least in diluted sulphuric acid solution, some orthonitrodimethylaniline, which product is not readily nitrated any further. As nitric acid of

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[1]) Diss. Leiden, 1877.

[2]) Ber. d D. Chem. Ges. **19**, 2123 (1886).

[3]) Rec. d. Trav. Chim. **5**, 240 (1886).

[4]) Ber. d. D. Chem. Ges. **32**, 1666 (1899).

low concentration, such as used in the above experiment, may act as an oxidiser, it is likely to attack this *o*-nitrodimethylaniline in the still unoccupied *para*-positions and cause the formation of *o.o'*-dinitrotetramethylbenzidine, which is more readily capable of further nitration, particularly in the presence of nitrous acid. As is well-known, the nitro-group, in this prolonged nitration, exerts an influence of such a kind that the newly entered nitro-groups arrange themselves *meta* in regard to the previous ones.

It may also be possible that the dimethylamine itself is oxidised directly to a benzidine derivative of which it may be assumed (in analogy with different other benzene derivatives in which the *para*-position in regard to the aminogroup has been occupied) that the nitration will take place in a corresponding manner. Hence, I have tried in the first place to prepare the 3.3'.5.5' tetranitrotetramethylbenzidine synthetically.

After several vain efforts, to which I will not now refer, I have taken the following course.

I started from p.-diphenoldiethylether, which I prepared according to Hirsch's directions¹) and then treated with fuming nitric acid. The dark coloured solution, on heating soon became pale yellow and on cooling the tetranitrodiphenoldiethylether crystallises in long, transparent colourless needles melting at 256°—257°.

Analysis:			
found	45.6 % C.	3.5 % H	13.5 % N.
calculated for $C_{16}H_{14}N_4O_{10}$	45.5 ,,	3.3 ,,	13.3 ,,

Of the tetranitrodiphenolether, I placed 2 grams in a tube of resistance glass and added a solution of 1 gram of dimethylamine in 25 cc. of alcohol. The sealed tube was first placed in a boiling water-bath, which caused the contents to slowly turn an orange-red. I further also heated for some hours at 120° when it appeared that a red crystalline mass had deposited. This product was collected and washed with warm alcohol and warm water, when it appeared that the compound dissolved in the latter. On addition of strong hydrochloric acid to the red coloured solution, a yellow coloured compound was precipitated which could be recrystallised from acetic acid, and melted at 223°. It struck me as not being inprobable that this product was tetranitrodiphenol and indeed it caused no lowering of the melting point when mixed with this substance.

As to its structure, the opinions remained, however, divided. By boiling it with strong nitric acid I succeeded, as did Schmidt and Schultz²), in converting it into picric acid, so that the position of the

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¹) Ber d. D. Chem. Ges. **22**, 335 (1889).

²) Ann. d. Chemie **207**, 334 (1881).

nitro-groups in this tetranitrodiphenol, and therefore also in the ether obtained by me, must be 3.3'.5.5'.

No tetranitrotetramethylbenzidine had formed meanwhile. Hence, I made another experiment where I allowed monomethylamine to act on the tetranitrodiphenoldiethylether. The contents of the tube also turned orange-red when immersed in the boiling water-bath and after the operation a red crystalline mass had again deposited in the tube.

Again I washed with warm alcohol and warm water, but the latter soon ran through colourless whilst a dark red crystalline mass was left behind on the filter. It could be recrystallised from phenol. The compound so obtained decomposed at 282°.

Hence, the synthesis of tetranitrodimethylbenzidine had been successful and now it was also proved beyond doubt that it was a 3.3'.5.5' compound, which, of course, also applies to the tetranitrotetramethylbenzidine and its derivatives.

The difficult decomposition by boiling aqueous potassium hydroxide must be most likely attributed to the slight solubility of this compound.

The above cited experiments now also paved the way for the synthesis of all kinds of tetranitroalkylbenzidines.

For instance, I allowed ethylamine to act on the tetranitrodiphenolether and obtained a compound which, when recrystallised from ethyl benzoate, crystallises in yellowish-red small needles, which melt at 248° with decomposition. This same substance, I also could prepare from tetraethylbenzidine.

I have also allowed propyl-, *iso*propyl- *iso*butyl- and allylamine to react. The compounds so obtained are united in the following table in which are also included the final nitration compounds (nitramines) generated from the different products. All these nitramines are of an extremely pale yellow colour.

	Monoalkyl compounds			corresponding nitramines	
Methyl	red	284°	(with decomp.)	230°	(with decomp.)
ethyl	yellowish-red	248°	,, ,,	230°	,, ,,
propyl	dark-red	202°		213°	,, ,,
isopropyl	,,	250°	,, ,,	209°	,, ,,
isobutyl	,,	194°		205°	,, ,,
allyl	yellowish-red	208°	,, ,,	100°	,, ,,

With tin and hydrochloric acid the tetranitrotetramethyl- and the tetranitrodimethylbenzidine may be reduced, also the end nitration product obtained from these compounds.

As these substances are practically insoluble in hydrochloric acid the reaction proceeds very slowly; the two last named compounds must be boiled for a considerable time before everything has passed into solution. On cooling, the tin double salts crystallise in colourless scales. I removed the tin with hydrogen sulphide and on adding strong hydrochloric acid to the filtrates, I obtained the hydrochlorides of tetraminotetramethyl- and of tetraminodimethylbenzidine in beautiful, small, colourless needles.

The first product begins to darken at 240° and decomposes at 251°. It contains 4 mols. of hydrogen chloride and 2 mols. of water,

Analysis: Found:	$39.4\,^0/_0\,C$	$6.7\,^0/_0\,H$	$17.5\,^0/_0\,N$
Calculated for $C_{16}H_{32}N_6O_2Cl_4$	39.8 ,,	6.6 ,,	17.4 ,,

The tetraminodimethylbenzidine which is formed both from the tetranitrodimethylbenzidine and from the end product, crystallises with 4 mols. of hydrogen chloride and 1 mol. of water.

Analysis: Found:	$38.8\,^0/_0\,C$	$6.4\,^0/_0\,H$	$19.3\,^0/_0\,N$
Calculated for $C_{14}H_{26}N_6OCl_4$	38.5 ,,	5.8 ,,	19.3 ,,

I happened to succeed in diazotising these amino-compounds and preparing from the same a number of colouring matters varying in shade from red to bluish-violet, by linking them to suitable substances such as the various naphthylaminosulphonic acids and naphtholsulphonic acid. Some of these colouring matters exhibit the property of dyeing cotton without the aid of a mordant.

Further particulars as to the compounds described in this article will be published before long in the Rec. d. Trav. Chim.

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Physics. — "*On the field of two spherical fixed centres in* EINSTEIN'*s theory of gravitation*". By J. DROSTE. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of October 30, 1915).

In a former communication[1] I calculated the field of a single spherical centre and I investigated the motion of a particle in it. I now proceed to calculate the field of two fixed spherical centres according to the method followed by LORENTZ in calculating the field of a single centre consisting of an incompressible fluid. It

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[1] Vol. XVII, page 998.

differs from my former method in not using the symmetry of the field for decreasing the number of functions to be calculated. This would scarcely be an advantage here, the functions having all the same to be calculated from *partial* differential equations.

I have worked out the calculation on the supposition that the bodies have invariable shape and volume, and I have carried the calculation only to such an extent as is required by the precision with which we are going to calculate the equations of motion of a particle in it. As to this precision it will be sufficient that it furnishes a first correction on the equations of motion as defined by classical mechanics and NEWTON's law.

§ 1. We call $g^{(0)}_{\sigma\nu}$, $\gamma^{(0)}_{\sigma\nu}$, c the values of the quantities $g_{\sigma\nu}, \gamma_{\sigma\nu}, \sqrt{-g}$, as they would be if both centres were absent. If only the first centre existed, these quantities would be $g^{(0)}_{\sigma\nu}+g^{(1)}_{\sigma\nu}$, $\gamma^{(0)}_{\sigma\nu}+\gamma^{(1)}_{\sigma\nu}$, $c+c^{(1)}$; when we have only the second centre we represent them by $g^{(0)}_{\sigma\nu}+g^{(2)}_{\sigma\nu}$, $\gamma^{(0)}_{\sigma\nu}+\gamma^{(2)}_{\sigma\nu}$, $c+c^{(2)}$, and in the case of both centres we put:

$$g_{\sigma\nu}=g^{(0)}_{\sigma\nu}+g^{(1)}_{\sigma\nu}+g^{(2)}_{\sigma\nu}+\bar{g}_{\sigma\nu}\,,\ \gamma_{\sigma\nu}=\gamma^{(0)}_{\sigma\nu}+\gamma^{(1)}_{\sigma\nu}+\gamma^{(2)}_{\sigma\nu}+\bar{\gamma}_{\sigma\nu}\,,\ \sqrt{-g}=c+c^{(1)}+c^{(2)}+\bar{c} \quad (1)$$

The quantities $g^{(0)}_{\sigma\nu}$, $\gamma^{(0)}_{\sigma\nu}$, c are constants. We know already $g^{(1)}_{\sigma\nu}$, $\gamma^{(1)}_{\sigma\nu}$, $c^{(1)}$, $g^{(2)}_{\sigma\nu}$, $\gamma^{(2)}_{\sigma\nu}$, $c^{(2)}$; they do not contain terms of order zero. (We name one the order of a term such as k/r or v^2/c^2). The quantities $\bar{g}_{\sigma\nu}$, $\bar{\gamma}_{\sigma\nu}$, $\bar{c}$ finally do not contain any terms of lower order than the second; it is they that must be calculated.

We now have to substitute the expressions (1) in the equations

$$\sum_{\alpha\beta\mu} \frac{\partial}{\partial x_\alpha}\left(\sqrt{-g}\;\gamma_{\alpha\beta}\, g_{\sigma\mu}\, \frac{\partial \gamma_{\mu\nu}}{\partial x_\beta}\right) = \varkappa\,(\mathfrak{T}_{\sigma\nu} + \mathfrak{t}_{\sigma\nu}) \quad . \quad . \quad . \quad . \quad (2)$$

Omitting all terms of higher order than the second, we have

$$\sqrt{-g}\;\gamma_{\alpha\beta}\, g_{\sigma\mu}\, \frac{\partial \gamma_{\mu\nu}}{\partial x_\beta} =$$

$$(c+c^{(1)}+c^{(2)})(\gamma_{\alpha\beta}{}^{(0)}+\gamma_{\alpha\beta}{}^{(1)}+\gamma_{\alpha\beta}{}^{(2)})(g_{\sigma\mu}{}^{(0)}+g_{\sigma\mu}{}^{(1)}+g_{\sigma\mu}{}^{(2)})\left(\frac{\partial \gamma_{\mu\nu}{}^{(1)}}{\partial x_\beta}+\frac{\partial \gamma_{\mu\nu}{}^{(2)}}{\partial x_\beta}+\frac{\partial \bar{\gamma}_{\mu\nu}}{\partial x_\beta}\right)$$

$$= c\gamma_{\alpha\beta}{}^{(0)}\, g_{\sigma\mu}{}^{(0)}\, \frac{\partial \bar{\gamma}_{\mu\nu}}{\partial x_\beta} + (c+c^{(1)})(\gamma_{\alpha\beta}{}^{(0)}+\gamma_{\alpha\beta}{}^{(1)})(g_{\sigma\mu}{}^{(0)}+g_{\sigma\mu}{}^{(1)})\, \frac{\partial \gamma_{\mu\nu}{}^{(1)}}{\partial x_\beta}$$

$$+\ (c+c^{(2)})\,(\gamma_{\alpha\beta}{}^{(0)}+\gamma_{\alpha\beta}{}^{(2)})\,(g_{\sigma\mu}{}^{(0)}+g_{\sigma\mu}{}^{(2)})\, \frac{\partial \gamma_{\mu\nu}{}^{(2)}}{\partial x_\beta}$$

$$+\ (c\gamma_{\alpha\beta}{}^{(0)}\, g_{\sigma\mu}{}^{(2)} + c g_{\sigma\mu}{}^{(0)}\, \gamma_{\alpha\beta}{}^{(2)} + \gamma_{\alpha\beta}{}^{(0)}\, g_{\sigma\mu}{}^{(0)}\, c^{(2)})\, \frac{\partial \gamma_{\mu\nu}{}^{(1)}}{\partial x_\beta} +$$

$$+\ (c\gamma_{\alpha\beta}{}^{(0)}\, g_{\sigma\mu}{}^{(1)} + c g_{\sigma\mu}{}^{(0)}\, \gamma_{\alpha\beta}{}^{(1)} + \gamma_{\alpha\beta}{}^{(0)}\, g_{\sigma\mu}{}^{(0)}\, c^{(1)})\, \frac{\partial \gamma_{\mu\nu}{}^{(2)}}{\partial x_\beta}.$$

We represent these five terms successively by A, B, C, D, E. Substituting equations (1) in

$$-\varkappa\, \mathfrak{t}_{\sigma\nu} = \tfrac{1}{2} \sqrt{-g} \sum_{\beta\tau\rho} \gamma_{\beta\nu} \frac{\partial g_{\tau\rho}}{\partial x_\sigma} \frac{\partial \gamma_{\tau\rho}}{\partial x_\beta} - \tfrac{1}{4}\, \delta_{\sigma\nu} \sqrt{-g} \sum_{\alpha\beta\tau\rho} \gamma_{\alpha\beta} \frac{\partial g_{\tau\rho}}{\partial x_\alpha} \frac{\partial \gamma_{\tau\rho}}{\partial x_\beta}$$

($\delta_{\sigma\nu} = 1$, when $\sigma = r$; $\delta_{\sigma\nu} = 0$, when $\sigma \neq r$) we obtain

$$-\varkappa\, \mathfrak{t}_{\sigma\nu} = \tfrac{1}{2} c \sum_{\beta\tau\rho} \gamma_{\beta\nu}{}^{(0)} \left(\frac{\partial g_{\tau\rho}{}^{(1)}}{\partial x_\sigma} + \frac{\partial g_{\tau\rho}{}^{(2)}}{\partial x_\sigma} \right) \left(\frac{\partial \gamma_{\tau\rho}{}^{(1)}}{\partial x_\beta} + \frac{\partial \gamma_{\tau\rho}{}^{(2)}}{\partial x_\beta} \right)$$

$$- \tfrac{1}{4}\, \delta_{\sigma\nu}\, c \sum_{\alpha\beta\tau\rho} \gamma_{\alpha\beta}{}^{(0)} \left(\frac{\partial g_{\tau\rho}{}^{(1)}}{\partial x_\alpha} + \frac{\partial \gamma_{\tau\rho}{}^{(2)}}{\partial x_\alpha} \right) \left(\frac{\partial \gamma_{\tau\rho}{}^{(1)}}{\partial x_\beta} + \frac{\partial \gamma_{\tau\rho}{}^{(2)}}{\partial x_\beta} \right) =$$

$$= -\varkappa\, \mathfrak{t}_{\sigma\nu}{}^{(1)} - \varkappa\, \mathfrak{t}_{\sigma\nu}{}^{(2)} - \tfrac{1}{2} c \sum_{\tau\rho} \left(\frac{\partial g_{\tau\rho}{}^{(1)}}{\partial x_\sigma} \frac{\partial \gamma_{\tau\rho}{}^{(2)}}{\partial x_\nu} + \frac{\partial g_{\tau\rho}{}^{(2)}}{\partial x_\sigma} \frac{\partial \gamma_{\tau\sigma}{}^{(1)}}{\partial x_\nu} \right)$$

$$+ \tfrac{1}{4}\, \delta_{\sigma\nu}\, c \sum_{\alpha\tau\rho} \left(\frac{\partial g_{\tau\rho}{}^{(1)}}{\partial x_\alpha} \frac{\partial \gamma_{\rho\tau}{}^{(2)}}{\partial x_\alpha} + \frac{\partial g_{\tau\rho}{}^{(2)}}{\partial x_\alpha} \frac{\partial \gamma_{\tau\rho}{}^{(1)}}{d x_\alpha} \right),$$

where $\mathfrak{t}_{\sigma\nu}{}^{(1)}$ and $\mathfrak{t}_{\sigma\nu}{}^{(2)}$ represent the values of $\mathfrak{t}_{\sigma\nu}$ in the case of only the first or second centre. We put

$$-\varkappa\, \mathfrak{t}_{\sigma\nu} = -\varkappa\, \mathfrak{t}_{\sigma\nu}^{(1)} - \varkappa\, \mathfrak{t}_{\sigma\nu}^{(2)} + p + q.$$

In calculating p and q we have considered, that $\gamma_{\beta\nu}^{(0)}$ and $\gamma_{\alpha\beta}^{(0)}$ are zero, except when $\beta = r$ resp. $\beta = \alpha$. Moreover as terms to be differentiated with respect to x_4 give zero, the field being stationary, we might everywhere replace $\gamma_{\nu\nu}^{(0)}$ and $\gamma_{\alpha\alpha}^{(0)}$ by -1.

When we now put

$$\mathfrak{T}_{\sigma\nu} = \mathfrak{T}_{\sigma\nu}^{(1)} + \mathfrak{T}_{\sigma\nu}^{(2)} + \overline{\mathfrak{T}}_{\sigma\nu},$$

(2) becomes

$$\sum_{\alpha\beta\mu} \frac{\partial}{\partial x_\alpha} (A+B+C+D+E) = \varkappa(\mathfrak{T}_{\sigma\nu}^{(1)} + \mathfrak{t}_{\sigma\nu}^{(1)}) + \varkappa(\mathfrak{T}_{\sigma\nu}^{(2)} + \mathfrak{t}_{\sigma\nu}^{(2)}) - p - q + \varkappa \overline{\mathfrak{T}}_{\sigma\nu}.$$

As the field of each centre separately satisfies (2) we have

$$\sum_{\alpha\beta\mu} \frac{\partial B}{\partial x_\alpha} = \varkappa \left(\mathfrak{T}_{\sigma\nu}^{(1)} + \mathfrak{t}_{\sigma\nu}^{(1)} \right) \text{and} \sum_{\alpha\beta\mu} \frac{\partial C}{\partial \varkappa_\alpha} = \varkappa \left(\mathfrak{T}_{\sigma\nu}^{(2)} + \mathfrak{t}_{\sigma\nu}^{(2)} \right)$$

and so we obtain

$$\sum_{\alpha\beta\mu} \frac{\partial}{\partial x_\alpha} (A+D+E) = -p - q + \varkappa \overline{\mathfrak{T}}_{\sigma\nu},$$

or, by further reduction of A,

$$c g_{\sigma\sigma}^{(0)} \Delta \overline{\gamma}_{\sigma\nu} = \sum_{\alpha\beta\mu} \frac{\partial D}{\partial x_\alpha} + \sum_{\alpha\beta\mu} \frac{\partial E}{\partial x_\alpha} + p + q - \varkappa \overline{\mathfrak{T}}_{\sigma\nu} \quad . \quad . \quad . \quad (3)$$

We now have to consider that in neglecting terms of the second and higher orders $g^{(1)}_{ab} = \gamma^{(1)}_{ab} = g^{(2)}_{ab} = \gamma^{(2)}_{ab} = 0$ if not $a = b = 4$. This involves, exact up to terms of the second order inclusive,

$$\sum_{\alpha\beta\mu} \frac{\partial D}{\partial x_\alpha} = \sum_{\alpha\beta\mu} \frac{\partial E}{\partial x_\alpha} = 0,$$

when not $\sigma = \nu = 4$. In the latter case

$$\sum_{\alpha\beta\mu} \frac{\partial D}{\partial x_\alpha} = -c g_{44}^{(2)} \Delta \gamma_{44}^{(1)} - c \sum_\alpha \frac{\partial g_{44}^{(2)}}{\partial x_\alpha} \frac{\partial \gamma_{44}^{(1)}}{\partial x_\alpha} - c^2 c^{(2)} \Delta \gamma_{44}^{(1)} - c^2 \sum_\alpha \frac{\partial c^{(2)}}{\partial x_\alpha} \frac{\partial \gamma_{\mu\nu}^{(1)}}{\partial x_\alpha}$$

and

$$\sum_{\alpha\beta\mu} \frac{\partial E}{\partial x_\alpha} = -c g_{44}^{(1)} \Delta \gamma_{44}^{(2)} - c \sum_\alpha \frac{\partial g_{44}^{(1)}}{\partial x_\alpha} \frac{\partial \gamma_{44}^{(2)}}{\partial x_\alpha} - c^2 c^{(1)} \Delta \gamma_{44}^{(2)} - c^2 \sum_\alpha \frac{\partial c^{(1)}}{\partial x_\alpha} \frac{\partial \gamma_{\mu\nu}^{(2)}}{\partial x_\alpha}.$$

For p and q we find for the same reasons

$$p = -\tfrac{1}{2} c \left(\frac{\partial g_{44}^{(1)}}{\partial x_\sigma} \frac{\partial \gamma_{44}^{(2)}}{\partial x_\nu} + \frac{\partial g_{44}^{(2)}}{\partial x_\sigma} \frac{\partial \gamma_{44}^{(1)}}{\partial x_\nu} \right)$$

and

$$q = \tfrac{1}{4} \delta_{\sigma\nu} c \sum_\alpha \left(\frac{\partial g_{44}^{(1)}}{\partial x_\alpha} \frac{\partial \gamma_{44}^{(2)}}{\partial x_\alpha} + \frac{\partial g_{44}^{(2)}}{\partial x_\alpha} \frac{\partial \gamma_{44}^{(1)}}{\partial x_\alpha} \right).$$

Now, putting

$$g_{44}^{(1)} = -c^2 \lambda \text{ and } g_{44}^{(2)} = -c^2 \mu,$$

and neglecting quantities of order 2 in $g_{44}^{(1)}, g_{44}^{(2)}, \gamma_{44}^{(1)}, \gamma_{44}^{(2)}, c^{(1)}$ and $c^{(2)}$, we find

$$\gamma_{44}^{(1)} = \frac{\lambda}{c^2},\ \gamma_{44}^{(2)} = \frac{\mu}{c^2},\ c^{(1)} = -\tfrac{1}{2} c\lambda,\ c^{(2)} = -\tfrac{1}{2} c\mu$$

and so

$$p = \tfrac{1}{2} c \left(\frac{\partial \lambda}{\partial x_\sigma} \frac{\partial \mu}{\partial x_\nu} + \frac{\partial \mu}{\partial x_\sigma} \frac{\partial \lambda}{\partial x_\nu} \right),\ q = -\tfrac{1}{2} \delta_{\sigma\nu} c \sum_\alpha \frac{\partial \lambda}{\partial x_\alpha} \frac{\partial \mu}{\partial x_\alpha}$$

and in the case $\sigma = \nu = 4$

$$\sum_{\alpha\beta\mu} \frac{\partial D}{\partial x_\alpha} = \tfrac{3}{2} \mu \Delta \lambda + \tfrac{3}{2} c \sum_\alpha \frac{\partial \lambda}{\partial x_\alpha} \frac{\partial \mu}{\partial x_\alpha}, \quad \sum_{\alpha\beta\mu} \frac{\partial E}{\partial x_\alpha} = \tfrac{3}{2} c \lambda \Delta \mu + \tfrac{3}{2} c \sum_\alpha \frac{\partial \lambda}{\partial x_\alpha} \frac{\partial \mu}{\partial x_\alpha}.$$

In consequence to all these considerations we get

$$g_{\sigma\sigma}^{(0)} \Delta \overline{\gamma}_{\sigma\nu} = \tfrac{3}{2} \delta_{\sigma 4} \delta_{\nu 4} \left(\mu \Delta \lambda + \lambda \Delta \mu + 2 \sum_\alpha \frac{\partial \lambda}{\partial x_\alpha} \frac{\partial \mu}{\partial x_\alpha} \right) +$$

$$+ \tfrac{1}{2} \left(\frac{\partial \lambda}{\partial x_\sigma} \frac{\partial \mu}{\partial x_\nu} + \frac{\partial \mu}{\partial x_\sigma} \frac{\partial \lambda}{\partial x_\nu} \right) - \tfrac{1}{2} \delta_{\sigma\nu} \sum_\alpha \frac{\partial \lambda}{\partial x_\alpha} \frac{\partial \mu}{\partial x_\alpha} - \varkappa \mathfrak{T}^{\nu\sigma\nu}.$$

Now, if everywhere we replace $2 \sum_\alpha \frac{\partial \lambda}{\partial x_\alpha} \frac{\partial \mu}{\partial x_\alpha}$ by $\Delta (\lambda\mu) - \mu \Delta \lambda - \lambda \Delta \mu$, we obtain

$$\triangle \left(g_{\sigma\sigma}^{(0)} \gamma_{\sigma\nu} - \tfrac{3}{2}\, \delta_{\sigma 4} \delta_{\nu 4} \lambda\mu + \tfrac{1}{4}\, \delta_{\sigma\nu} \lambda\mu\right) =$$
$$= \tfrac{1}{4}\, \delta_{\sigma\nu} (\mu \triangle \lambda + \lambda \triangle \mu) + \tfrac{1}{2} \left(\frac{\partial \lambda}{\partial x_\sigma} \frac{\partial \mu}{\partial x} + \frac{\partial \mu}{\partial x_\sigma} \frac{\partial \lambda}{\partial x_\nu}\right) - \varkappa\, \overline{\mathfrak{T}}_{\sigma\nu} \quad . \; . \; (4)$$

§ 2. We now have to substitute in (4) for λ and μ values that are exact including terms of the first order. We find them from (2) by omitting all terms of higher orders than the second. This gives us

$$- c g_{\sigma\sigma}^{(0)} \triangle \gamma_{\sigma\nu}^{(1)} = \varkappa \mathfrak{T}_{\sigma\nu}^{(1)} \text{ and } - c g_{\sigma\sigma}^{(0)} \triangle \overline{\gamma}_{\sigma\nu}^{(2)} = \varkappa \mathfrak{T}_{\sigma\nu}^{(2)}.$$

When $\sigma = \nu = 4$ this becomes

$$\triangle \lambda = - \frac{\varkappa \varrho_1}{c} \text{ or } 0 \text{ and } \triangle \mu = - \frac{\varkappa \varrho_2}{c} \text{ or } 0 \quad . \; . \; . \; (5)$$

In these equations ϱ_1 and ϱ_2 represent positive constants; the right member of the first equation is different from zero only in the interior of a sphere of radius R_1 and the righthand member of the other equation is different from zero only in a sphere of Radius R_2. From (5) we have

$$\lambda = \frac{\varkappa \varrho_1}{3c} \frac{R_1^3}{r_1} \text{ and } \mu = \frac{\varkappa \varrho_2}{3c} \cdot \frac{R_2^3}{r_2} \quad . \; . \; . \; . \; . \; . \; . \; (6)$$

Each equation (6) is valid only at a point outside the sphere the radius of which occurs in it; within that sphere is

$$\lambda = \frac{\varkappa \varrho_1}{6c} (3R_1^2 - r_1^2) \text{ and } \mu = \frac{\varkappa \varrho_2}{6c} (3R_2^2 - r_2^2) \quad . \; . \; . \; (6a)$$

We now substitute this in the righthand member of (4). Within the first sphere that second member becomes

$$- P_{\sigma\nu} = - 3 \delta_{\sigma\nu} \frac{\omega_1 \omega_2}{R_1^3 r_2} + 2 \frac{\omega_1 \omega_2}{R_1^3} \cdot \frac{r_1}{r_2^2} \left(\frac{\partial r_1}{\partial x_\sigma} \frac{\partial r_2}{\partial x_\nu} + \frac{\partial r_2}{\partial x_\sigma} \frac{\partial r_1}{\partial x_\nu}\right) - \varkappa \overline{\mathfrak{T}}_{\sigma\nu},$$

when we put

$$\omega_1 = \frac{\varkappa \varrho_1 R_1^3}{6c} \text{ and } \omega_2 = \frac{\varkappa \varrho_2 R_2^3}{6c}.$$

In the interior of the second sphere we find in the same way $- R_{\sigma\nu}$. Outside both spheres the right member of (4) will be

$$- Q_{\sigma\nu} = 2 \omega_1 \omega_2 \left(\frac{\partial \frac{1}{r_1}}{\partial x_\sigma} \frac{\partial \frac{1}{r_2}}{\partial x_\nu} + \frac{\partial \frac{1}{r_2}}{\partial x_\sigma} \frac{\partial \frac{1}{r_1}}{\partial x_\nu}\right).$$

Considering (6) we thus find outside both spheres

$$g_{\sigma\sigma}^{(0)} \overline{\gamma}_{\sigma\sigma} = (6 \delta_{\sigma 4} \delta_{\nu 4} - \delta_{\sigma\nu}) \frac{\omega_1 \omega_2}{r_1 r_2} + \int\limits_{(1)} \frac{P_{\sigma\nu} dS_1}{4\pi r} + \int\limits_{(2)} \frac{R_{\sigma\nu} dS_2}{4\pi r} + \int \frac{Q_{\sigma\nu} dS}{4\pi r}; \; \ldots \; (7)$$

the first integral is to be extended over the volume of the first sphere, the second over the volume of the second, and the third over the whole space outside both spheres. $P_{\sigma\nu}$ must be calculated at a point near dS_1; in the same way $Q_{\sigma\nu}$ near dS and $R_{\sigma\nu}$ near dS_2. r in each expression represents the distance from the point, at which $\bar{\gamma}_{\sigma\nu}$ is to be calculated, to the point near which the element of volume is situated.

§ 3. From (7) we are able to calculate the function $\gamma_{\sigma\nu}$ for all values of σ and ν. For the motion of a particle in the field of the two centres only $\bar{\gamma}_{44}$ is to be calculated if no terms of higher order than the second are required. For this reason we will finish only the calculation of $\bar{\gamma}_{44}$; at the same time we introduce the supposition $\varepsilon_{44}=0$, which, in connexion with the supposition already used of both centres remaining spherical under each other's influence, comes to the same thing as exclusion of any variation of shape and volume. We then find

$$c^2\bar{\gamma}_{44}=\frac{5\omega_1\omega_2}{r_1r_2}+\frac{3\omega_1\omega_2}{4\pi R_1^3}\int\limits_{(1)}\frac{dS_1}{rl_2}+\frac{3\omega_1\omega_2}{4\pi R_2^3}\int\limits_{(2)}\frac{dS_2}{rl_1}, \quad . \quad . \quad . \quad (7a)$$

where l_2 denotes the distance from dS_1 to the centre of the second sphere, and l_1 the distance from dS_2 to that of the first. In case the mutual distance l of the centres or the distances r_1 and r_2 of these centres from the point, in which γ_{44} is required, is large with respect to R_1 and R_2 the value of the first integral will be $4\pi R_1^3 : 3r_1 l$ and of the second $4\pi R_2^3 : 3r_2 l$. In this case we have

$$\bar{\gamma}_{44}=\frac{\omega_1\omega_2}{c^2}\left(\frac{5}{r_1r_2}+\frac{1}{lr_1}+\frac{1}{lr_2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For the calculation of the quantity γ_{44} itself it is sufficient now to know $\gamma_{44}^{(1)}$ and $\gamma_{44}^{(2)}$. From the equation

$$s=\frac{1}{c^2}+\frac{\varkappa a_\infty}{c^3 r}+\frac{\varkappa^2}{4c^4 r}\int\limits_0^\infty\frac{a^2}{r^2}\,dr+\frac{5\varkappa^2 a_\infty^2}{8c^4 r^2},$$

occurring on p. 1006 of my former communication, quoted above, it follows that

$$\gamma_{44}^{(1)}=\frac{2\omega_1}{c^2 r_1}\left(1+\frac{3\omega_1}{5R_1}\right)+\frac{5\omega_1^2}{2c^2 r_1^2} \quad \text{and} \quad \gamma_{44}^{(2)}=\frac{2\omega_2}{c^2 r_2}\left(1+\frac{3\omega_2}{5R_2}\right)+\frac{5\omega_2^2}{2c^2 r_2^2}$$

and from this and (8), in connexion with (1),

$$\gamma_{44} = \frac{1}{c^2}\left\{1 + \frac{2\omega_1}{r_1}\left(1 + \frac{3\omega_1}{5R_1}\right) + \frac{2\omega_2}{r_2}\left(1 + \frac{3\omega_2}{5R_2}\right) + \right.$$

$$\left. + \frac{5\omega_1{}^2}{2r_1{}^2} + \frac{5\omega_1{}^2}{2r_2{}^2} + \frac{5\omega_1\omega_2}{r_1r_2} + \frac{\omega_1\omega_2}{lr_1} + \frac{\omega_1\omega_2}{lr_2}\right\} \quad . \quad . \quad (9)$$

If now we put

$$c^2\omega_1\left(1 + \frac{3\omega_1}{5R_1} + \frac{\omega_2}{2l}\right) = k_1 \text{ and } c^2\omega_2\left(1 + \frac{3\omega_2}{R_2} + \frac{\omega_1}{2l}\right) = k_2,$$

we may replace $\omega_1{}^2, \omega_2{}^2$ and $\omega_1\omega_2$ by $k_1{}^2 : c^4$, $k_2{}^2 : c^4$ and $k_1k_2 : c^4$ in the terms $5\omega_1{}^2 : 2r_1{}^2$, $5\omega_2{}^2 : 2r_2{}^2$ and $5\omega_1\omega_2 : r_1r_2$, and so we have

$$\gamma_{44} = \frac{1}{c^2}\left\{1 + \frac{2}{c^2}\left(\frac{k_1}{r_1} + \frac{k_2}{r_2}\right) + \frac{5}{2c^4}\left(\frac{k_1}{r_1} + \frac{k_2}{r_2}\right)^2\right\} \quad . \quad . \quad . \quad (10)$$

and from this

$$g_{44} = c^2\left\{1 - \frac{2}{c^2}\left(\frac{k_1}{r_1} + \frac{k_2}{r_2}\right) + \frac{3c^4}{2}\left(\frac{k_1}{r_1} + \frac{k_2}{r_2}\right)^2\right\} \quad . \quad . \quad . \quad (11)$$

§ 4. We now proceed to the calculation of the field of the equations of motion of a particle in the field of the two fixed centres. We put for abbreviation

$$\frac{k_1}{c^2r_1} + \frac{k_2}{c^2r_2} = w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

w is a function of the coordinates. Let v be the velocity of the particle and x, y, z the cartesian coordinates. For L we then get the expression

$$L = \sqrt{c^2 - 2c^2w + \tfrac{3}{2}w^2 - v^2}$$

and from this, expanding the root and neglecting terms of higher order than the second,

$$P = c^2(1 - L/c) = \tfrac{1}{2}v^2 + c^2w - \tfrac{1}{4}c^2w^2 + \tfrac{1}{2}wv^2 + \frac{v^4}{8c^2}.$$

Instead of L we may use P in the principle of HAMILTON and thus we find

$$\frac{d}{dt}\left(\frac{\partial P}{\partial \dot{x}}\right) = \frac{\partial P}{\partial x}, \; \frac{d}{dt}\left(\frac{\partial P}{\partial \dot{y}}\right) = \frac{\partial P}{\partial y} \text{ and } \frac{d}{dt}\left(\frac{\partial P}{\partial \dot{z}}\right) = \frac{\partial P}{\partial z} \quad . \quad . \quad (13)$$

The first of these equations is

$$\ddot{x} + w\ddot{x} + \frac{v^2}{2c^2}\ddot{x} + \dot{x}\left(\dot{x}\frac{\partial w}{\partial x} + \dot{y}\frac{\partial w}{\partial y} + \dot{z}\frac{\partial w}{\partial z}\right) +$$

$$+ \frac{v\dot{v}}{c^2}\dot{x} = c^2\frac{\partial w}{\partial x} - \tfrac{1}{2}c^2w\frac{\partial w}{\partial x} + \tfrac{1}{2}v^2\frac{\partial w}{\partial x}.$$

Neglecting in these and the two other equations any terms of the second order we get

$$\ddot{x} = c^2 \frac{\partial w}{\partial x}, \quad \ddot{y} = c^2 \frac{\partial w}{\partial y}, \quad \ddot{z} = c^2 \frac{\partial w}{\partial z} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and so

$$v\dot{v} = c^2 \left(\dot{x} \frac{\partial w}{\partial x} + \dot{y} \frac{\partial w}{\partial y} + \dot{z} \frac{\partial w}{\partial z} \right) \quad . \quad . \quad . \quad . \quad . \quad (14a)$$

We now may everywhere replace in the terms of the second order in the complete equations the quantities $\ddot{x}, \ddot{y}, \ddot{z}$ and $v\dot{v}$ by the values taken from (14) and (14a). We then find

$$\left.\begin{aligned}
\ddot{x} + 2\dot{x} \left(\dot{x} \frac{\partial w}{\partial x} + \dot{y} \frac{\partial w}{\partial y} + \dot{z} \frac{\partial w}{\partial z} \right) &= c^2 \frac{\partial w}{\partial x} - \tfrac{3}{2} c^2 w \frac{\partial w}{\partial x} \\
\ddot{y} + 2\dot{y} \left(\dot{x} \frac{\partial w}{\partial x} + \dot{y} \frac{\partial w}{\partial y} + \dot{z} \frac{\partial w}{\partial z} \right) &= c^2 \frac{\partial w}{\partial y} - \tfrac{3}{2} c^2 w \frac{\partial w}{\partial y} \\
\ddot{z} + 2\dot{z} \left(\dot{x} \frac{\partial w}{\partial x} + \dot{y} \frac{\partial w}{\partial y} + \dot{z} \frac{\partial w}{\partial z} \right) &= c^2 \frac{\partial w}{\partial z} - \tfrac{3}{2} c^2 w \frac{\partial w}{\partial z}
\end{aligned}\right\} \quad . \quad (15)$$

These are the equations of motion required. From them we can deduce the equation of energy by multiplying the first by $\dot{x}$, the second by $\dot{y}$, and the third by $\dot{z}$, and then adding them. So we get

$$\frac{d}{dt} \left(\tfrac{1}{2} v^2 \right) + 2 v^2 \frac{dw}{dt} = c^2 \frac{dw}{dt} - \tfrac{3}{2} c^2 w \frac{dw}{dt}.$$

In connection with (14a) we write the second term in the form

$$2v^2 \frac{dw}{dt} = \frac{2v^3 \dot{v}}{c^2} = \frac{d}{dt} \left(\frac{v^4}{2c^2} \right)$$

and this gives us

$$\frac{d}{dt} \left[\tfrac{1}{2} v^2 + \frac{v^4}{2c^2} - c^2 w + \tfrac{3}{4} c^2 w^2 \right] = 0 \quad . \quad . \quad . \quad . \quad . \quad (16)$$

On the other side we find from (13)

$$\frac{d}{dt} \left(\dot{x} \frac{\partial P}{\partial \dot{x}} + \dot{y} \frac{\partial P}{d \dot{y}} + \dot{z} \frac{\partial P}{d \dot{z}} - P \right) = 0$$

or

$$\frac{d}{dt} \left[\tfrac{1}{2} v^2 + \tfrac{1}{2} v^2 w + \frac{3v^4}{8c^2} - c^2 w + \tfrac{1}{4} c^2 w^2 \right] = 0. \quad . \quad . \quad (16a)$$

This agrees with (16) because the difference

$$\frac{d}{dt} \left(\frac{v^4}{8c^2} - \tfrac{1}{2} v^2 w + \tfrac{1}{2} c^2 w^2 \right)$$

is equal to

$$\frac{1}{2c^2}\frac{d}{dt}\left[\left(\tfrac{1}{2}\, v^2 - c^2 w\right)^2\right],$$

being zero on account of (14a) when terms of higher order than the second are neglected.

§ 5. The equation of energy (together with the integral of angular momentum) of the motion of a particle in the field of two fixed centres can be obtained rigorous in the following way.

It is clear that, whatever may be the influence of both centres on each other, their field will be symmetrically situated, about an axis. Choosing this axis for axis of x and calling r the distance of the particle from that axis, φ the angle between a fixed plane through the axis and the plane through the axis and the particle, we obtain

$$L = (u\dot{x}^2 + 2p\,\dot{x}\dot{r} + v\dot{r}^2 + qr^2\dot{\varphi}^2 + s)^{\frac{1}{2}},$$

u, p, v, q, s being functions of x and r. This will yield at once the equations of motion

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) = \frac{\partial L}{\partial x}\ ,\quad \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{r}}\right) = \frac{\partial L}{\partial r}\ ,\quad \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\varphi}}\right) = 0.$$

From the third we get

$$\frac{\partial L}{\partial \dot{\varphi}} = \frac{qr^2\dot{\varphi}}{L} = -A\,h, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and by multiplying them in succession by $\dot{x}$, $\dot{r}$, $\dot{\varphi}$ and adding them we obtain

$$\frac{s}{L} = h\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Here h and A are constants. From (17) and (18) it follows that

$$\frac{-qr^2}{s}\,\dot{\varphi} = A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

(18) represents the equation of energy, (19) the equation which corresponds to the integral of angular momentum. With the approximation with which we have contented ourselves in the former §§ $q = -1$ and

$$s = c^2\,(1 - 2w + \tfrac{3}{2}\,w^2).$$

so that we obtain

$$r^2\dot{\varphi} = Ac^2\,(1 - 2w + \tfrac{3}{2}\,w^2)\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19a)$$

Without difficulty one sees that (18) agrees with (16a). (19) enables us to eliminate the variable $\dot{\varphi}$ from the equations of motion.

I take the opportunity to correct an error in my former communication (quoted above). On page 1003 in the equation that follows equation (11) and in the next equation $3\,r^2\,P$ instead of $r^2\,(2P+Q)$ is to be read. This makes (12) valid in any case (and not only in the case of a liquid), even when $S \neq 0$ r being $< R$. (13) of course is valid only, as before, in the case of S being zero outside a sphere of radius R at points in which $r > R$.

Mathematics. — "*On a linear integral equation of* Volterra *of the first kind, whose kernel contains a function of* Bessel." By Dr. J. G. Rutgers. (Communicated by Prof. W. Kapteyn).

(Communicated in the meeting of September 25, 1915).

Among the few applications given of Sonine's extension of Abel's integral equation [1]) we may arrange the integral equation:

$$f(x) = \Gamma(1-\lambda)\left(\frac{z}{2}\right)^{\lambda}\int\limits_a^x (x-\xi)^{-\frac{\lambda}{2}} I_{-\lambda}(z\sqrt{x-\xi})\,u(\xi)d\xi \quad . \quad . \quad (1)$$

with the solution:

$$u(x) = \frac{\sin\lambda\pi}{\pi}\,\Gamma(\lambda)\left(\frac{iz}{2}\right)^{1-\lambda}\int\limits_a^x (x-\xi)^{-\frac{1-\lambda}{2}} I_{-(1-\lambda)}(iz\sqrt{x-\xi})\,f'(\xi)\,d\xi. \quad (2)$$

in which it is supposed: $0 < \lambda < 1$, and the given function $f(x)$ must satisfy the conditions that $f(x)$ is an analytical function, $f'(x)$ finite with at most a finite number of discontinuities for $a \leq x \leq b$, and $f(a) = 0$.

In what follows we shall prove that (1) and (2) may be directly deduced by means of relations known in the theory of the functions of Bessel. In this deduction it will moreover appear that the solution of (1) only becomes the form (2) if a definite value is avoided and consequently a great restriction is imposed on a certain parameter, what is not strictly necessary. This special selection has moreover the drawback that we only come to the solution of (1) under the very restrictive condition $0 < R(\lambda) < 1$, whereas the more general expression which we may find in this way, gives a solution under the far more extensive condition $R(\lambda) < 1$. The conditions which the given function $f(x)$ must satisfy will manifest themselves.

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[1]) Sonine: Acta Matem. 4 (1884). These Proceedings XVI p. 583 (1913).

We shall also apply VOLTERRA's method to (1) and so we shall be led to important conclusions.

1. We premise the well-known relation[1]:

$$I_{\nu+\rho+1}(y)=\frac{\left(\frac{y}{2}\right)^{\rho+1}}{\Gamma(\rho+1)}\int_0^1 \alpha^{\frac{\nu}{2}}(1-\alpha)^{\rho} I_\nu(y\sqrt{\alpha})\,d\alpha,\quad \begin{cases} R(\nu)>-1 \\ R(\rho)>-1 \end{cases}. \qquad (3)$$

substitute in it: $\alpha=\frac{x-\xi}{x-a}$, $y=z\sqrt{x-a}$, and replace ν by $-\lambda$, ρ by $n+m$ (n and m positive integers or zero), so as to get:

$$\left.\begin{aligned} &I_{n+m+1-\lambda}(z\sqrt{x-a})= \\ &=\frac{\left(\frac{z}{2}\right)^{n+m+1}}{(n+m)!\,(x-a)^{\frac{n+m+1-\lambda}{2}}}\int_a^x (x-\xi)^{-\frac{\lambda}{2}} I_{-\lambda}(z\sqrt{x-\xi})(\xi-a)^{n+m}d\xi, R(\lambda)<1 \end{aligned}\right\} (4)$$

We multiply both members of (4) by $\frac{1}{n!}\left(\frac{z\sqrt{x-a}}{2}\right)^n$ and summate afterwards from $n=0$ to $n=\infty$. The first member may be reduced by means of the relation[2]:

$$\sum_{n=0}^{\infty}\frac{\left(\frac{y}{2}\right)^n}{n!}I_{n+\nu}(y)=\frac{\left(\frac{y}{2}\right)^{\nu}}{\Gamma(\nu+1)}$$

and in the second member summation under the integral sign is allowed on account of uniform convergence of the series arisen.

After some reduction we find:

$$\left.\begin{aligned} &\frac{\left(\frac{iz}{2}\right)^m (x-a)^{m+1-\lambda}}{\Gamma(m+2-\lambda)}= \\ &=\left(\frac{z}{2}\right)^{\lambda}\int_a^x (x-\xi)^{-\frac{\lambda}{2}} I_{-\lambda}(z\sqrt{x-\xi}).(\xi-a)^{\frac{m}{2}} I_m(iz\sqrt{\xi-a})d\xi,\ R(\lambda)<1. \end{aligned}\right\} (5)$$

If we further substitute in (3) $\alpha=\frac{x-\xi}{x-a}$, $y=iz\sqrt{x-a}$, and replace ν by $\mu-1$, ρ by $m-\mu$ (m again positive integer or zero), we get:

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[1] NIELSEN: Handb. der Cylinderfunktionen 1904, p. 181 (8) slightly altered.

[2] NIELSEN. l. c. p. 97 (6).

$$\left.\begin{gathered}(x-a)^{\frac{m}{2}} I_m (iz\sqrt{x-a}) = \\ = \frac{\left(\frac{iz}{2}\right)^{m+1-\mu}}{\Gamma(m+1-\mu)} \int\limits_a^x (x-\xi)^{-\frac{1-\mu}{2}} I_{-(1-\mu)} (iz\sqrt{x-\xi}) \,.\, (\xi-a)^{m-\mu}\, d\xi, \\ 0 < R(\mu) < m+1.\end{gathered}\right\} \quad . \ (6)$$

These expressions (5) and (6), which in a sense may be considered as each other's reverses, enable us to arrive at (1) and (2).

For this purpose we multiply both members of (5) by $a_m\left(\frac{iz}{2}\right)^m \Gamma(1-\lambda)$ and afterwards summate from $m=s$ to $m=\infty$ (in the second member under the integral sign). Let us write:

$$f(x) = \sum_{m=s}^{\infty} (-1)^m a_m \frac{\Gamma(1-\lambda)}{\Gamma(m+2-\lambda)} \left(\frac{z}{2}\right)^{2m} (x-a)^{m+1-\lambda}, \quad . \ . \ . \ (7)$$

$$u(x) = \sum_{m=s}^{\infty} a_m \left(\frac{iz\sqrt{x-a}}{2}\right)^m I_m (iz\sqrt{x-a}), \quad . \ . \ . \ . \ (8)$$

then we get already:

$$f(x) = \Gamma(1-\lambda) \left(\frac{z}{2}\right)^{\lambda} \int\limits_a^x (x-\xi)^{-\frac{\lambda}{2}} I_{-\lambda} (z\sqrt{x-\xi})\, u(\xi)\, d\xi, \ R(\lambda) < 1. \quad (1)$$

If we multiply both members of (6) by $a^m\left(\frac{iz}{2}\right)^m$, the first member by summation from $m=s$ to $m=\infty$ passes on account of (8) into $u(x)$, and if we execute the summation in the second member under the integral sign, we find:

$$\left.\begin{gathered}u(x) = \left(\frac{iz}{2}\right)^{1-\mu} \int\limits_a^x (x-\xi)^{-\frac{1-\mu}{2}} I_{-(1-\mu)} (iz\sqrt{x-\xi})\, g(\xi)\, d\xi, \\ \text{in which } g(\xi) = \sum_{m=s}^{\infty} \frac{(-1)^m a_m \left(\frac{z}{2}\right)^{2m}}{\Gamma(m+1-\mu)} (\xi-a)^{m-\mu}\end{gathered}\right\} \quad . \ . \ . \ (9)$$

$$0 < R(\mu) < s+1 \ (s \text{ positive integer or zero}).$$

It clearly appears now that only on account of the special selection $\mu=\lambda$ this expression on account of (7) passes into:

$$u(x) = \frac{\sin\lambda\pi}{\pi} \Gamma(\lambda) \left(\frac{iz}{2}\right)^{1-\lambda} \int\limits_a^x (x-\xi)^{-\frac{1-\lambda}{2}} I_{-(1-\lambda)} (iz\sqrt{x-\xi}) f'(\xi) d\xi, \quad (2)$$

but we see at the same time arise as a condition $R(\lambda) > 0$; and as in (1) $R(\lambda) < 1$ was necessary, so we find apart from other conditions, that (2) is a solution of (1), provided $0 < R(\lambda) < 1$.

2. If we do not impose that great restriction on μ in (9) (viz. $\mu = \lambda$), but if we maintain its independence in reference to λ, (9) even in this case, apart from other conditions, represents a solution (1) provided $R(\lambda) < 1$ is satisfied.

A simpler form may be given to (9) by using the following definition:

$$D_x^q\, x^p = \frac{\Gamma(p+1)}{\Gamma(p-q+1)}\, x^{p-q}$$

for all values of p and q, which form exactly indicates for positive integer values of q the q^{th} differential quotient of x^p. For the series occurring in the second member of (9) under the integral sign, we may then write:

$$\left.\begin{aligned} &\sum_{m=s}^{\infty} \frac{(-1)^m a_m \left(\frac{z}{2}\right)^{2m}}{\Gamma(m+1-\mu)}\, (\xi-a)^{m-\mu} = \\ &= D_\xi^{\mu+1-\lambda} \sum_{m=s}^{\infty} \frac{(-1)^m a_m \left(\frac{z}{2}\right)^{2m}}{\Gamma(m+2-\lambda)}\, (\xi-a)^{m+1-\lambda} = \frac{1}{\Gamma(1-\lambda)}\, D_\xi^{\mu+1-\lambda} f(\xi) \end{aligned}\right\} \quad (10)$$

on account of (7), or again $= \frac{1}{\Gamma(1-\lambda)} f^{(\mu+1-\lambda)}(\xi)$ according to the well-known notation by the whole index.

So we get for (9) the form:

$$u(x) = \frac{\sin \lambda\pi}{\pi}\, \Gamma(\lambda) \left(\frac{iz}{2}\right)^{1-\mu} \int_a^x (x-\xi)^{-\frac{1-\mu}{2}}\, I_{-(1-\mu)}(iz\sqrt{x-\xi})\, f^{(\mu+1-\lambda)}(\xi)\, d\xi, \quad (11)$$

$$0 < R(\mu) < s+1.$$

We now recognize at once (2) from (11) for $\mu = \lambda$.

The remaining conditions, under which (11) will be a solution of (1), are implied in the way of deducing these relations from (5) and (6), in which we have carried out summations under the integral sign.

So it is necessary that in (11) the series for $f^{(\mu+1-\lambda)}(x)$, cf. (10), converges uniformly for $a \leq x \leq b$; if this condition is satisfied, the series (8) for $u(x)$ is uniformly convergent, as in the second member of (11): $(x-\xi)^{-\frac{1-\mu}{2}} I_{-(1-\mu)}(iz\sqrt{x-\xi})$ is of order $\dfrac{1}{(x-\xi)^{1-\mu}}$ and μ satisfies $R(\mu) > 0$.

As a condition in the deducing of (1) from (5) it arises that (8) must be uniformly convergent for $a \leq x < b$, which has the consequence: $f(x)$ continuous as $R(\lambda) < 1$.

We may therefore agree upon the following:

I. If $\dfrac{f(x)}{(x-a)^{1-\lambda}}$ is an analytical function, regular for $a \leq x < b$, having $x = a$ as zero of order s [so that development (7) obtains], and if the series, which we may draw up according to our definition for $f^{(\mu+1-\lambda)}(x)$ [cf. (10)], converges uniformly for $a < x \leq b$, — (11) will be a continuous solution of (1), provided $R(\lambda) < 1$ and $0 < R(\mu) < s+1$.

3. For $z = 0$, (1) passes into Abel's integral equation:

$$f(x) = \int_a^x \frac{u(\xi)}{(x-\xi)^{\lambda}}\, d\xi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

for which we now find the solution in a general form by substituting in (11) also $z = 0$, viz.

$$u(x) = \frac{\sin \lambda\pi}{\pi}\, \frac{\Gamma(\lambda)}{\Gamma(\mu)} \int_a^x \frac{f^{(\mu+1-\lambda)}(\xi)}{(x-\xi)^{1-\mu}}\, d\xi, \quad . \quad . \quad . \quad . \quad (13)$$

available under the same conditions as mentioned under I (§ 2). Abel solved (12) on the supposition $0 < R(\lambda) < 1$, and found as solution (13), in which $\mu = \lambda$.

Liouville[1]) extended Abel's problem to the supposition $n < R(\lambda) < -n+1$ (n positive integer or zero) and found as solution (13), in which $\mu = n + \lambda$.

4. Let us now take (1) as a special case of Volterra's integral equation of the first kind, which has the general form:

$$f(x) = \int_a^x K(x,\xi)\, u(\xi)\, d\xi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

then (1) appears to ensue from this, if we take as kernel

$$K(x,\xi) = \Gamma(1-\lambda)\left(\frac{z}{2}\right)^{\lambda} (x-\xi)^{-\frac{\lambda}{2}} I_{-\lambda}(z\sqrt{x-\xi}). \quad . \quad . \quad (15)$$

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[1]) Journ. de l'Ec. Polytechn, Cah. 21 (1832).

As to (14) the following theorems[1]) obtain.

A. If $K_0(x,\xi)=K(x,\xi)$, $K_1(x,\xi)=\frac{\partial K(x,\xi)}{\partial x}, \dots K_n(x,\xi)=\frac{\partial^n K(x,\xi)}{\partial x^n}$ are continuous and $K_{n+1}(x,\xi)=\frac{\partial^{n+1} K(x,\xi)}{\partial x^{n+1}}$ is finite for $a \leq \xi \leq x \leq b$, and the discontinuities of $K_{n+1}(x,\xi)$, if it has any, are regularly distributed[2]), and if moreover $K_0(x,x)=0$, $K_1(x,x)=0, \dots$ $\xi \dots$ $K_{n-1}(x,x)=0$, but $K_n(x,x) \neq 0$ for $a \leq x \leq b$, (14) will have only *one* continuous solution under the necessary and sufficient conditions: $f(x)$, $f'(x), \dots f^{(n+1)}(x)$ continuous for $a < x \leq b$ and $f(a)=f'(a)=\dots =f^{(n)}(a)=0$. And this solution will be represented by the only possible continuous solution of the integral equation of the second kind:

$$f^{(n+1)}(x)=K_n(x.x)\,u(x)+\int_a^x K_{n+1}(x,\xi)\,u(\xi)\,d\xi \quad . \quad . \quad (16)$$

B. If $K_0(x,\xi)=K(x,\xi)$, $K_1(x,\xi)=\frac{\partial K(\xi,\zeta)}{\partial x}, \dots K_{n-1}(x,\xi)=\frac{\partial^{n-1} K(x\xi)}{\partial x^{n-1}}$, are continuous for $a \leq \xi \leq x \leq b$ and $K_n(x,\xi)=\frac{\partial^n K(x,\xi)}{\partial x^n}=\frac{G(x,\xi)}{(x-\xi)^{\lambda_n}}$ $(0<R(\lambda_n)<1)$, in which $G(x,\xi)$ and $\frac{\partial G(x,\xi)}{\partial x}$ are also continuous for $a \leq \xi \leq x \leq b$, and if moreover $K_0(x,x)=0$, $K_1(x,x)=0, \dots K_{n-1}(x,x)=0$, but $G(x,x) \neq 0$ for $a \leq x \leq b$, — then (14) will have only *one* continuous solution under the necessary and sufficient conditions: $f(x), f'(x) \dots f^{(n)}(x)$ and $\frac{d}{dx}\int_a^x \frac{f^{(n)}(\xi)}{(x-\xi)^{1-\lambda_n}}\,d\xi$ continuous for $a \leq x \leq b$, and $f(a)=f'(a)=\dots=f^{(n)}(a)=0$. And this solution will be represented by the only possible continuous solution of the integral equation of the first kind:

$$F(x)=\int_a^x L(x,\xi)\,u(\xi)\,d\xi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

in which:

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[1]) See for instance M. Bôcher: An introduction to the study of integral equations (1904) §§ 13, 14.

[2]) Viz. that the discontinuities lie on a finite number of curves with continuously turning tangents in the space of the $x\xi$-plane considered, which are intersected by lines // x- of ξ-axis always in a finite number of points.

$$F(x) = \int_a^x \frac{f^{(n)}(\xi)}{(x-\xi)^{1-\lambda_n}}\, d\xi \; . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and

$$L(x,\xi) = \int_\xi^x \frac{G(y,\xi)}{(x-y)^{1-\lambda_n}(y-\xi)^{\lambda_n}}\, dy \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Theorem A may again be applied to equation (17), as the kernel $L(x,\xi)$ satisfies already for $n=0$ the conditions written down for $K(x,\xi)$.

We may moreover observe that, as sufficient though not necessary condition for the continuity of $\frac{d}{dx}\int_a^x \frac{f^{(n)}(\xi)}{(x-\xi)^{1-\lambda_n}}\, d\xi$ obtains: $f^{(n)}(x)$ continuous and $f^{(n+1)}(x)$ finite with only a finite number of discontinuities for $a \leq x \leq b$.

In the first place we shall now prove that the special value (15) for the kernel $K(x,\xi)$ satisfies the conditions mentioned in theorem A or B and that in proportion as $\lambda = -n$ or $-n < R(\lambda) < -n+1$ (n positive integer or zero).

a. Let us suppose $\lambda = -n$, (15) passes into:

$$K(x,\xi) = n!\left(\frac{z}{2}\right)^{-n}(x-\xi)^{\frac{n}{2}}\, I_n(z\sqrt{x-\xi}) = n!\sum_{m=0}^{\infty}\frac{(-1)^m\left(\frac{z}{2}\right)^{2m}}{m!\,(m+n)!}\,(x-\xi)^{m+n}$$

and we find:

$$K_p(x,\xi) = \frac{\partial^p K(x,\xi)}{\partial x^p} = n!\sum_{m=0}^{\infty}\frac{(-1)^m\left(\frac{z}{2}\right)^{2m}}{m!\,(m+n-p)!}\,(x-\xi)^{m+n-p} =$$

$$= n!\left(\frac{z}{2}\right)^{-n+p}(x-\xi)^{\frac{n-p}{2}}\, I_{n-p}(z\sqrt{x-\xi}),$$

so that:

$K_0(x,\xi),\ K_1(x,\xi) \ldots K_{n+1}(x,\xi)$ are continuous for $a \leq \xi \leq x \leq b$, moreover $K_0(x,x) = 0$, $K_1(x,x) = 0, \ldots\ldots K_{n-1}(x,x) = 0$, but $K_n(x,x) \neq 0$ for $a \leq x \leq b$.

Consequently for $\lambda = -n$ the suppositions mentioned in theorem A are satisfied by $K(x,\xi)$, also if $z=0$.

b. Let us further suppose $\lambda = -n + \lambda_n$ $(0 < R(\lambda_n) < 1)$, then:

$$K(x,\xi) = \Gamma(n+1-\lambda_n)\left(\frac{z}{2}\right)^{-n+\lambda_n}(x-\xi)^{\frac{n-\lambda_n}{2}} I_{n-\lambda_n}(z\sqrt{x-\xi}) =$$

$$= \Gamma(n+1-\lambda_n)\sum_{m=0}^{\infty}\frac{(-1)^m\left(\frac{z}{2}\right)^{2m}}{m!\,\Gamma(m+n+1-\lambda_n)}(x-\xi)^{m+n-\lambda_n}$$

and consequently:

$$K_p(x,\xi) = \Gamma(n+1-\lambda_n)\sum_{m=0}^{\infty}\frac{(-1)^m\left(\frac{z}{2}\right)^{2m}}{m!\,\Gamma(m+n-p+1-\lambda_n)}(x-\xi)^{m+n-p-\lambda_n} =$$

$$= \Gamma(n+1-\lambda_n)\left(\frac{z}{2}\right)^{-n+p+\lambda_n}(x-\xi)^{\frac{n-p-\lambda_n}{2}} I_{n-p-\lambda_n}(z\sqrt{x-\xi}),$$

so that:

$K_0(x,\xi)$, $K_1(x,\xi) \ldots K_{n-1}(x,\xi)$ are continuous for $a \leq \xi \leq x < b$, moreover $K_0(x,x) = 0$, $K_1(x,x) = 0, \ldots K_{n-1}(x,x) = 0$ for $a \leq x \leq b$, while $K_n(x,\xi) = \dfrac{G(x,\xi)}{(x-\xi)^{\lambda_n}}$, in which:

$$G(x,\xi) = \Gamma(n+1-\lambda_n)\left(\frac{z}{2}\right)^{\lambda_n}(x-\xi)^{\frac{\lambda_n}{2}} I_{-\lambda_n}(z\sqrt{x-\xi})$$

and

$$\frac{\partial G(x,\xi)}{\partial x} = -\Gamma(n+1-\lambda_n)\left(\frac{z}{2}\right)^{1+\lambda_n}(x-\xi)^{-\frac{1-\lambda_n}{2}} I_{1-\lambda_n}(z\sqrt{x-\xi}),$$

so that:

$G(x,\xi)$ and $\dfrac{\partial G(x,\xi)}{\partial x}$ are continuous for $a < \xi < x < b$, and $G(x,x) \neq 0$ for $a \leq x \leq b$.

Consequently for $-n < R(\lambda) < -n+1$ the suppositions mentioned in theorem B are satisfied by $K(x,\xi)$, also if $z = 0$.

Summarizing we can already state that (1) has only one continuous solution, provided $R(\lambda) < 1$ and certain conditions for $f(x)$ are satisfied.

These necessary and sufficient conditions for $f(x)$ mentioned in A or B are doubtlessly satisfied if we impose on $f(x)$ the conditions mentioned under I (§ 2), so that we can complete I in this way that (11) under the conditions mentioned there is the only possible continuous solution of (1). [This holds good for (13) as a solution of (12)]. As a consequence of this (11) is invariable by changing μ within the limits indicated.

In order to determine the solution of (1) according to VOLTERRA's method we have to investigate again the cases a and b separately.

a. Supposing that $\lambda = -n$ and the given function $f(x)$ satisfies the conditions mentioned in theorem A, we have to consider the equation of the second kind into which (16) passes for our case, viz.

$$u(x) = \frac{f^{(n+1)}(x)}{n!} + \frac{z}{2} \int_a^x \frac{I_1(z\sqrt{x-\xi})}{\sqrt{x-\xi}} u(\xi)\, d\xi \quad . \quad . \quad (20)$$

Its solution is the absolutely and uniformly convergent series:

$$u(x) = \frac{f^{(n+1)}(x)}{n!} + \frac{1}{n!} \sum_{m=1}^{\infty} \left(\frac{z}{2}\right)^m \int_a^x \frac{I_1(z\sqrt{x-\xi})}{\sqrt{x-\xi}} \int_a^{\xi} \frac{I_1(z\sqrt{\xi-\xi_1})}{\sqrt{\xi-\xi_1}} \cdot \cdot \cdot$$

$$\cdot \cdot \cdot \cdot \int_a^{\xi_{m-1}} \frac{I_1(z\sqrt{\xi_{m-1}-\xi_m})}{\sqrt{\xi_{m-1}-\xi_m}} f^{(n+1)}(\xi_m)\, d\xi_m \cdot \cdot \cdot \cdot d\xi_1\, d\xi. \quad . \quad . \quad (21)$$

which now moreover represents the only possible continuous solution of (1) for $\lambda = -n$.

b. Supposing that $\lambda = -n + \lambda_n$ $(0 < R(\lambda_n) < 1)$ and $f(x)$ satisfies the conditions mentioned in theorem B, we arrive at equation (17), in which the kernel, represented by (19), passes for our case into

$$L(x, \xi) = \Gamma(n + 1 - \lambda_n) \left(\frac{z}{2}\right)^{\lambda_n} \int_{\xi}^{x} \frac{I_{-\lambda_n}(z\sqrt{y-\xi})}{(x-y)^{1-\lambda_n}(y-\xi)^{\lambda_n}}\, dy =$$

$$= \Gamma(n + 1 - \lambda_n)\, \Gamma(\lambda_n)\, I_0(z\sqrt{x-\xi})$$

so that (17) becomes:

$$F(x) = \Gamma(n + 1 - \lambda_n)\, \Gamma(\lambda_n) \int_a^x I_0(z\sqrt{x-\xi})\, u(\xi)\, d\xi \, . \, . \quad . \quad (22)$$

This integral equation of the first kind has as kernel:

$$K(x, \xi) = \Gamma(n + 1 - \lambda_n)\, \Gamma(\lambda_n)\, I_0(z\sqrt{x-\xi}),$$

so that $K_0(x, x) \neq 0$ and we consequently arrive at its solution by determining the solution of (16), in which $n = 0$ and f has been replaced by F; if we replace moreover λ_n by $n+\lambda$, (16), considering (18), assumes the following form:

$$u(x) = \frac{1}{\Gamma(1-\lambda)\, \Gamma(n+\lambda)} \frac{d}{dx} \int_a^x \frac{f^{(n)}(\xi)}{(x-\xi)^{1-(n+\lambda)}}\, d\xi + \frac{z}{2} \int_a^x \frac{I_1(z\sqrt{x-\xi})}{\sqrt{x-\xi}} u(\xi)\, d\xi \; (23)$$

Its solution is the absolutely and uniformly convergent series:

$$\left.\begin{aligned} u(x) &= \frac{1}{\Gamma(1-\lambda)\,\Gamma(n+\lambda)} \frac{d}{dx} \int_a^x \frac{f^{(n)}(\xi)}{(x-\xi)^{1-(n+\lambda)}}\, d\xi + \\ &+ \frac{1}{\Gamma(1-\lambda)\,\Gamma(n+\lambda)} \sum_{m=1}^{\infty} \left(\frac{z}{2}\right)^m \int_a^x \frac{I_1(z\sqrt{x-\xi})}{\sqrt{x-\xi}} \int_a^{\xi} \frac{I_1(\sqrt{\xi-\xi_1})}{\sqrt{\xi-\xi_1}} \cdots \\ &\cdots \int_a^{\xi_{m-1}} \frac{I_1(z\sqrt{\xi_{m-1}-\xi_m})}{\sqrt{\xi_{m-1}-\xi_m}} \cdot \frac{d}{d\xi_m} \int_a^{\xi_m} \frac{f^{(n)}(\xi_{m+1})}{(\xi_m-\xi_{m+1})^{1-(n+\lambda)}}\, d\xi_{m+1}\, d\xi_m \ldots d\xi_1\, d\xi, \end{aligned}\right\} \quad (24)$$

which now represents moreover the only possible continuous solution of (1) for $-n < R(\lambda) < -n+1$.

It is moreover important to observe, that though (1) for $z=0$ passes into the equation of Abel (12), the substitution of $z=0$ in (21) and (24) does not lead to its solution. As we saw, the kernel $K(x, \xi)$ continues to satisfy the conditions mentioned in theorem *A* or *B* if $z=0$, but, for $\lambda = -n$ and $z=0$, $K_{n+1}(x, \xi) = 0$, so that (16) is cancelled.

And if $-n < R(\lambda) < -n+1$ and $z=0$, (17) passes into

$$\int_a^x \frac{f^{(n)}(\xi)}{(x-\xi)^{1-(n+\lambda)}}\, d\xi = \Gamma(1-\lambda)\,\Gamma(n+\lambda) \int_a^x u(\xi)\, d\xi\,,$$

from which the solution ensues directly:

$$u(x) = \frac{\sin \lambda\pi}{\pi} \frac{\Gamma(\lambda)}{\Gamma(n+\lambda)} \frac{d}{dx} \int_a^x \frac{f^{(n)}(\xi)}{(x-\xi)^{1-(n+\lambda)}}\, d\xi$$

under the conditions for $f(x)$ mentioned in theorem *B*.

5. The expressions (21) and (24) may not be easily reduced, even though we should make use of (7) and so we accept the conditions mentioned under I (§ 2) for $f(x)$. As in this case (11) must represent the same $u(x)$ we arrive at the following conclusions:

1. Not only (21) but also (11) with $\lambda = -n$ represents the only possible continuous solution of (20), if the conditions mentioned under I hold good for $f(x)$. If we introduce some simplification here by supposing $\dfrac{f^{(n+1)}(x)}{n!} = \varphi(x)$, we can say that the integral equation of the second kind:

$$u(x) = \varphi(x) + \frac{z}{2}\int_a^x \frac{I_1(z\sqrt{x-\xi})}{\sqrt{x-\xi}}\, u(\xi)\, d\xi \,. \quad . \quad . \quad . \tag{25}$$

has the only possible continuous solution:

$$u(x) = \left(\frac{iz}{2}\right)^{1-\mu} \int_a^x (x-\xi)^{-\frac{1-\mu}{2}} I_{-(1-\mu)}(iz\sqrt{x-\xi})\,\varphi^{(\mu)}(\xi)\,d\xi\,,\ 0<R(\mu)<s+1 \tag{26}$$

if the conditions are satisfied:

II. $\varphi(x)$ is an analytical function, regular for $a \leq x \leq b$, which has $x=a$ as zero of order s; and the series for $\varphi^{(\mu)}(x)$, which we may draw up by means of our definition, is uniformly convergent for $a \leq x \leq b$.

So, not only (24) but also (11) with $-n < R(\lambda) < -n+1$ represents the only possible continuous solution of (23), if the conditions mentioned under I hold good for $f(x)$. Here too we can introduce some simplification by writing $\dfrac{f^{(n)}(x)}{\Gamma(1-\lambda)\,\Gamma(n+\lambda)} = \varphi(x)$, so that of the integral equation:

$$\left.\begin{aligned} u(x) &= \frac{d}{dx}\int_a^x \frac{\varphi(\xi)}{(x-\xi)^{1-(n+\lambda)}}\, d\xi + \frac{z}{2}\int_a^x \frac{I_1(z\sqrt{x-\xi})}{\sqrt{x-\xi}}\, u(\xi)\, d\xi, \\ &-n < R(\lambda) < -n+1 \ (n \text{ pos. integer or zero}) \end{aligned}\right\} . \tag{27}$$

the only possible continuous solution may be written in the form:

$$\left.\begin{aligned} u(x) = \Gamma(n+\lambda)\left(\frac{iz}{2}\right)^{1-\mu} \int_a^x (x-\xi)^{-\frac{1-\mu}{2}} I_{-(1-\mu)}(iz\sqrt{x-\xi})\,\varphi^{(\mu+1-n-\lambda)}(\xi)\,d\xi\,. \\ 0 < R(\mu) < s+1 \end{aligned}\right\} \tag{28}$$

under the conditions:

III. $\dfrac{\varphi(x)}{(x-a)^{1-(n+\lambda)}}$ is an analytical function, regular for $a<x<b$, having $x=a$ as zero of order s; and the series ensuing from it for $\varphi^{(\mu+1-n-\lambda)}(x)$ is uniformly convergent for $a \leq x \leq b$.

2. As (21) with $\dfrac{f^{(n+1)}(x)}{n!} = \varphi(x)$ and (26) both represent the only possible continuous solution of (25), in the same way (24) with $\dfrac{f^{(n)}(x)}{\Gamma(1-\lambda)\ \Gamma(n+\lambda)} = \varphi(x)$ and (28) both the only possible continuous

solution of (27), we arrive at the two important relations:

$$\left.\begin{aligned} & q(x) + \sum_{m=1}^{\infty} \left(\frac{z}{2}\right)^m \int_a^x \frac{I_1(z\sqrt{x-\xi})}{\sqrt{x-\xi}} \int_a^{\xi} \frac{I_1(z\sqrt{\xi-\xi_1})}{\sqrt{\xi-\xi_1}} \cdots \\ & \qquad \cdots \int_a^{\xi_{m-1}} \frac{I_1(z\sqrt{\xi_{m-1}-\xi_m})}{\sqrt{\xi_{m-1}-\xi_m}} q(\xi_m)\, d\xi_m \ldots d\xi_1 d\xi = \\ & \doteq \left(\frac{iz}{2}\right)^{1-\mu} \int_a^x (x-\xi)^{-\frac{1-\mu}{2}} I_{-(1-\mu)}(iz\sqrt{x-\xi})\, q^{(\mu)}(\xi) d\xi, \end{aligned}\right\} \quad . \quad . \quad (29)$$

in which $0 < R(\mu) < s+1$, $z \neq 0$, and the conditions mentioned under II obtain.

$$\left.\begin{aligned} & \frac{d}{dx}\int_a^x \frac{q(\xi)}{(x-\xi)^{1-(n+\lambda)}} d\xi + \sum_{m=1}^{\infty} \left(\frac{z}{2}\right)^m \int_a^x \frac{I_1(z\sqrt{x-\xi})}{\sqrt{x-\xi}} \int_a^{\xi} \frac{I_1(z\sqrt{\xi-\xi_1})}{\sqrt{\xi-\xi_1}} \cdots \\ & \cdots \int_a^{\xi_{m-1}} \frac{I_1(z\sqrt{\xi_{m-1}-\xi_m})}{\sqrt{\xi_{m-1}-\xi_m}} \cdot \frac{d}{d\xi_m} \int_a^{\xi_m} \frac{q(\xi_{m+1})}{(\xi_m-\xi_{m+1})^{1-(n+\lambda)}}\, d\xi_{m+1} d\xi_m .\, d\xi_1 d\xi = \\ & = \Gamma(n+\lambda)\left(\frac{iz}{2}\right)^{1-\mu} \int_a^x (x-\xi)^{-\frac{1-\mu}{2}} I_{-(1-\mu)}(iz\sqrt{x-\xi})\, q^{(\mu+1-n-\lambda)}(\xi) d\xi, \end{aligned}\right\} \quad (30)$$

in which $-n < R(\lambda) < -n+1$ (n positive integer or zero), $0 < R(\mu) < s+1$, $z \neq 0$ and the conditions mentioned under III obtain.

Anatomy. — "*On the conus medullaris of the domestic animals.*"

By Dr. H. A. Vermeulen. (Communicated by Prof. C. Winkler).

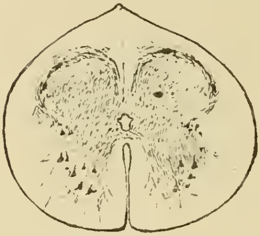
(Communicated in the meeting of October 30, 1915).

The material used in this research was derived from 4 horses, a calf's foetus of $4^1/_2$ months, 2 goats, 2 sheep, a pig's foetus of 3 months, 3 dogs and a cat. Of that of 2 horses, 1 dog and 1 sheep longitudinal sections were made, that of the other animals was cut into transverse sections. (Paraffine inclusion, sections of 12—18 μ, colouring with cresil violet.)

In all our domestic animals the spinal cord reaches further in the spinal canal than in human beings. Whereas in the latter the conus medullaris reaches the second lumbal segment, in the carnivori this passes the whole or almost all of the lumbar region of the vertebral column, which in these animals is generally built up of seven, sometimes of 6 vertebrae, while in the Ungulata, it can be traced as far as the middle of the sacral portion of the vertebral column.

Similarly, the continuation of the conus and that of the surrounding membranes, the filum terminale, extends in these animals, owing to the stronger development of the tail column, further than in the corresponding part of the human body.

Equus caballus. In the last lumbal segment the transverse section of the medulla of the horse shows a heart shape, with the basis turned ventrally (anterior) and the blunt point dorsally (posterior). The anterior horns are well developed, the posterior horns are large, with rounded, much broadened tops turned towards the periphery; the substantia gelatinosa is characterised by a sharply outlined fibre system. As well as in the ventral and in the ventro-lateral portion of the anterior horn, numbers of large cells are met with on the border of the anterior and posterior horns; in the posterior horn we see scattered cells generally of a somewhat smaller type. Occasionally these are fusiform or egg-shaped, or more or less round, and they exhibit a marked accumulation of pigment, which causes a morphological resemblance to the cells of the spinal ganglion of the horse. Frequently we see a few cells, sometimes clustered in small groups and of a narrow fusiform, in the border zone of the posterior horn, most of them on its posterior and outside edge. The septum longitudinale posterius is very thin and the fissura longitudinalis anterior much narrower on the periphery than in the more central portion of it (fig. 1). The canalis centralis is not obliterated, small coagulations are visible in the centrum but the ciliated epithelium is quite intact. Remarkable is the great number of small blood-vessels situated in its immediate neighbourhood. It shows a peculiar form (fig. 2). The posterior portion of it is broad and rounded, and possesses two small pointed lateral recessus, the anterior portion is smaller and likewise rounded off. At its greatest breadth it measures 0.315 mm., while the greatest depth is 0.365 mm. At the commencement of the sacral medulla the heart shape becomes more distinct on section as the posterior pole becomes more pointed. The canalis has shifted from the centrum in a forward direction and has become rather narrower; the above dimensions now are 0.216 mm. and 0.315 mm. respectively; the section is that of a spindle with irregular walls, and the side projections in the posterior portion are but faintly indicated. The septum posterior has meanwhile disappeared and the number of cells in

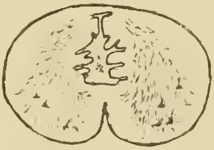

Equus (Fig. 1).


Equus (Fig. 2).

the anterior horn have greatly decreased, clusters of cells can be seen longest ventrally and dorso-laterally on the border of the anterior and posterior horns. In the sensory zone the large cells, mentioned above, can still be seen, though not constantly, both in the centrally situated cells and the fusiform border-cells.

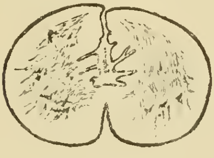
Likewise fairly large oval, or more or less round cells, containing pigment, can still be seen occasionally. The fissura longitudinalis anterior is unchanged. In the following portion of the sacral medulla these conditions are the same, with the exception of the section of the central canal. This is now widest in the ventral (anterior) portion, for there the wall is gently curved ventrally or flattened, the dorsal (posterior) pole a blunt curve, and the side walls exhibit several bulges. These at first number two on either side, one half way up and one on the ventrally pointing basis. In many sections they are seen symmetrically. The number of cells in the anterior horn has grown small again, while in the sensory zone the various kinds of cells appear now and then as before. This sensory zone has grown much more massive, owing to the commissura grisea having become thicker, the fissura anterior is smaller and no longer shows the broadened central portion. Further back the sensory horns merge almost to one mass, in which however, the two horns can still be separately distinguished for some time, as the round-fibred systems keep their individuality (fig. 3). The conus which gradually decreases in diameter, still exhibits the heartshaped form in section. The anterior horn cells seen occasionally are few, and the central and border cells are also scarce in the sensory area. The projections of the central canal are larger, the epithelium is intact and soon a third set of projections makes its appearance. The number of cells decreases, especially in the sensory portion, while the section loses its heart-shaped form, owing to the conus becoming flatter. As the fissura anterior is still present and the back wall of the conus rounds off, the whole, on a section, now has the appearance of a kidney. The flattening is a result of the diminishing of the sensory area. The sectional view of the central canal again changes. The posterior portion grows out in a point and before long almost touches the posterior periphery of the conus, the side projections again increase in number, new ones appear among the first, but neither constantly nor symmetrically, while also small projections grow out of the posterior top which has become flat. The canal now measures at the deepest part, 830 m.m., and its maximum breadth is 0.217 m.m. In another horse these measurements were at this place 1.13 and 0.398 m.m. The folds, four, five, and sometimes six in number on each side, vary in size, the longer having secondary smaller ones (fig. 4).

Equus (Fig. 3)

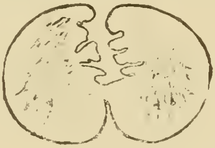


Equus (Fig. 4)

The conus is still kidney-shaped on section, occasionally a few cells still occur, the posterior zone having no more large cells. After this the canal breaks through on the posterior side, which break



Equus (Fig. 5).

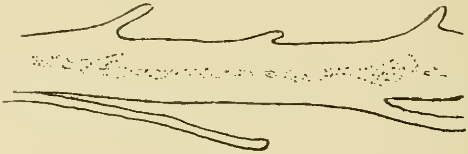


Equus (Fig. 6).

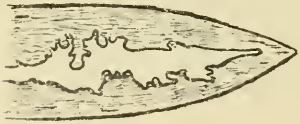
can be seen in a series of 62 consecutive sections of $18\,\mu$, for a length of fully 1 m.m. The opening, very narrow at first, gradually widens to a maximum of 0.3 m.m. after which it becomes narrower and the canal closes again, continuing for $^1/_2$ m.m. nearly to the apex of the conus.

The ciliated epithelium can still be seen quite intact in many sections as far as the break in the border. In the conus medullaris of the horse there is thus a cleft-like open communication of about 1 m.m. long and with a maximum breadth of 0.3 m.m. After this cleft has closed the central canal attains its greatest depth, viz. 1.33 m.m., with a breadth of 0.332 m.m. The fissura anterior has disappeared after the rupture, the kidney-form in section gives place to an irregular round shape and afterwards, when the cross diameter of the conus grows shorter, to a pear shape. Finally the anterior portion of the canal is also pointed, whereby the frontal wall is almost reached, but not broken through. The ventriculus terminalis measures about 5.5 mm.

In two horses the end of the sacral medulla was cut longitudinally for a length of 3.5 cm. Here too it is seen that the central canal, before it widens at the end of the conus into a ventriculus terminalis is not everywhere equally wide. Cranially from the ventriculus terminalis more widenings occur, in one case there was even an elongated spindle-shaped widening, 2.5 m.m. in length, to be seen right in front of the ventricle. Since the ventriculus proper was here only 2.8 m.m., it is not impossible that this extreme broadening belongs to it and that the ventriculus in this horse showed a bend. The folds vary greatly in size, the smaller ones protruding at right angles, the larger ones at an acute angle, while the longest runs nearly parallel to the conus (fig. 7). The longest which I observed was 5 mm. in length with a breadth of 0.250 mm. In one case a narrow fold was to be seen close to the end of the canal, so that the latter ended here in the form of a pitch-fork. The wall of the ventriculus is much folded, some folds branch off again till the whole has a very odd appearance (fig. 8). The rupture seems to take place near the end of the ventriculus. Behind the ventriculus the conus continues for 0.5 mm. more (fig. 8). Neither is the ventriculus obliterated, although the epithelium here shows signs of degeneration.



Equus. Fig. 7.



Equus. Fig. 8.

Especially in the longitudinal sections fine large round cells containing a great quantity of pigment are to be seen. It is not improbable that these are central ganglion cells of spinal ganglions.

Bos taurus. (foetus of $4^1/_2$ months). On the border of the lumbal and sacral portion the medulla shows a sectional view which resembles exactly that of the closed portion of the medulla oblongata of the cow, in the reverse way, however, for the cleft is caused by the fissura anterior and thus lies here on the frontal side. The walls of this fissure diverge widely and gradually slope into the frontal wall. The strongly developed anterior horns are extremely rich in cells in the ventral portion; latero-dorsally on the border of anterior and posterior horns no cells of a large type are met with. As a rule three sharply defined cell-groups may be distinguished in the anterior horn, one ventro-medial, one ventro-lateral and one dorsally at the last-named. This dorso-lateral group is the most constantly round in form and contains 30—40 cells, the two other differ greatly in size and shape, owing to their often possessing continuations which continue along the lateral and medial walls respectively. The dorsal horns are broad and carry a heavy cap of substantia gelatinosa Rolando, always clearly circumscribed on the periphery by a fibre system. These horns are also rich in cells, of a smaller type, however, than those of the anterior horns. The canalis centralis is a recumbent oval in section, in width it measures 0.1 mm. and in depth 0.07 mm.; the ciliated epithelium is very well developed. The fissura anterior is shallow, regular in section and proceeds, as has been remarked, with a pronounced curve into the frontal wall of the medulla. In this foetal tissue the commissura grisea is very slightly developed, when, strongly magnified, but few commissure fibres can be detected, a circumstance which can be observed also in the whole of the lumbal segment (fig. 9).

Caudally the cross diameter of the conus decreases, whereby the form on section becomes compact, the central canal shifts in a ventral direction and on section is seen to be round; the cell groups

Fig. 9. Fig. 10.

Bos taurus (Embryo $4^1/_2$ months).

in the anterior horn have grown fewer in number and smaller, the commissura grisea begins to be clearly visible on the peripheral portion and further develops rapidly and grows very rich in small cells. The border zone of the posterior horns lies directly against the periphery. Further caudally, in the medio-ventral portion of the anterior horn, many cells again appear, and conspicuous is a well-defined cell-group right and left of the canalis centralis. These groups built up of typical anterior horn cells, can be traced for many sections (fig. 10).

The conus then becomes roundish in form, only broken in its frontal wall by the shallow fissura anterior, the central canal has become egg-shaped on section with the blunt end pointing ventrally; the septum posterius has disappeared; the commissura grisea is very broad and rich in small cells, in the anterior horn a varyingly large number of cells occur of a smaller type than before; after this the conus flattens and its section shows the form of a kidney, the central canal keeps its diameter and remains free; the number of cells has diminished very greatly everywhere; in the anterior horn we see exclusively small cells of 10—12 μ, sometimes in groups 3—5. By the time the fissura anterior has disappeared, the frontal wall of the conus is flattened, the posterior wall remains rounded, the central canal is then rather wider, (0.13 × 0.1 mm.) and is also flattened on the frontal side. Now the canal begins gradually to widen into the ventriculus terminalis. First egg-shaped on section with the pointed end towards the front, it further on expands backwards whereby the posterior wall of the canal becomes flat. At the base traces of folds can now and then be seen (fig. 11). The breadth diameter of the conus diminishes greatly so that, when the canal has reached its maximum breadth and its front and back walls have very nearly reached the periphery, the whole canal is surrounded by a narrow strip of conus-tissue (fig. 12). The ventriculus is then 1.16 mm. deep and 0.250 mm. broad; the epithelium here shows signs of degeneration, and cell remnants are present in the ventriculus. Then the latter decreases in width and gradually becomes a narrow groove; before the end, however, a slight widening takes place,

Fig. 11.

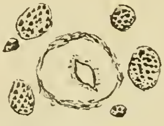


Fig. 12.

Bos taurus Embryo $4^1/_2$ month.

which bears traces of folds, and in which the epithelium appears again to be quite intact. The whole ventriculus has a length of 3 mm., and there is no sign of any rupture. At the end of the conus we find outside the continuation of the dura numerous spinal ganglions, the largest with a diameter of 0.750 mm., while a few smaller ones can be seen caudally from the conus (fig. 12).

Capra hircus. On the border of the last lumbal and the first sacral segment the medulla is roundish on section, the anterior horns are well developed and almost reach the periphery; they are very rich in large cells, which also occur in the so-called middle-horn; the posterior horns, with their round, cap-like, broadened tops partly, and rather more caudally entirely, reach the periphery. They contain few large cells; the fibre-system round the substantia gelatinosa Rolandi is also distinctly present. The section shows the canalis as an upright oval, at this place it is 0.270 mm. deep and 0.1 mm. wide. The septum posterius is very thin and the fissura anterior very narrow. The canal is quite free, ventro-laterally we find on the right and left a sharply defined fibre bundle, more or less round, with a diameter of 0.2 mm. These bundles are also present in the lumbal medulla and can be traced far back [1]). Also in the second series they can equally clearly be seen. Owing to the canal deepening caudally they gradually come to lie right and left beside the canal (fig. 13). In this level the conus is still round in section and numerous cells, though in general of a smaller type than before, are met with in the anterior horns, as also in the middle-horn and dorsally from the central canal. The posterior horns are still poor in cells. More caudally the septum posterius disappears and the whole posterior portion of the conus is taken up by the sensory area, in which the two horns have merged into one, the fissura anterior has grown very shallow, the central canal has shifted further ventrally and has become wider,

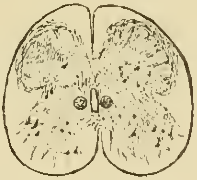


Fig. 13. Capra hircus.

Fig. 14. Capra hircus.

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[1]) According to Dexler these sharply circumscribed "intra kommissurale Ventralbündel" occur constantly in the Ruminants and in Pigs. (Ellenberger, Handbuch der vergleichenden mikroskopischen Anatomie der Haustiere, Vol. II, Page 214). In the calf's foetus they were not present.

especially in the ventral portion, in which portion folds occur. In this respect there appear to be individual differences. In one series they are very distinct. The posterior portion grows out in a point, stretches as far as the back wall of the conus and even pushes the latter outwards in a point at some places; the anterior portion sends out strong folds at its base and somewhat higher (fig. 14). Further back these increase till finally the whole ventricle wall is folded. The greatest depth here measures 0.550 mm. the greatest width 0.140 mm. In the other series the canal appeared less deep here, though more than twice as broad; here the measurements were 0.480 and 0.3 mm. respectively; the folds occur later, are less numerous and much smaller. The ventriculus terminalis of the goat is about 3 mm. long. The canal is not obliterated.

Ovis aries. The end of the lumbal medulla on section is round, as is also the central canal. The latter is partially obliterated and the epithelium also exhibits distinct signs of degeneration. As in the goat, clearly defined bundles also occur ventrally from the canal: here however, they lie nearer the median line and do not reach so far caudally. The grey matter is less well developed than in the goat and cells are fewer in number. The septum posterius is partially cleft-shaped, the fissura anterior, as in the horse, is much wider in the more central portion than at the surface.

Caudally the conus becomes heart-shaped in section, the canal shifts in a ventral direction, deepens and broadens ventrally, and then becomes bell-shaped in section, owing to the flattening of the broad lower wall. Its depth and breadth are here 0.2 and 0.170 mm. respectively. In this region we see, at the back, indications of folds and the above-mentioned bundles will be found to lie immediately against each other and right against the lower wall. More caudally the canal becomes narrower again, the septum posterius here is a cleft almost as well developed as the fissura anterior, still further back, the septum becomes shorter and we frequently see the remainder of it as a small cleft-like space connected with the posterior wall by a fine pia-bundle. At this juncture the conus is distinctly kidney-shaped on section, cells are still present in all the sections, the majority in the anterior horn but a few also in the posterior horn. The central canal widens into the ventriculus terminalis, deepens as it proceeds backwards and soon reaches the posterior circumference, many sections show the wall at this place bulged in a point by the ventriculus. Here shallow folds and short bulges are present in the ventricle wall. (Fig. 15). The back wall of the conus is hereby rendered so thin that a break seems to have taken place repeatedly. In the continuous series, however, we see distinctly that there have been ruptures, the remains of which are frequently to be seen, but where such is not the case or is doubtful, such sections are followed by others in which the canal is closed. The greatest depth of the ventriculus in this series is 0.670 mm. and the maximum width is 0.250 mm., after which the canal grows narrower. Although the walls are often irregular, distinct folds no longer occur. The ventriculus is about 4 mm. long. Even at the end of the conus an occasional cell is to be found. Immediately behind the end of the conus, beyond the continuation of the dura lies a spinal ganglion which contains about 60 cells. In a longitudinal section we see that the central canal itself is very irregular in width, and that the folds are small and few in number.

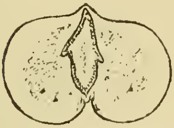
Fig. 15. Ovis aries.

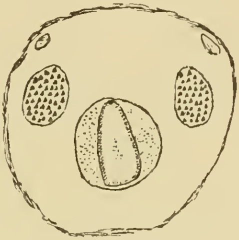
Fig. 16. Sus scrofa domesticus (foetus 3 months).

Sus scrofa domesticus (foetus of 3 months). This material appears to have suffered greatly and only the series of the last portion of the conus has been successful. At this place the conus is ¾ mm. in diameter, and round in section, the septum posterius is not present and of the fissura anterior only a shallow groove is left. No cells are to be observed. The canal no longer lies in the centrum, it is a fairly narrow ellipsis in section, 0.3 mm. deep and 0.07 mm. wide. Towards the back it widens 0.16 mm. and the section becomes egg-shaped. On this level and also further backwards we constantly find in the durapocket one or two spinal ganglions of 0.250 mm. in diameter. The canal continues till it strikes against the front and back walls of the conus (fig. 16), then it widens in a ventral direction and finally decreases in width and depth, at the end it is surrounded only by an extremely fine layer of conus tissue. The widened portion of the canal is 1.5 mm. long, the greatest depth measures 0.4 and the greatest breadth 0.18 mm. No folds of the wall, nor any indications of such can be noticed. Cell-remnants are present in the ventriculus. No more spinal ganglions are seen at or near the top of the conus.

Canis familiaris. In carnivori the conus does not reach the sacral canal. In the middle the lumbal medulla is heart-shaped on section with the blunt point directed backwards. The grey matter is very strongly developed. Owing to the presence of the big commissura grisea the fine septum posterius is very small. The central canal is an irregular round, frequently it is a distinct pentagon on section, the epithelium is poorly developed and even lost in several places; many remnants of it are found in the central canal, which is also wholly, or nearly wholly, obliterated, its depth and breadth are practically equal, the diameter measures 0.17 mm. In the strongly developed motor horns we find large cells ventrally only. The posterior horns touch a large part of the back wall of the conus, the border zone is not so sharply marked as in the Ungulates. In this area too a few large cells occur. In general the medulla is poorer in cells than the sacral medulla of ruminants (fig. 17). Further back the conus becomes kidney-shaped on section and the canal measures more in width than in depth, the broad base sometimes arched, sometimes flat, measures 0.250 mm. and the depth 0.125 mm. Here we find traces of folding at the base and sometimes also above. Now the formation of the ventricle commences, the canal deepens towards the back; at first it is pointed in front and rounded at the back, so that the whole in section becomes pear-shaped; later the base also rounds off so that it becomes an elongated oval, after which it gradually decreases. In three dogs the measurements were as follows: from the number of transverse sections the


Fig. 17. Canis familiaris.

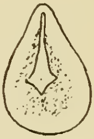
Fig. 18. Felis catis domest.

length of the ventriculus of one could be calculated to be 2.5 mm. of another 2.25 mm. while of the third dog the longitudinal section measured 3 mm. In the two first cases the greatest depth and breadth were 0.4—0.17 mm. and 0.5—0.15 mm. respectively, and the greatest depth in longitudinal section 0.515 mm. In longitudinal section it further appears that the canal does not run quite to the point of the conus, but stops 0.225 mm. from it and that the portion of the canal behind the ventricle exhibits slight differences in depth. Past the conus very small ganglions are seen outside the membranes.

Felis catis domestica. In general we find here the same conditions as in the dog. Owing as the fissura anterior disappears earlier the section does not show the kidney shape after the heart shape, but the conus here is more or less flattened at both poles, and later it becomes oval and pear-shaped on section. Further the central canal in the cat appears to have different diameter measurements at several places, and is mostly obliterated. At first fusiform on section with a depth of 0.30 mm. and a width of 0.166 mm. towards the back it becomes roundish, with a section of 0.230 mm. and then points in a ventral direction. At several places it exhibits small folds in many sections of the ventriculus, these are symmetrically present in the posterior third portion (fig. 18). Here the ventricle is 0.558 mm. deep and 0.250 mm. wide, after which it gradually narrows to a fine cleft which has also small folds. The whole ventriculus is 2.25 mm. long. At the end of the conus a few ganglion cells are observed.

We see thus that of our domestic animals the horse exhibits various peculiarities in the structure of the conus. Although the length of the ventriculus terminalis is very small compared to that of human beings at least, (man 8—10 mm., horse 5.5 mm.) this difference is certainly fully compensated by the particularly strong folds of the ventricle walls and the numerous, frequently even strongly developed folds of the canal before the ventricular widening. This fold formation can be seen in a more or less degree in all the other domestic animals with the exception perhaps of the pig, but in none in such a degree of development as in the horse. Further the rupture of the canal, the presence in the horse of a neuroporus posterior and the striking abundance of blood-vessels in the immediate proximity of the central canal. As regards the rupture, Stilling has observed that the central canal breaks through at the end of the conus, in some animals at the back wall, on others at the frontal wall. Stilling's observations have been repeatedly refuted by others, and hitherto the theory generally held was that such a rupture does not occur, and that what Stilling had seen were only artefacta, which need occasion no surprise since the conus wall, which surrounds the ventricle, is often extremely thin. In my opinion the rupture is undeniable in the horse and I connect it with the unusually rich fold formation, the presence of numerous recessus and the great quantity of blood. For, owing to these conditions, the resorption surface of the liquor cerebro-spinalis and the degree of the power of resorption increases of the relative tissues, which for an animal used for long and heavy labour and therefore provided with a very powerful metabolism, cannot be otherwise than of the greatest use. To this opinion I will here add in passing that in none of our domestic animals are such frequent disturbances of the central nervous system caused by stopping of the liquor cerebro-spinalis to be met with as in the horse.

Remarkable is the occurrence of sharply defined bundles in the motory region and in the immediate neighbourhood of the central canal and the lumbal and sacral medulla of ruminants and pig, as also the fact that about half-way in the development the commissura grisea in the cow is locally developed and at other places has still to be formed.

It is known that in human beings spinal ganglia can be seen at the end of the medulla inside the dura-pocket. As regards the horse I can give no information on this point because the material of these animals has been prepared for the investigation. Of the other animals numerous spinal ganglia occurred intra-durally only in the pig (foetus): in several, these ganglia are seen caudally from the conus. It is certainly remarkable that these ganglia, which in higher levels have shifted peripherally into the foramina vertebralia, have remained at the end of the medulla nearer their origin or have been left behind at the end of the spinal canal. The fact that they even remain within the membranes entitles us to assume that the spinal ganglion cells of the terminal part of the medulla are more inclined to keep their connection with the spinal cord, for which reason I venture to express the possibility that the cells rich in pigment as described in the horse even might be central ganglion cells.

Chemistry. — *"On Critical Endpoints in Ternary Systems"*. III.

By Prof. A. Smits. (Communicated by Prof. J. D. van der Waals.)

(Communicated in the meeting of October 30, 1915).

1. *Projections on the concentration triangle.*

Already in a few earlier communications I have written on the occurrence of critical endpoints in ternary systems[1]), specially because this subject is of great importance for *petrography* and particularly for the chemistry of the magma.

In my latest communication six cases have been successively discussed, the sixth of which referred to the occurrence of a binary compound as solid phase.

The consideration of a case that a ternary compound occurs as solid phase was then postponed till later, because it seemed to me that this case would not be a subject of study for the present.

Soon after, however, Dr. Morey informed me that he was engaged in the study of the ternary system $H_2O—SiO_2—K_2O$ in the Geophysical Laboratory of the Carnegie Institution of Washington, in the course of which research he met with a case that had not yet been treated by me, so that it had become desirable to extend my earlier considerations.

I greatly desired, particularly because I knew Dr. Morey would be interested, to undertake this work immediately after his communication, but want of time compelled me to put this off until now.

7th *Case.* Continuing our earlier considerations we shall therefore begin with the case that the volatile component A gives critical endpoints neither with B nor with C, but that a ternary compound D_3 occurs, which more or less dissociates in the liquid and the vapour phase, and which presents critical endpoints with A. This case is schematically represented in fig. 1.

In this figure in the first place the ternary eutectic liquid and vapour lines are given, so the liquids and the vapours that coexist with two solid substances. In the second place the critical endpoint curve has been given.

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[1]) These Proc. XIII, p. 342 and XV, p. 184.

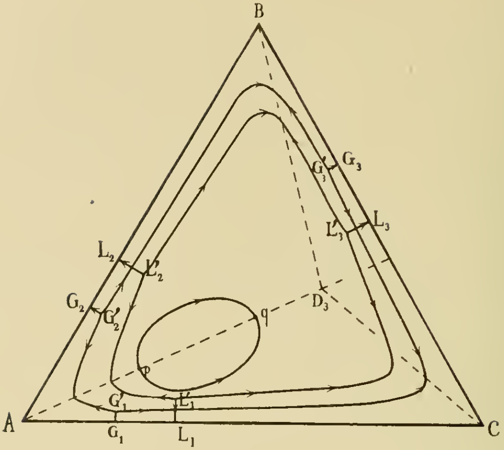

Fig. 1.
D_3 the least volatile; B more volatile than C; A very volatile.

The lines $L_1'L_2'$ and $G_1'G'_2$	refer to the liquid resp. vapour phases coexisting with	$A+D_3$
" " $L_2'L_3'$ " $G_2'L_3'$		$B+D_3$
" " $L_1'L_3$ " $G_1'G_3'$		$C+D_3$
" " L_1L_1' " G_1G_1'		$A+C$
" " L_2L_2' " G_2G_2'		$A+B$
" " L_3L_3' " G_3G_3'		$B+C$

The arrows on every curve indicate the direction towards higher temperature.

The closed curve pq is the critical endpoint curve with the ternary compound as solid phase. Hence critical phenomena take place by the side of the solid ternary compound D_3 along this line. The critical endpoints which are found starting from the ternary compound D_3 and pure A lie in the points p and q. On addition of B, as well as of C these points approach each other, till they finally coincide. Now it has been assumed here that the ternary compound can exist up to the highest eutectic temperature that occurs in the ternary sytem.

If this is not the case, however, and if the ternary compound decomposes before this temperature has been reached, so that a double salt D_2 occurs as solid phase, the figure becomes as indicated in fig. 2.

Now the transformation points L'_4 and G'_4 resp. L'_3 and G'_3 occur on the liquid and vapour lines which indicate the liquids and the vapours coexisting with $D_3 + C$ and $D_3 + B$, from which points new eutectic lines start indicating the following coexistences.

L'_4L_4 and G''_4G_4 for liquid or resp. vapour phases with $C + D_2$
L'_3L_3 ,, G''_3G_3 ,, ,, ,, ,, ,, ,, ,, $B + D_2$
and $L'_3L'_4$,, $G''_3G''_4$,, ,, ,, ,, ,, ,, ,, $D_3 + D_2$

It might happen that now again critical endpoints occur, and now by the side of D_2 as solid substance, but this case we leave out of consideration for the moment.

It is still noteworthy here that the critical endpoint curve might also have been drawn in this way, that it intersects the lines G''_4. G''_3 and L'_4 L'_3. This intersection would then, however, have had no physical signification, as the latter lines refer to other temperatures than those for which the critical endpoint curve holds.

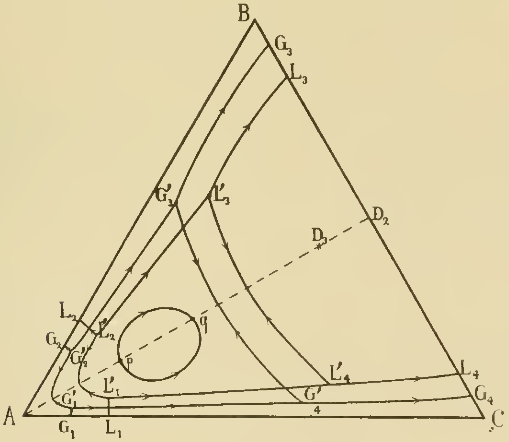

Fig. 2.

D_3 the least volatile; D_2 less volatile than B and C;
B more volatile than C; A very volatile.

8th *Case.* We *will*, however, examine the case that presents itself when in the preceding case the ternary compound D_6 decomposes before the critical endpoint q is reached, and when at higher temperatures critical phenomena with solid D_2 occur instead of with solid D_3. When this case presents itself fig. 2 is changed into fig. 3.

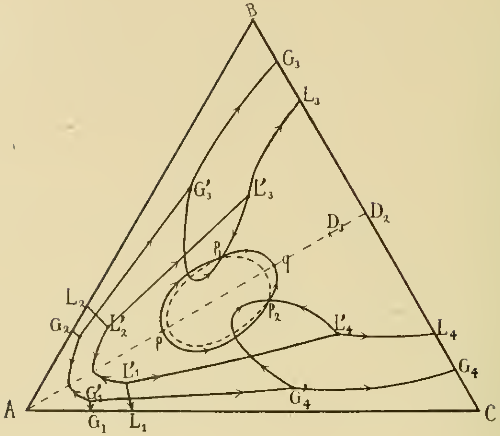

Fig. 3.
D_3 the least volatile; D_2 less volatile than B and C;
B more volatile than C; A very volatile.

The particularity is here that the eutectic liquid-vapour lines referring to the coexistence with $D_3 + D_2$, merge continuously into each other in the points p and p_2, which are therefore two *double critical endpoints.*

In these two points the two critical endpoint curves, that of D_3 and of D_2, intersect.

9th *Case.* Just as in the preceding case two double critical endpoints can present themselves, when besides the ternary compound, also the component C with A exhibits critical endpoints. We then get a structure as given in fig. 4.

The double-critical endpoints P_1 and P_2 are the points of intersection of two critical endpoint curves.

For one critical endpoint curve the ternary compound D_3 occurs as solid phase, and for the other the component C. Of course the corresponding continuous eutectic liquid vapour lines pass through the two points of intersection. It has further been assumed in this figure that just as in the preceding case a binary compound D_2 is formed from the ternary compound at a temperature above the critical endpoint p. If in the binary system $A—B$ also critical endpoints occur, two double critical endpoints may arise also on that side of the triangle, which we need not specially indicate here.

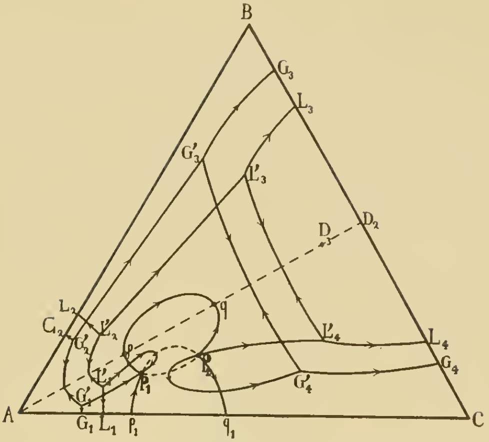

Fig. 4.
D_3 the least volatile; D_2 less volatile than B and C;
B more volatile than C; A very volatile.

Besides a combination with fig. 3 can occur, but this case too follows so easily from the preceding ones that this does not call for a separate discussion either.

Thus it will also be clear that in the last case the two endpoint curves coming from the sides AC and AB, which refer to the coexistence of a critical phase with solid C resp. with solid B, can come in contact with each other, as was drawn by me already before, (fig. 5 in communication II), and then this case can occur e.g. combined with case 7 or 8.

What is, however, of more importance at the moment is the fact that Dr. MOREY in his study of the system $H_2O—SiO_2—K_2O$, found phenomena which point to this that this system as far as its main points are concerned, must be probably classed with fig. 4, when we namely put that $A = H_2O$, $C = SiO_2$ and $B = K_2O$. The system H_2O—SiO_2 gives two critical endpoints; further Dr. MOREY has found that in this system a ternary compound $KHSi_2O_5$ occurs, which probably also shows two critical endpoints, the former lying at ± 365°, the latter at ± 500°. He has further found that this ternary compound splits up at higher temperatures into the binary compound $K_2Si_2O_5$, and a solution rich in SiO_2. Of course the critical endpoint curve of the compound need not come in contact with that of SiO_2; this is however probably the case, and then fig. 4 represents the phenomena schematically perfectly, at least as far as the principal features are concerned, though the situation of the vapour lines is much more one-sided than has been drawn here. It is, however, not impossible, as Dr. Morey observes, that also the binary compound yields critical endpoints, but this being still unknown at the moment, we can leave this possible complication undiscussed for the present. Now the system studied by Dr. Morey. however, is certainly still somewhat more complicated than that indicated in fig. 4, for there occurs another ternary compound there, viz. $K_2Si_2O_5H_2O$. This ternary compound gives no critical endpoints. The figure, however, changes only little, also when this compound is considered.

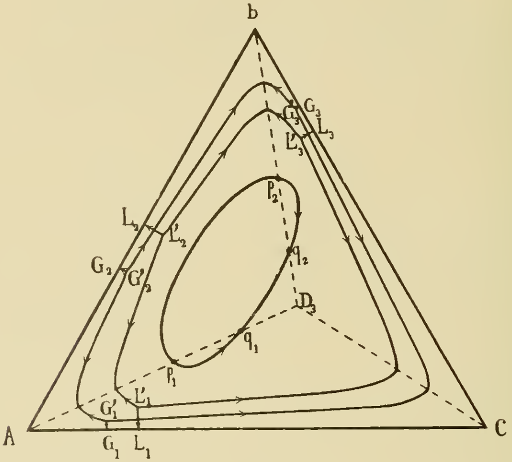

Fig. 5.

D_3 the least volatile; B more volatile than C; A very volatile.

This change will be applied later when the system has been more closely investigated; probably $K_2Si_2O_5H_2O$ will occur at lower temperature, $KHSi_2O_5$ at higher temperature.

In any case it seems probable to me that what is typical of the said ternary system is indicated by fig. 4, and so this figure can probably render good services as a guide in the continued research.

Case 10. Up to now cases have been considered which may present themselves for ternary systems with one volatile component.

Now we will suppose that both A and B are volatile, and that a ternary compound D_3 occurs, giving critical endpoints with A and B, whereas C presents critical endpoints neither with A nor with B. We then get fig. 5, which does not call for further elucidation.

Case 11. The case we are going to consider now only differs from the preceding one in this that in the binary system $A—C$ critical endpoints occur. The critical endpoint curve for solid D and solid C intersect, and give then rise to the origin of two double critical endpoints P_1 and P_2.

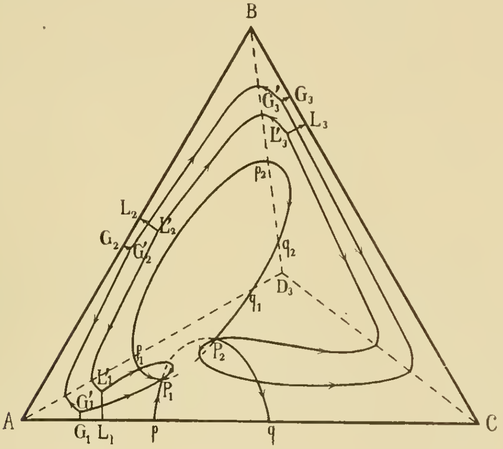

Fig. 6.
D_3 the least volatile; B more volatile than C; A very volatile.

As it has been supposed that also B is volatile, critical endpoints could also occur in the binary system BC, with this result that also on this side double critical endpoints make their appearance.

Case 12. We shall now proceed to the case that the three components are volatile, but form a ternary compound melting at a high temperature and much less volatile, which yields critical endpoints with the three components. Here too, as in the preceding cases, unmixing in the liquid phases is excluded.

Fig. 7 represents the case supposed here in drawing, and shows that the ternary compound D_3 with all the mixtures gives critical endpoints, so that two closed critical endpoint curves are formed, an inner q-curve and an outer p-curve.

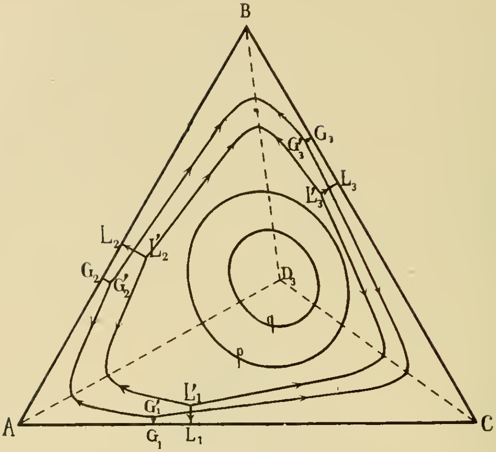

Fig. 7.

D_3 very little volatile; *A*, *B*, and *C* very volatile.

If now in one of the binary systems a maximum critical temperature occurs, the possibility still exists that the ring is opened in consequence of the continuous merging into each other of the *p*- and the *q*-curve at two places.

Though the cases discussed here might be supplemented by a number of others, I shall for the present drop the subject here, and resume it again as soon as the experiment renders it desirable to enter more deeply into these considerations or to extend them.

II. *The P, T-figure.*

Four phase lines and critical endpoint curves.

As in Dr. Morey's research *P-T*-lines are determined it was desirable to represent also these curves i. e. the *four phase lines* in drawing for a few of the cases considered here.

When we examine the projections of the eutectic liquid and vapour lines, taking the direction into account in which the temperature rises, and bear in mind that where a eutectic line is cut by a line joining the two coexisting solid phases with each other a maximum temperature prevails, this derivation can on the whole easily be given roughly, provided the rules are made use of, giving the relative situation of the four-phase lines round a definite quintuple point.

I will therefore first devote a few moments to the discussion of the derivation of these rules.

If the concentrations of the coexisting phases in a system of an arbitrary number of components have been given, there exist in the *P,T*-figure definite relations for the relative situation of the lines for monovariant equilibria. For quadruple points Dr. SCHEFFER has derived a rule which indicates this relation, and which renders the construction of the three phase lines possible, if the succession in concentration of the four phases is known.[1] Afterwards the same rule derived and formulated in a slightly different way, was given by SCHREINEMAKERS.[2] The situation of the four phase lines round a quintuple point has already been described by SCHREINEMAKERS in "Heterogene Gleichgewichte III 1", the relations holding for them have been lately elucidated further by him.[3]

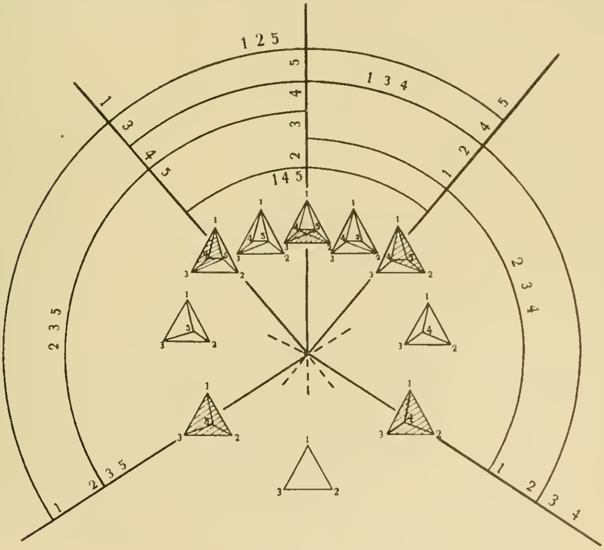

Fig. 8.

For the construction of the subjoined *P.T*-figures I have used these relations availing myself of the following figures, which

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[1] These Proc. XV, p. 389. Z. f. phys. Chem 84. 707 (1913).

[2] Z. f phys. Chem. 82, 59 (1913).

[3] Verslag Kon. Akademie 25 Nov. 1915. (Not yet translated.)

Dr. Scheffer had already derived in his cited investigation, but which had been left unpublished, as the essential part appeared to have been published already by Schreinemakers, and the derivation of which only differs somewhat in form. In his investigation on the quadruple point rule Scheffer demonstrated that no two-phase coexistence can exist over a spacial angle greater than 180°. Making use of the filling up of the space round the quadruple line by two-phase coexistences, he came to the quadruple point rule. The following figures have been constructed by him through application of the same principles for the quintuple points. The P,T-figures round the quintuple point were derived through the application of the principle of the filling up of the space round the quintuple point, which is now four-dimensional, and must consist of three-phase coexistences, combined with the rule that three phase coexistences in stable state can only occur over angles which are smaller than 180°.

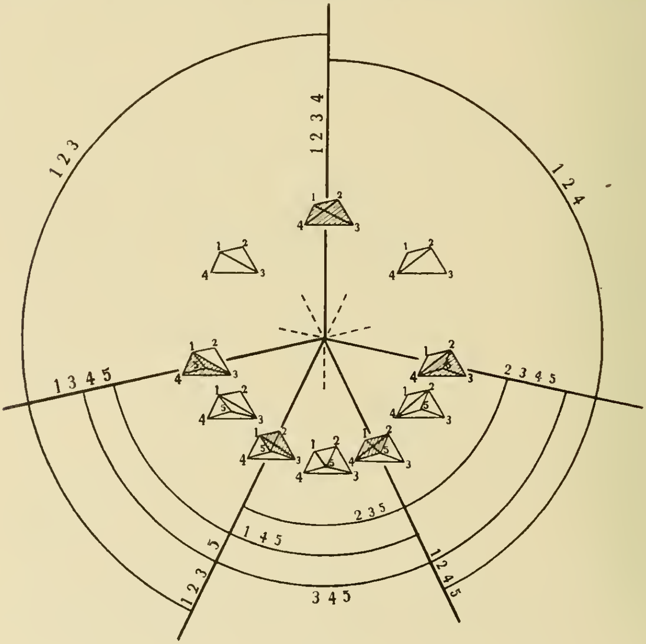

Fig. 9.

In the figures 8, 9, and 10 are given three-phase-coexistences which successive regions have in common and which must lie within an angle smaller than 180°. The coexistences between immediately following four-phase lines have been omitted for the sake of clearness.

If we know the situation of the five phases in the plane of concentration, it is easy to construct the subjoined *P-T* figures. The five points can namely lie in three different ways: they can form a triangle with two points inside, a quadrangle with one point inside it, or a pentagon.

These three cases correspond resp. with the figures 8, 9, and 10. For the first case the figure is e.g. constructed in the following way. We consider a certain division of the triangle in three phase regions; this situation is then possible in one angle at the quintuple point. If we now pass round the quintuple point it is possible that by the side of three of the coexisting phases a fourth exists. This fourth phase can lie inside or outside the three-phase coexistence in question. We then get either a quadrangle, of which the four

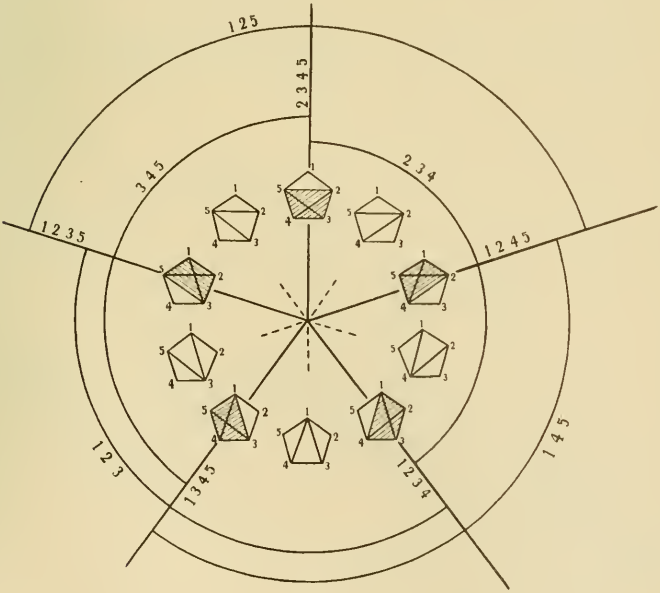

Fig. 10.

phases can exist simultaneously, or a triangle with a point inside it, which are all at the same time stable. If we take a definite division as point of issue, the new division can come about in two different ways.

In the P-T-figures this comes to this that the region is enclosed by two four-phase lines. The question is therefore reduced to this: divide the concentration figure into triangles, and gradually change this division, so that every time one fourphase coexistence shows the transition. When the division has been modified five time, we have passed round the quintuple point, and we have again the original division.

In this way the three figures are easy to reconstruct. In the figures the corresponding division is indicated in every region and it has been indicated by hatching on the quadruple lines what four phase coexistences make the transition between successive divisions possible. Strictly speaking regions of one single homogeneous phase and the two-phase coexistence would still have to be indicated in the concentration figures; for the survey and the construction these are, however, not necessary. [When the four-phase line is passed some three-phase coexistences are left undisturbed repeatedly. Thus it will be clear among others that in fig. 10 the coexistence 125 is not disturbed by the four-phase line 2345; it occurs both on the left

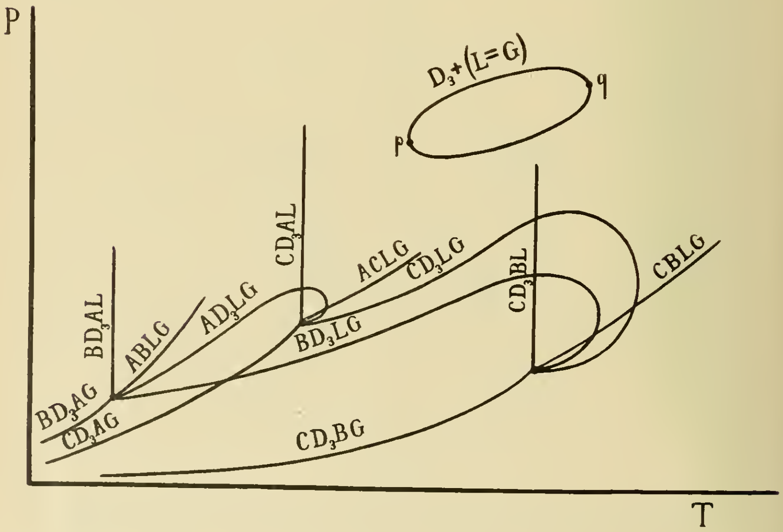

Fig. 1*a*.

and on the right of the four-phase line in question.

The reproduction of these figures 8, 9, 10, which were not published by Dr. Scheffer, seemed desirable to me, because though they do not contain anything new, they can render good services in the application on account of their great lucidity.

We can now represent the four-phase lines schematically for the different cases.

Fig. 1*a* agrees with the case considered in fig. 1. Particularities do not present themselves; it is only worthy of note that the four-

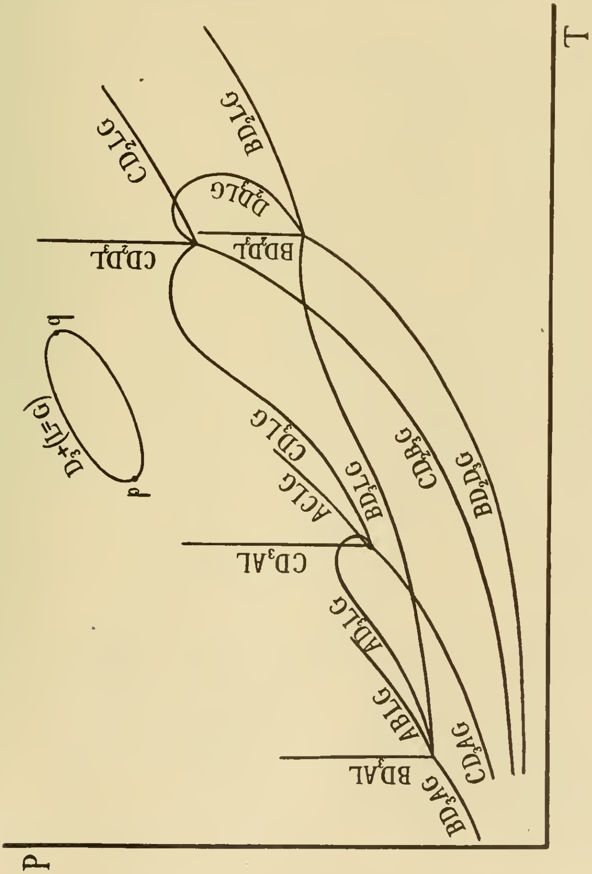

Fig. 2*a*.

phase lines of AD_3LG, CD_3LG, and BD_3LG possess temperature maxima.

The ternary critical endpoint curve for the coexistence of the solid ternary compound with the critical fluid phase is indicated by a closed line, on which the critical endpoints p and q occur. By the side of this line the symbol $D_3 + (L = G)$ is written.

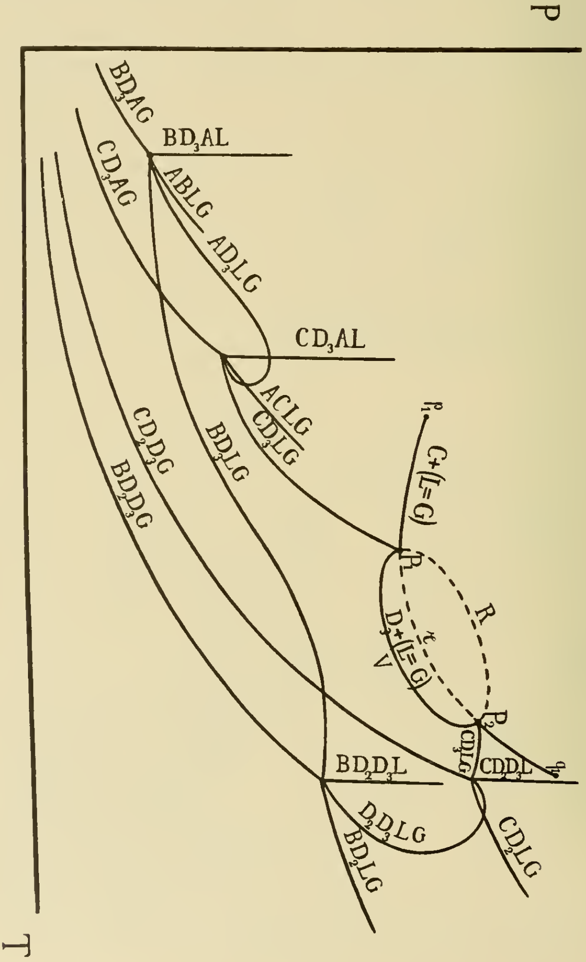

Fig. 4a.

Fig. $2a$ is a little more intricate, because here the binary compound D_2 is formed from the ternary compound D_3 at higher temperature. This gives rise to two new quintuple points CD_2D_3LG and BD_2D_3LG. Now the temperature maxima of the four phase lines CD_3LG and BD_3LG have disappeared, and instead of this the four-phase line D_2D_3LG now possesses a temperature-maximum.

Of the greatest importance, however, is the P-T fig. $4a$, which corresponds with fig. 4.

In a binary system occur the critical endpoints $S+(L=G)$, in consequence of the three-phase line $S+L+G$ meeting the plaitpoint curve $L=G$, just as for the system ether-anthraquinone. In a ternary system the critical endpoints $S_1+S_2+(L=G)$ occur, which I have called *double critical endpoints*, when the four-phase line $S_1\,S_2\,L\,G$ meets the critical endpoint curves $S_1+(L=G)$ and $S_2+(L=G)$, which meeting must of course take place simultaneously. In fig. $4a$ the lines p_1rq_1 and $P_1RP_2VP_1$, refer to the critical endpoint curves $C+(L=G)$ and $D_3+(L=G)$.

Where the four-phase line CD_3LG meets these critical endpoint curves, the double critical endpoints $C+D_3+(L=G)$ occur, from which it therefore follows that this meeting must take place in the points of intersection of the critical endpoint curves mentioned. The double critical endpoints P_1 and P_2 are connected by the critical endpoint curve P_1VP_2 the other half of this curve is metastable.

As has been said it is very well possible that this case occurs in the system H_2O—SiO_2—K_2O, but it is also possible that the critical endpoint curves p_1rq_1 and $P_1RP_2VP_1$ do not intersect, and in this case the four-phase line CD_3LG proceeds undisturbed from one quintuple point to the other.

Dr. MOREY's investigation will be able to decide this point.

Anorganic Chemical
Amsterdam, Oct. 28, 1915. *Laboratory of the University.*

Chemistry. — "*The Periodic Passivity of Iron.*" By Prof. A. SMITS and C. A. LOBRY DE BRUYN. (Communicated by Prof. VAN DER WAALS).

(Communicated in the meeting of October 30, 1915).

1. *The periodic passivity on anodic polarisation.*

As was already communicated before [1]) the passive state of iron can be abolished by bringing the iron into contact with solutions

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[1]) Chem. Weekblad **12**, 678 (1915).

containing Cl′ — Br′ and I′-ions, which ions must therefore be considered as catalysts for the conversion of *passive* iron into *active* iron.

In the course of the investigation on the passivity of iron the question rose whether it would not be possible to call forth periodic phenomena for instance by the addition of Cl-ions to the electrolyte during the anodic polarisation.

According to our recent views the internal equilibrium in the iron surface is namely disturbed during the anodic polarisation, in consequence of this that practically exclusively ferro-ions go into solution, and the comparatively slow internal transformation ferri → ferro in the iron surface proceeds too slowly to keep pace with the going into solution of ferro-ions. Hence the iron surface becomes richer in ferro-ions and the potential difference iron electrolyte becomes less strongly negative or positive.

Let us suppose that the electrolyte is *ferrosulphate,* and during the anodic polarisation of an iron electrolyte with a very small surface, we add *ferrochloride*, then the catalytic influence exercised by the chlorine ion becomes noticeable by a decrease of the positive potential difference, and when the addition of ferrochloride is continued, a pretty rapid and considerable decrease of the potential difference appears at a given moment, and the iron has passed from the passive state into the active state.

Without our entering into any further details it is clear that at a velocity of solution of the iron determined by the density of current it must be possible to find a concentration of chlorine ions, at which at a definite moment the chance that the iron remains passive is just as great as the chance that it becomes active or vice versa. Let us now suppose that at this moment the density of the current is somewhat diminished, then it may be expected that the transition passive-active takes place, and while the iron-anode in the passive state only goes exceedingly little into solution, the iron, having now become active, will be sent into solution to a very great degree in the form of ferro-ions. Hence the *contact* of the Cl′-ions with the iron-surface will *diminish*, and in consequence of this the iron will again be brought back to the passive state.

As has been said, the iron dissolves but very sparingly in this passive state, and the processes which now take place at the anode, consist first of all in the discharge of the SO_4-ions with the subsequent O_2-generation, and secondly in an increase of concentration of the Cl′-ions. This latter process will then again give rise to activation and so on. This supposition was fully confirmed, and as the following

A. SMITS and C. A. LOBRY DE BRUYN: "Activation curves of iron".

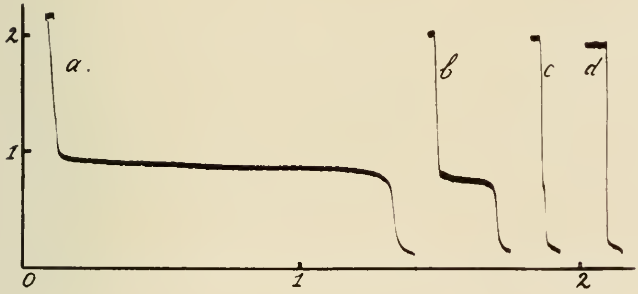

Fig. 2.

Activation curves of iron after anodic polarisation in $FeSO_4$ (0.473 gr. mol. p. L.)
a. „ „ „ „ „ „ „ without $FeCl_2$
b. „ » „ „ „ „ „ + 0.00024 gr. mol. „
c. „ „ „ „ „ „ „ + 0.00036 „ „ „
d. „ „ „ „ „ „ „ + 0.00048 „ „ „

The potential is indicated on the y-axis in Volt. with respect to the potential of active iron in the same solution. The time is indicated on the x-axis in minutes.

A. SMITS and C. A. LOBRY DE BRUYN: "The periodic passivity of iron."

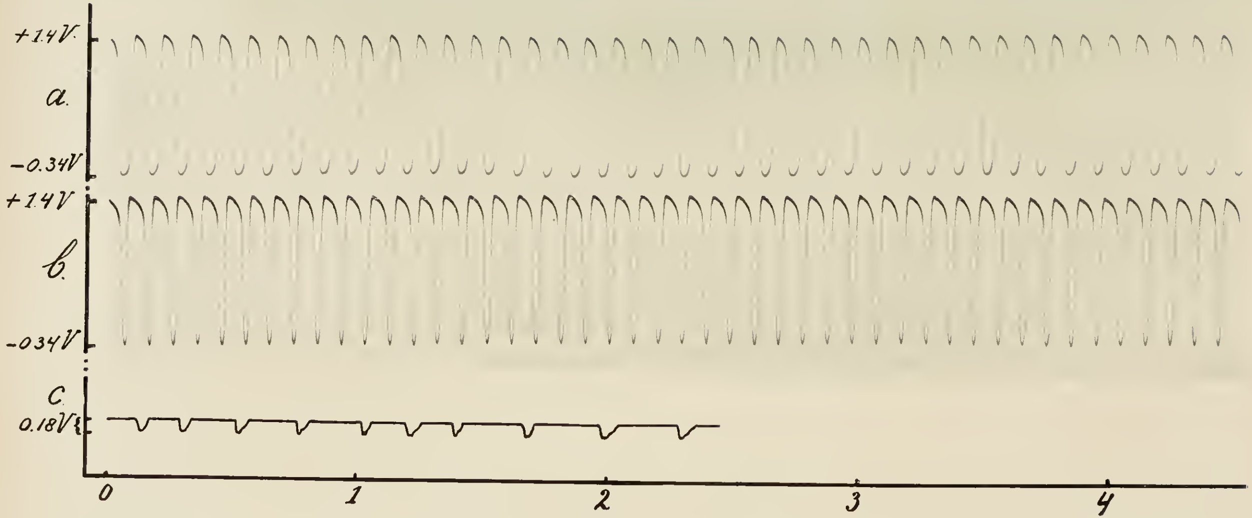

Fig. 1. Periodic variations in te potential difference metal-solution for anodic polarisation of iron in a solution of 0.473 gr. mol. $FeSO_4$ + 0.023 gr. mol. $FeCl_2$ in 1 Liter of H_2O. The potential is given in Volt. with respect to the 1 norm. calomelelectrode (E_h = + 0.286 V).

a. Currrent density 0.155 Amp. c.M.^{2} (passive) – 0.195 Amp. c.M.^{2} (active). Duration of a period = 6.54 sec. — About equally long passive as active. Difference of the extreme values = 1.74 Volt.

b. Density of current 0.180 Amp c.M.^{2} (passive) – 0.255 Amp c.M.^{2} (actiev). Duration of a period = 5.8 sec. — Longer passive than active. Difference of the extreme values = 1.74 Volt.

c. Periodic variations observed by ADLER. Difference of the extrema values 0.180 Volt.

photographic reproductions (fig. 1) show, we have complete control over the phenomenon [1]).

For a definite Cl-ion concentration the density of current is to be chosen so that the time during which the most passive state prevails, is about equally long as that during which the most active state continues to exist. See fig. *1a*.

If the density of current is made slightly greater, the passive state continues to exist longer than the active state, which appears very clearly from fig. *1b*. In the maxima the iron is passive, and in the minima active. The oscillations in the potential which we have observed here, are very great; the maxima and the minima lie 1,74 Volts apart, the duration of the periods amounting to 6.54 and 5.8 seconds. It is self-evident that the periodic phenomenon described here only manifests itself clearly when the iron-surface is small. The larger the iron-surface the smaller the chance that the iron is passive or active all over its surface at the same moment; hence this phenomenon is less regular as the surface is taken larger, and vanishes entirely for a large surface.

We will point out here that periodic phenomena during the electrolytic solution of passifiable electrodes have already been observed by different investigators, but none of these investigators has succeeded in calling forth a periodic phenomenon of such large regular oscillations as here.

ADLER [2]), who has perhaps done the most meritorious work in this region, obtained periodic oscillations in the potential difference anode-electrolyte among others for iron by generating hydrogen at the backside of the iron wall, part of which acted as anode. The explanation is as follows: The hydrogen diffuses through the iron, and arriving at the anodeside it can then exert its catalytic action. Though ADLER's view was different from ours we may say that here too the periodic phenomenon was obtained by the use of a catalyst, but here the catalyst enters *through* the metal, hence the phenomenon is brought about in another way than ours.

Further the iron in ADLER's experiments remained a long time passive and a very short time active, and the potential difference only amounted to 180 millivolts, the phenomenon being besides less regular than ours. The curve found by him is represented to scale

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[1]) The iron rod was not suspended on a platinum wire, but was cemented with shellac in the short leg of a U-shaped tube. After it had appeared that electrolytic iron behaves perfectly uniformly to iron with a small carbon-content, we have afterwards always used the latter.

[2]) Z. f. phys. Chem. **80**, 385 (1912).

in fig. 1*c*. The oscillations found by us are, as is shown in the drawing, about ten times greater.

2. *The influence of the Cl'-ion concentration on the shape of the curve of activation.*

Another question which likewise incited to research, was this:

When iron is made passive by anodic polarisation, e. g. in a solution of ferro-sulphate, and then the current is interrupted, the potential difference diminishes rapidly at first, then it changes little for a short time, after which it finally descends again rapidly.

This discontinuity has been accounted for by SMITS and ATEN[1]), the explanation coming to this that in the transition *passive* → *active* a state must be passed through at which two metal phases exist side by side, which, in case electromotive equilibrium continued to exist all the time, would have to give rise to a temporary occurrence of a *constant* potential difference.

When now chlorine ions in the form of ferro-chloride are added to the solution of ferro-sulphate it may be expected that, the Cl'-ions accelerating the internal transformation in the iron surface, this discontinuity will become less distinct, and *apparently* vanishes entirely at a certain Cl'-ion concentration.

As the curves fig. 2 show this expectation has been entirely realized.

It is clear that the discontinuity which seems to have entirely disappeared on the last photo, *d* fig. 2, would manifest itself again clearly, when the velocity of revolution of the registration cylinder was increased. We shall return to this later on. [2])

That these remarkable results recorded here, which strongly support the new views of the passivity, can be stated in such a way that every particularity which the different figures contain, is essential to the phenomenon, and is not a consequence of the inertia of the galvanometer, we owe to this that the research could be made with Dr. MOLL's excellent galvanometer, which through its quick and moreover perfectly aperiodic indication was eminently suitable for these experiments.

The photographic representations have been made with Dr. MOLL's

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[1]) These Proc. Vol. XVII, p. 680.
Chem Weekblad 31, 678 (1915).

[2]) The curve *d* exhibits a hardly visible thickening on the original photo at the place of the halting-point. In a subsequent communication the influence of the extent of the iron-surface on the periodicity will be more particularly dealt with, and further the periodic passivity at anodic polarisation of iron, the unprotected surface of which is only partially immerged in a ferro-sulphate solution.

photographic registering apparatus, which he very kindly placed at our disposition, and for which we gladly express our sincere thanks to him once more here.

Anorg. Chem. Laboratory of the University.

Amsterdam, Oct. 28, 1915.

Physiology. — "*On after-sounds.*" By Dr. F. Roels. (Communicated by Prof. Dr. H. Zwaardemaker).

(Communicated in the meeting of October 30, 1915).

In daily life after-sounds are rarely perceptible to the ear of normal man and even then they are vague and comparatively feeble after violent detonations. We, therefore, had to apply rather potent stimuli and to screen our subjects from all disturbances above all from the ordinary street-noises.

The Galton- and Edelmann-whistles gave most satisfaction. The subject was placed in the camera silenta of the Physiological Laboratory at Utrecht; the head was fixed, the right ear at 2 cm. distance and right in front of the embouchure of the whistle. At every time an airstream of equal force was urged through the whistle by the experimenter outside the camera. In the first experiments the whistle was put into operation inside the camera by the experimenter, who also recorded the phenomena perceived by the subject. Although we used our utmost endeavour to do this as noiselessly as possible, it was detrimental to the production as well as to the observation of the phenomena. We, therefore, resolved to separate the experimenter from the subject. They spoke to each other by telephone, which enabled the experimenter to perform the time-measurements by means of a chronometer. The subject used the telephone only for these measurements; for the description of the nature of the phenomena he relied entirely upon his memory after the experiment. This procedure was not open to objection as the phenomena never took more time than $1^1/_2$ minute.

Before entering upon our experiment proper a series of respectively 100 and 50 preliminary tests were performed with our two subjects, Prof. Dr. A. Michotte from Louvain and Dr. Bakker from Batavia. The total number of the subsequent conclusive tests amounted for M to 143 and for B to 129.

They are distributed among the various stimuli as follows:

	M.	B.		M.	B.		M.	B.		M.	B.
e_2	7	6	cis_3	8	6	e_4	8	6	f_5	10	12
f_2	8	6				f_4	12	6	a_5	8	12
g_2	8	6	a_3	12	7	a_4	20	22	e_6	8	16
a_2	8	6	c_4	7	6	d_5	17	12	c_7	2	

The order of the stimuli varied regularly. As a rule stimuli of the same pitch acted on the subject in 2 or 3 consecutive tests. From 6 to 12 experiments were made in succession.

e_2. B. The after-sound immediately following the stimulus is short (1 sec.), feeble, and indistinct. Sometimes a short and slight sensation of strain is perceived directly after or simultaneously with the after-sound. Most often the subject announces a period of absolute or relative silence (total absence or considerable decrease of intensity of the murmurs usually perceived during a stay of some length in the camera silenta). This interval generally links itself to the after-sound. In half the cases it continues from 10—16 sec. Little by little the normal noises return intensified.

M. Directly after the stimulus an after-sound, being a typical murmur with pitch (± fis_4). The pitch disappears after a rather short time; the murmur continues and while being broken from time to time by feeble boundary tones, pulsations and the like, passes into the normal noises after 15 to 27 sec.

f_2 B. The after-sound follows the stimulus instantaneously; it is a short (± 1 sec.), feeble, shrill sound. It is closely followed by a period of absolute or relative silence (1—$13^1/_2$ sec.), which is gradually filled by reinforced normal noises. During the interval of silence the subject is generally conscious of a slight sensation of strain. Occasionally the reinforced noises are interrupted by a musical sound, of a pitch lying between that of the stimulus and that of the succeeding after-sound.

M. In 5 out of 10 cases a typical murmur with pitch, is yielded directly after the stimulus. The intensity of tone rapidly diminishes, so that at last only the murmur remains. The tone heard in the murmur, is higher than *fis*, and afterwards recurs once or twice. In the other cases a tone is heard directly after the stimulus which, while lowering rapidly, sinks into the afore-said typical murmur.

In its turn the latter gets lost again in the ordinary entotic noises.

g_2. B. Very likely the after-sound comes close upon the stimulus. It is short (± $1^1/_4$ sec.) and very high. Less often than in the case of f_4 it is followed directly by an interval of absolute or relative silence, as mostly a feeble musical tone is heard whose pitch lies between that of the after-sound and the stimulus and whose duration varies from 2—$3^1/_2$ sec.

Whenever the musical tone is not heard, the normal noises, which, while intensifying gradually, follow the after-sound directly or are heard after a space of absolute or relative silence, possess a certain pitch. Eventually the space of silence lasts 5—9,5 sec.

M. In three cases a tone is heard instantly after the whistle is blown. It is rather higher than fis_4, gradually grows less intense, to be replaced after 4—7 seconds by a typical murmur. In the other cases the tone and the typical murmur occur simultaneously. Its pitch (invariably ± fis_4) gets lost after 6—8 sec., when the pure murmur continues to flow (as is ever the case) into the normal noises; sometimes a strain is felt.

a_2. B. The after-sound is short (± $1^1/_3$ sec.), feeble, and high-pitched. Only twice a vague sensation of strain is announced. Close upon the after-sound follows a "dark" space (period of absolute or relative silence of 10.5—11 sec.). At times it is succeeded by a feeble musical tone by the side of which the normal noises are generated and reinforced so as to supersede the tone, whose pitch lies between that of the after-sound and the stimulus. Every now and then a high bird's note interferes with these noises.

M. In every experiment the subject notices immediately after the stimulus a murmur, with markedly varying pitch and intensity, the former fluctuating between d_6 and a_2. The pitch gradually disappears so that only the typical murmur is left. Occasionally a great strain, which sometimes causes pain.

cis_3 B. Short (± 1 sec.) and feeble after-sound, followed in 5 out of 6 cases by a "dark" space, which lasts from 13 to 16 seconds. Little by little the normal noises recur with growing intensity.

M. Immediately after the stimulus in all cases a murmur, evidently of a definite pitch; it most often belongs to the 6th octave. The intensity of the tone decreases by degrees, so that at last only a typical murmur remains, in which, however, a pitch is still plainly discernible. At times the quality of this murmur is modified, both the intensity and the richness being diminished; the pitch also is gradually lowered.

a_3 B. The after-sound is short (± 1.1 sec.), feeble and high. Sometimes it is followed by a feeble musical tone ($3^{1}/_{2}$—4 sec.). Then a period of absolute or relative silence sets in. In almost all cases this "dark" interval commences immediately when the after-sound has ceased; it takes $19^{1}/_{2}$—$20^{1}/_{2}$ sec. Then the normal noises recur, gradually intensified. Feeble bird's notes of distinctly varying pitch often mingle with the noises at more or less regular intervals. Sometimes a strongly marked sensation of strain occurs in the gap of absolute or comparative silence.

M. A murmur with pitch in almost all cases directly after the production of the stimulus. The pitch is about $1^{1}/_{2}$ octave higher than fis_4. At times only a tone is heard, succeeded by a murmur after 14—17 sec.

The pitch of the tone is modified in a few cases: being rather low at first, it rises up to $\pm d_6$. The intensity of tone and murmur gradually lessens. The pulsations heard anterior to the production of the stimulus recur during the experiment with augmented intensity and with a decided pitch. Only once or twice the subject makes mention of a sensation of strain.

c_4 B. The after-sound is short ($\pm$ 1,1 sec.), feeble, and shrill. In 4 out of 6 cases it passes into a very feeble tone of different pitch (lower than the after-sound, higher than the stimulus), lasting from 4—$7^{1}/_{2}$ sec. A gap of absolute or relative silence immediately links itself to it. The gap covers 14 to 25 seconds, whereas only 13—15 seconds are taken by the "dark" interval that follows the after-sound. Ultimately the normal noises return gradually with augmented intensity, intermitted by several high and feeble musical tones. In one case only a slight sensation of strain.

M. Frequently, directly after the production of the stimulus a murmur with pitch ($\pm c_5, d_5$; duration 24—31 sec.) In a few cases a pure tone is heard, which only somewhat later makes way for the typical murmur, which in its turn passes into the normal noises, broken now and again by pulsations and feeble cricket-chirps.

e_4 B. The duration of the after-sound, mostly forcible and very high, averages 2 sec. Directly after it a constantly feeble, musical tone with a pitch, intermediate between that of the after-sound and the stimulus. Sometimes the after-sound coalesces with the musical tone so gradually that is seems to sound musical at the outset. The tone continues from 1 to 18 seconds and is succeeded by a gap of absolute or relative silence lasting from 3 to 34 sec. Finally the normal noises slowly return with augmenting intensity. Only once a sensation of strain is recorded.

M. Almost always directly after the emission of the stimulus a murmur with pitch (± c_5). Both tone and murmur soon get weaker and weaker; when they have disappeared the normal noises are heard.

f_4 B. The after-sound is very forcible and high; its time averages $1^3/_4$ sec. It always makes way for a musical sound of a pitch lying between that of after-sound and stimulus. Its intensity lessens gradually, so that finally (in 3 cases after 4, 7 and $20^1/_2$ min.) an absolute or relative silence ensues. This interval lasts about 6 sec., after which not the normal noises are perceived, but again a musical sound whose length varies from 7 to 18 sec., and with which the gradually reinforced normal noises coalesce, while being interrupted every now and then by feeble bird's notes. Ultimately the musical tone flows together with the normal noises.

M. Only rarely does the subject observe a murmur with pitch directly after the emission of the stimulus. While maintaining its pitch (± c_5) till the end it gets gradually fainter and finally makes way for the normal noises. Oftenest, however, the subject observes instantly after the stimulus a powerful, highpitched tone (6th Octave) of fairly long duration (7—9 sec.), fading away slowly. In the end the normal noises return.

a_4 B. The after-sound heard directly after the stimulus, is high and powerful; its duration averages ± $1^1/_4$ sec. In well nigh all cases it is succeeded by a musical sound of a pitch lying between that of the after-sound and the stimulus and of a duration varying from 2 to 4 sec. This sound makes way for a period of absolute or relative silence, which is gradually filled by intensified normal noises.

M. In 17 out of 20 cases a tone is heard instantly after the stimulus is emitted. It gradually swells up to a maximum, reached after 2 or 3 seconds. Then the tone dies out very slowly. Its pitch is about that of the stimulus. Its length is considerable (21—63 sec.) When lasting very long there is sometimes a breach of continuity; it is plainly audible, though it is, of course, comparatively feeble. When discontinuous it sounds like a succession of pulsations of the same periodicity with those observed by the subject when not experimented upon. In the end there is a recurrence of the ordinary entotic noises.

In 3 cases the subject is for about 20—58 sec. conscious of a powerful, typical blowing noise immediately after the stimulus issues from the whistle. It is discontinuous at rather regular intervals and makes way for the normal noises, in which it may be distinguished a few times.

d_5 B. The after-sound is very high and powerful; its time averages

± $1^1/_5$ sec. The subject often announces a regularly recurring intense strain, which vanishes by slow degrees. In 11 out of 12 cases the after-sound is succeeded by a pause of absolute or relative silence. In about half the cases it lasts 13—17 sec. when it is filled by the gradually intensifying murmur. In the remaining cases this pause is much shorter (8—10 sec.) and is filled not by the normal noises, but by a second after-sound, a continuous tone lasting ± 7—10 sec. and fading before the gradually intensifying normal noises. In only one case does the second after-sound follow the first immediately. Its pitch is lower than that of the first.

M. Close upon the issue of the stimulus a rapid tone, gradually growing less intense, lying somewhere about a_4. In well-nigh every case it is succeeded by a vigorous blowing noise, which lasts from 65—93 sec; the maximum of intensity is reached after $2^1/_2$—3 sec.; then it fades away extremely slowly and regularly. Sometimes it recurs once or twice. In synchronism with this blowing noise pulsations are audible, weak as compared with the force of the blowing noise (pitch ± a_4).

f_5. B. The average duration of the after-sound, appearing at the emission of the stimulus, is 2 sec. It is high (cricket-chirp), vigorous, often extremely so. It is constantly succeeded by a period of absolute or relative silence, (5—16 sec.); in this pause a strong sensation of strain is often perceived. In some cases a second after-sound is heard after the first, lower but of longer duration (3—7 sec.). In the majority of cases the pause is filled by gradually intensifying normal noises broken by a few bird's notes.

M. In some cases directly after the emission of the stimulus a high-pitched tone, followed immediately by a typical, continuous blowing noise (duration 69—87 sec.). Mostly this noise is heard close upon the stimulus. It is very powerful, sometimes with pitch especially at the beginning. At times it is interrupted by the ordinary pulsations. Finally the normal murmur returns.

a_5. B. The after-sound is comparatively long (± 3 sec.), powerful and high-pitched (cricket-chirp) and seems to follow the stimulus immediately. In most cases it is succeeded by a period of absolute or relative silence (3—$12^1/_2$ sec.), In one third of the cases, however, the normal noises recur, either to continue with growing intensity, or to make way for a second after-sound, most often a musical sound lower and feebler than the first.

This after-sound covers about 4—13 sec. Ultimately it is also replaced by the gradually intensifying normal noises.

M. Only in one of the 10 cases does the subject announce a short

Subject B.

	Duration of the first after-sound	Intensity of the first after-sound	Sensation of strain	Period of absolute or relative silence	2nd after-sound	Blowing noise.
e_2 (6)	1	feeble	rarely, short and slight	10—16 after 1st after-sound		
f_2 (6)	1	feeble	most often, not very great	6—13.5 after 1st after-sound		
g_2 (6)	1.25	feeble		5—9.5 after 1st after-sound	2—3.5 mostly after 1st after-sound	
a_2 (6)	1.3	feeble	rarely, slight	10.5—11 after 1st after-sound	Short, after the period of silence	
cis_3(6)	1	feeble		13—16 after 1st after-sound		
a_3 (7)	1.1	feeble	distinct, rather slight	19.5—20.5 In 6 cases after the 1st after-sound. In one case after the musical tone following the after-sound.	3.5—4 occasionally, feeble, directly after the first after-sound	
c_4 (6)	1.1	feeble	rarely, rather slight	13—15 In 4 cases after the musical tone. 14—25 In 2 cases after the 1st after-sound	4—7.5 In 4 cases directly after the 1st after-sound	
e_4 (6)	2	mostly intense	rarely	3—34 after the musical tone following the after-sound	1—18 always after the 1st after-sound	
f_4 (6)	1.75	intense	most often, sometimes very intense	6 after the musical tone	4—20.5 always after the 1st after-sound	
a_4(22)	1.25	intense	sometimes	6 almost always after the musical tone	18 always after the 1st after-sound	
d_5(12)	1.8	intense	regularly	almost always after the 1st after-sound; in 6 cases: 8—10; in 5 cases: 5—16	7—10 in five cases after the period of silence	
f_5(12)	2	often very intense	regularly, often very great	after the 1st after-sound	3—7 in 3 cases after the period of silence	
a_5(12)	3	intense	rarely, slight	3—12.5 mostly after 1st after-sound	4—13 in 2 cases after the period of silence	
e_6(16)	2.6	intense	none	2—10 after the first hiss		3—7 During or after the 1st after-sound 15—40 Intermittent blow. sound.

Subject M.

	1st After-sound	Pitch of the after-sound	Duration of the after-sound (sec.)
e_2 (7)	In 6 cases murmur with pitch In 1 case: tone	slightly lower than fis_4	tone: 2 murmur: 15 - 21
f_2 (8)	In 5 cases murmur with pitch In 3 cases: tone	slightly higher than fis_4	
g_2 (8)	In 2 cases murmur with pitch In 6 cases: tone	slightly higher than fis_4	tone: 4—7 (6—8) murmur: 17—26
a_2 (8)	Murmur with pitch	between d_6 and fis_4	
cis_3 (8)	„ „ „	between d_6 and fis_4	
a_3 (12)	In 11 cases murmur with pitch In 1 case: tone	± 1½ octave higher than fis_4	tone: 14—17
c_4 (7)	In 4 cases murmur with pitch In 3 cases: tone	± c_5, d_5	tone: 24—31
e_4 (8)	In 6 cases murmur with pitch In 2 cases: tone	higher than c_5	
f_4 (12)	Nearly always tone	± 6th octave	tone: 7—9
a_4 (20)	In 17 cases: tone In 3 cases: blowing sound	mostly ± c_5	tone: 21—63 (not continuous)
d_5 (17)	Nearly always blowing sound		Blowing sound: 65—93
f_5 (10)	„ „ „ „		„ „ : 69—87
a_5 (8)	Always „ „		„ „ : 46—71 (not continuous)
c_6 (8)	„ „ „	higher than c_5	Blowing sound: 13—35
c_7 (2)	Typical murmur No blowing sound		

tone directly after the stimulus. In the other cases a vigorous blowing noise is observed, sometimes (especially at the commencement) of a certain pitch (a boundary tone). Mostly the blowing noise continues very vigorously, but not unintermittently, as in 5 of the 10 experiments it ceases altogether only after 46—71 sec. In three experiments the noise disappears after 15 or 15,5 sec. In its final stage other phenomena are also discernible, such as pulsations etc.

e_6. B. Immediately after the stimulus the after-sound, which is powerful and high-pitched (cricket-chirp) (duration $2^3/_5$ sec.).

A highly powerful blowing noise in conjunction with the after-sound and continuing when this has ceased. With one exception (15.5 sec.) it continues for 3—7 sec., to be succeeded by a gap of absolute or relative silence (2—10 sec.). Subsequently a second discontinuous blowing noise is distinguished, slightly differing in character from the first. The intervals are characterized by a slowly increasing murmur. The second blowing noise disappears entirely only after 15—40 sec. In the end the normal noises return while intensifying gradually.

M. Immediately when the stimulus is emitted a blowing noise is plainly audible, which especially in its initial phase, assumes a certain pitch (higher than c_5). The intensity of the noise lessens rapidly; after 2 or 3 sec. the subject has to concentrate his attention considerably to follow it; in 7 cases it is inaudible after 13—15 sec. Sometimes it is not continuous; the moment of its first disappearance occurs after 4—23 sec. Usually it is superseded by the normal noises.

c_7. M. Directly after the stimulus a typical murmur, heard also before the experiment but less vigorously.

In the foregoing tables we give the principal data regarding the character and the duration of the phenomena as apprehended by our subjects when acted upon by the stimuli applied.

CONCLUSIONS.

1. Invariably a constant after-sound, differing individually has been observed close upon the stimulus. With the lower stimuli it consists chiefly in a murmur of a certain pitch, while the latter prevails before the discant. At one stage after the discant the after-sound changes into a typical blowing noise.

The most forcible after-sound is yielded by the high discant. Its duration varies from 2 to 30 sec. As for the pitch of the after-sound, it is constantly higher than that of the stimulus. The lowest stimuli as a rule yield the lowest after-sound; the highest are produced by the highest stimuli.

2. An interval of 2—30 sec. is most often filled by a second after-sound, 'lower than the first, mostly of longer duration and much less distinguishable from the normal entotic noises.

Chemistry. — *"In-, mono- and divariant equilibria"*. III. By Prof. SCHREINEMAKERS.

(Communicated in the meeting of October 30, 1915).

Correction.

In the previous communication II, the figures 4 and 6, as will have been obvious to the reader, have to be changed mutually.

6. *Quaternary systems.*

In an invariant point of a quaternary system six phases occur, which we shall call A, B, C, D, E and F; consequently this point is a sextuplepoint. Six curves start from this point, therefore; in accordance with our previous notation we ought to call them (A), (B), ... (F); here, however we shall represent them by A', B', C', D', E' and F'. Further we find $\frac{1}{2}$ $(n+2)(n+1) = 15$ bivariant regions.

When we call the components K_1, K_2, K_3 and K_4 and when we represent them by the anglepoints of a regular tetrahedron, then we are able to represent each phase, which contains these four components, by a point in the space. As in a sextuplepoint six phases occur, consequently we have to consider six points in the space and their position with respect to one another.

In general this representation in space can lead to difficulties for the application to definite cases; for this reason we shall later indicate a method, which leads easily towards the purpose in every definite case. Here, however, we shall use the representation in space in order to deduce the different types of the possible P,T-diagrams.

When we consider the six points in the space, then they may be situated with respect to one another as in the figs. 1, 3, 5, and 7.

In figs. 1 and 3 they form the anglepoints of an octohedron, viz. of a solid which is limited by eight triangles. In each of these octohedrons we find twelve sides and three diagonals. [In fig. 1 AF, EC and BD are the diagonals, in fig. 3 AF, EC and EF]. In fig. 1 we find in each anglepoint four sides and one diagonal, in fig. 3 we find in the anglepoints E and F three sides and two diagonals, in the anglepoints A and C four sides and one diagonal and in the anglepoints B and D five sides only. As in fig. 1 the partition of the sides and the diagonals is a symmetrical one and, however, in fig. 3 an asymmetrical one, we shall call fig. 1 a symmetrical, fig. 3 an asymmetrical octohedron.

In fig. 5 five points form the anglepoints of a hexahedron within which the point F is situated. When we omit the side-plane BCD and when we unite F with B, C, and D, then again an octohedron arises, which we shall call monoconcave.

In fig. 7 four of the points form the anglepoints of a tetrahedron, within which the points E and F are situated. When we unite E with the points A, B and D, the point F with C, B and D, and when we omit the side-planes ABD and CBD, then a biconcave octohedron arises.

Type I. We shall deduce now the P,T-diagram, when the six phases form the anglepoints of a symmetrical octohedron (fig. 1). We may consider this solid as construed of the four tetrahedrons $CABD$, $EABD$, $FBCD$ and $FBED$, which terminate all in the side BD.

In order to determine the reaction between the phases of the monovariant equilibrium F', we consider the hexahedron $CADBE$; as the diagonal CE intersects the triangle ABD, this reaction is:

$$C + E \rightleftarrows A + B + D$$

Hence it follows:

$$C'\ E' \mid F' \mid A'\ B'\ D' \quad \ldots\ldots\ldots \quad (1)$$

In order to define the reaction between the phases of the monovariant equilibrium E', we take the tetrahedron $ACBDF$; as the diagonal AF intersects the triangle BCD, we find for this reaction:

$$B + C + D = A + F$$

Hence it follows:

$$B'\ C'\ D' \mid E' \mid A'\ F' \quad \ldots\ldots\ldots \quad (2)$$

We now draw in a P,T-diagram (fig. 2) in any way the curves E' and F'; for fixing the ideas we draw E' at the left of F'. [For the definition of "at the left" and "at the right" of a curve we have previously assumed that we find ourselves in the invariant point on this curve, facing the stable part]. In accordance with this assumption (1) and (2) have been written also at once in such a way that herein E' is situated at the left of F'.

It now follows from (1) and (2) that C' is situated at the left of F' and E'; C' is situated, therefore, as has also been drawn in fig. 2, between the stable part of E' and the metastable part of F'.

Further it follows from (1) and (2) that the curves B' and D' are situated at the right of F' and at the left of E'; they must, therefore, as is also drawn in fig. 2, be situated between the metastable parts of the curves E' and F'. The position of B' and D'

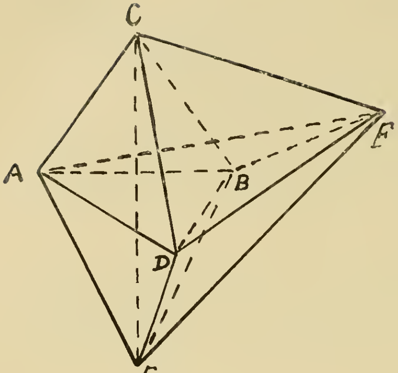

Fig. 1.

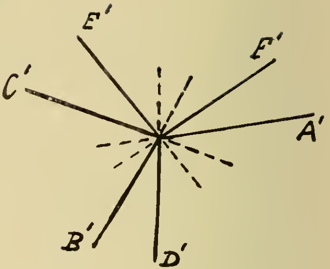

Fig. 2.

with respect to one another is, however, not yet defined, we shall refer to this later.

Further it follows from (1) and (2) that A' is situated at the right of F' and E'; consequently A' is situated within the angle, which is formed by the stable part of curve F' and the metastable part of curve E'. As however also the metastable part of curve C' is situated within this angle, we have still to define the position of A' with respect to this curve. For this we take the hexahedron $BCEFD$; as the diagonal BD intersects the triangle CEF, we find:

$$C'\,E'\,F' \mid A' \mid B'\,D' \,.\quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

Hence it is apparent that C', E' and F' must be situated at the one side, B' and D' at the other side of A'; consequently A' must be situated between the stable part of F' and the metastable part of C'.

In order to define the position of A' and C' with respect to one another, we might have considered also the hexadron $DCEFB$. As the diagonal BD intersects the triangle CEF, we find:

$$B'\,D' \mid C' \mid A'\,E'\,F' \,.\quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

In accordance with what has been deduced above we find here that B' and D' must be situated at the one side and A', E' and F' at the other side of curve C'.

In order to define the position of B' and D' with respect to one another, we have to know the reactions, which occur in the monovariant systems B' and D'; we shall refer to this later.

When we introduce, as in the case of ternary systems, the idea "bundle of curves", then we may express the results in the following way: when the six phases form the anglepoints of a symmetrical octahedron, then the six monovariant curves form in the P,T-diagram three "twocurvical" bundles.

Now we should yet also have to consider the bivariant regions; as, however, the reader can easily draw them in each of the P,T-diagrams, we shall omit this. Later we shall, however, refer to an example.

Type II. In fig. 3 the six phases form the anglepoints of an asymmetrical octohedron. We may consider this solid as to be composed of three tetrahedrons, which terminate in the side BD.

In order to define the position of the curves with respect to curve F', we consider the hexahedron $CADBE$, hence we find:

$$C'\,E' \mid F' \mid A'\,B'\,D' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In order to find the position of the curves with respect to curve E', we consider the hexahedron $ABDCF$; hence we deduce:

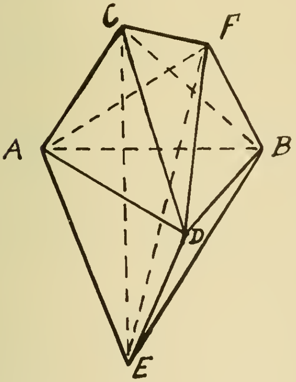

Fig. 3.

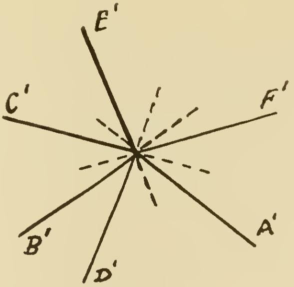

Fig. 4.

$$B'\,C'\,D' \mid E' \mid A'\,F' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Now we draw in a P,T-diagram (fig. 4) the curves E' and F' and we take in this case E' at the left of F'. For this reason (5) and (6) have been written also in such a way that herein E' is situated at the left of F'.

It follows from (5) and (6) that B' and D' are situated both at the right of F' and at the left of E'; consequently, as is also drawn in fig. 4, they must be situated between the metastable parts of E'' and F''. The position of B' and D' with respect to one another is, however, not yet defined by this; we shall refer to this later.

Further it follows from (5) and (6) that C'' is situated at the left of F'' and E''; consequently C'' is situated within the angle which is formed by the stable part of E'' and the metastable part of F''.

For the position of A' it follows from (5) and (6) that A' must be situated at the right of F'' and E''; consequently A' is situated in fig. 4 within the angle, which is formed by the stable part of F'' and the metastable part of E''. As however this angle, is divided into two parts by the metastable part of C'', we cannot tell yet within which of those two angles we have to draw curve A'. In order to examine this, we consider the hexahedron $EBDCF$; we find from this:

$$E''F''\,|\,A'\,|\,B'C''D' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence it is apparent that we must find at the one side of A' the curves E'' and F'', at the other side the curves B', C'' and D'. Consequently it follows from this that A' must be situated between the metastable parts of the curves C'' and E''.

We should have been able to find the same with the aid of the hexahedron $EABDF$; hence it follows:

$$E''F''\;C''\,|\,A'B'D' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Now it appears from this that we must find at the one side of C'' the curves E'' and F'', at the other side the curves A', B' and D'.

It is apparent from fig. 4 that we may express the previous results in the following way:

when the six phases form the anglepoints of an asymmetrical octohedron, then the six monovariant curves form in the P,T-diagram four onecurvical and one twocurvical bundle.

Type III. In fig. 5 the six phases form the anglepoints of the hexahedron $EABDC$, within which the point F is situated. In order to transform this hexahedron into an octohedron, we unite F with the three anglepoints of a definite side-plane of the hexahedron; we find this side-plane in the following way. In fig. 5 S represents the point of intersection of the diagonal CE with the triangle ABD. We imagine the hexahedron to be divided into six tetrahedrons, which terminate in the point S. As the point S is situated within the tetrahedron $SBDC$, we take for the side plane, mentioned above, the triangle BDC and we unite therefore the point F with the points B, C and D.

Consequently we may consider the solid as a monoconcave octohedron, which is composed of the tetrahedrons $EABD$ and $CABD$, diminished with $FBCD$; these tetrahedrons terminate again, the same as in the figs. 1 and 3 in the side BD.

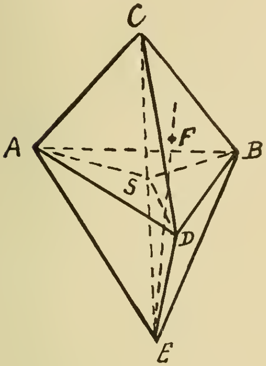

Fig. 5.

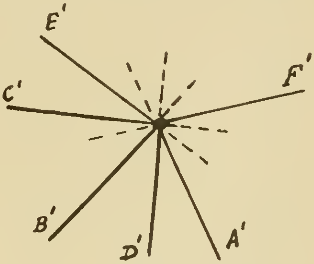

Fig. 6.

In order to define the position of the curves with respect to F' and E', we consider the hexahedron $EABDC$ and the tetrahedron $ABCD$, within which the point F is situated. We find:

$$C'E' \mid F' \mid A'B'D' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\text{and } A'B'C'D' \mid E' \mid F' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Now we draw again in a P,T-diagram the curves F' and E' (fig. 6) and we take again E' at the left of F'.

In this connection (9) and (10) have been written at once in such a way that also herein E' is at the left of F'.

It follows from (9) and (10) that C' must be situated at the left of F' and of E'; consequently C' must be situated within the angle, which is formed by the stable part of E' and the metastable part of F'.

Further it is apparent from (9) and (10) that A', B' and D' must be situated at the right of F', but at the left of E'; consequently they are situated, as is also drawn in fig. 6 within the metastable parts of E' and F'.

Now we have still to define the position of the three curves A', B' and D' with respect to one another. From the tetrahedron $CBDE$ within which the point F is situated, it follows:

$$F' \mid A' \mid B'C'D'E' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

so that at the one side of A' only F', at the other side B', C', D'

and E' must be situated. Consequently curve A' is situated as is drawn in fig 6.

The contemplation of the hexahedron $EABDF$ gives us:

$$E'F' \mid C' \mid A'B'D' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

but it does not teach us anything new.

Now we have still to define the position of B' and D' with respect to one another, we shall refer to this later.

When we summarize the obtained results, we may say:

when the six phases form the anglepoints of a monoconcave octohedron, then the six monovariant curves form in the P, T-diagram one threecurvical, one twocurvical and one onecurvical bundle.

Type IV. In fig. 7 the six phases form the anglepoints of the tetrahedron $ABCD$, within which the points E and F are situated. The line EF intersects the triangles ABD and CBD; now we unite E with A, B and D and also F with C, B and D. Consequently we may consider the solid as a biconcave octohedron, which is composed of the tetrahedron $ABCD$, diminished with the tetrahedrons $EABD$ and $FCBD$. These three tetrahedrons terminate again in the side BD.

From the position of the five phases of the equilibrium F' with respect to one another we find:

$$E' \mid F' \mid A'B'C'D' . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

It follows for the position of the equilibrium E':

$$A'B'C'D' \mid E' \mid F' . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Now we draw in a P,T-diagram (fig. 8) again the curves F' and E' and we take again E' at the left of F', in accordance with this also in (13) and (14) E' is taken at the left of F'.

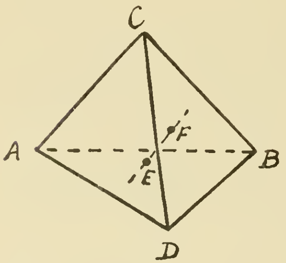

Fig. 7.

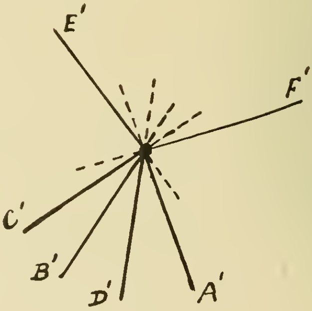

Fig. 8.

Now it follows from (13) and (14) that the bundle of the curves A', B', C' and D' must be situated at the right of F' and at the left of E'; therefore, these curves are situated, as is also drawn in fig. 8, within the angle, which is formed by the metastable parts of E' and F'.

Now we have still to define the position of those four curves with respect to one another. As the five phases of the equilibrium A' form a tetrahedron $EBCD$, within which the point F is situated, we find:

$$F' \mid A' \mid B'C'D'E' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

Hence it follows that curve A' must be situated as is drawn in the figure.

The five phases of the equilibrium C' form the tetrahedron $FABD$, within which the point E; hence it follows:

$$E' \mid C' \mid A'B'D'F' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

Hence it is apparent that curve C' must be situated as is drawn in the figure.

Later we shall define the position of the curves B' and D' with respect to one another.

We have found the following above:

when the six phases form the anglepoints of a biconcave octohedron, then the six monovariant curves form in the P,T-diagram one fourcurvical and two onecurvical bundles.

Though we have deduced the four types of the P,T-diagrams without knowing the position of the curves B' and D' with respect to one another, yet we shall define the position of the curves B' and D' with respect to one another. For this we have to consider the position of the five phases of each of the equilibria B' and D'.

For this we consider the line AF; this line intersects in each of the solids (figs. 1, 3, 5 and 7) either the triangle BCE or the triangle DCE. Now we assume that it intersects in each of these solids the triangle BCE.

As the five phases of the equilibrium D' form the hexahedron $ACEBF$, the diagonal of which intersects the triangle CEB, it follows:

$$A'F' \mid D' \mid B'C'E' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (17)$$

The five phases of the equilibrium B' form the anglepoints of the hexahedron $ACDEF$. As, in accordance with our assumption the line AF does not intersect the triangle CDE, the line CE will intersect the triangle AFD. Hence it follows:

$$A'D'F' \mid B' \mid C'E' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

It is apparent from (17) that in each of the figures 2, 4, 6 and

8, we must find at the one side of curve D' the curves A' and F' and at the other side the curves B', C' and E'. Therefore curve D' must be situated, as it is drawn in each of these figures. Consequently also by this the place of curve B' is defined.

We should have been able to deduce the same also from (18).

In each of the P,T-diagrams, when starting in a definite direction from B, the succession of the curves is: $B'D'A'F'E'C'$. In order to understand the meaning of this succession, we shall bear in mind the following. The points B,D, and A of the solids, are particular points, each defined in a particular way. BD is viz. the side in which terminate the tetrahedrons, of which we imagined each octohedron to be built up. On this side the point B occupies again a special place, as we have assumed that the line AF intersects the triangle BCE. Also the point A is a particular point, as the line AF intersects the triangle BCE.

When we compare the succession of the curves in the P,T-diagrams with the succession of the anglepoints of the solids then we go in these solids first along the sides from B towards D and afterwards towards A. Starting from A we go along a diagonal, consequently towards F; starting from F we go along the other diagonal, consequently towards E (figs. 3, 5 and 7) or, when no other diagonal starts from F (fig, 1) we go along a side towards the point, which is situated on the other side of the triangle ABD, consequently also towards E. At last we go, starting from E along a diagonal, consequently towards C.

When we summarize the results obtained above, the following is apparent:

1. There exist four types of P,T-diagrams. The six phases form the anglepoints of

a. a symmetrical octohedron (fig. 1); then in the P,T-diagram the six curves form three twocurvical bundles (fig. 2);

b. an asymmetrical octohedron (fig. 3); then in the P,T-diagram the six curves form one twocurvical and four onecurvical bundles (fig. 4);

c. a monoconcave octohedron (fig. 5); then in the P,T-diagram the six curves form one threecurvical, one twocurvical and one onecurvical bundle (fig. 6);

d. a biconcave octohedron (fig. 7); then in the P,T-diagram the six curves form one fourcurvical and two onecurvical bundles (fig. 8).

2. The four types are in accordance with one another in that respect that the curves succeed one another in a same definite succession. *(To be continued).*

Physics. — *"On the measurement of very low temperatures"*. XXVI. *The vapour-pressures of oxygen and nitrogen according to the pressure-measurements by* v. SIEMENS *and the temperature-determinations by* KAMERLINGH ONNES *c. s.* By Dr. G. HOLST. (Communications from the Physical Laboratory at Leiden. 148*a*). (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of Sept. 25. 1915.)

§. 1. *Introduction.* The main object of this communication is a correction of the calculation of the results contained in a paper by H. VON SIEMENS. Annalen der Physik Vol. 42, p. 871, 1913. SIEMENS determined the vapour-pressure as a function of the temperature for a number of substances using a platinum-resistance-thermometer. This thermometer had been reduced to the Leiden-standard-platinum-thermometer Pt_1 by means of NERNST's linear reduction-formula. For a handy calculation of the temperatures SIEMENS used an interpolation-table in which the resistance is given divided by the resistance at 0°C. below 80°K. for every two degrees and for temperatures between 80°K. and 290°K. for every five degrees. For this purpose he used the data of the Leiden-calibration of 1905—1906. It has appeared, however, afterwards that this calibration does not agree so well with subsequent ones as these among themselves and that, particularly in the oxygen-region, considerable deviations occur which must therefore also affect the results obtained by SIEMENS. We will therefore begin by a detailed examination of these deviations.

§ 2. *The calibration of* Pt_1.

The first comparison of this resistance-thermometer with the hydrogen-thermometer was carried out in 1905—1906 by KAMERLINGH ONNES, BRAAK and CLAY. The results are contained in the table on p. 44 of Comm. 95*c*. Subsequently Pt_1 broke and was then once more wound. The repaired thermometer was called Pt'_1. It was again compared with the hydrogen-thermometer in 1907. On page 5 of Comm. 101*a* its resistance at nine different temperatures is given. Small differences showed themselves at the time up to 0,04 of a degree. In the end of 1907 and the beginning of 1908 another calibration was performed at six different points: the results were published in Comm. 107*a* page 6.

In 1913 a new series of measurements was made by KAMERLINGH ONNES and HOLST, the results being contained in Table I Comm. 141*a* page 7.[1])

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[1]) An interpolation-formula representing these observations between 15° K. and 230°K. was given by ZERNIKE. (These Proceedings Kon. Ak. v. Wet. XXIII, p. 742, 1914).

TABLE I.

Resistance of the platinum-thermometer Pt'_1 by Kamerlingh Onnes c.s.

T abs. scala	$\frac{W}{W_0}$	diff.	T abs. scala	$\frac{W}{W_0}$	diff.
56° K.	0.10815	374	74° K.	0.18252	427
57	11189	394	75	18679	427
58	11583	401	76	19106	428
59	11984	406	77	19534	428
60	12390	409	78	19962	428
61	12799	411	79	20390	429
62	13210	412	80	20819	429
63	13622	414	81	21248	430
64	14036	416	82	21678	431
65	14452	417	83	22109	431
66	14869	418	84	22540	430
67	15287	420	85	22970	431
68	15707	421	86	23401	430
69	16128	423	87	23831	431
70	16551	424	88	24262	430
71	16975	425	89	24692	431
72	17400	426	90	25123	430
73	17826	426	91	25553	

On the basis of the results of the last three calibrations I have now computed a new interpolation-table, in which the resistance-ratio is given from 56° K. to 91° K. for every degree and from 90° K. to 270° K. for every five degrees. This table ought to replace the one given by Siemens and at the same time for temperatures below 80° K. supplement the full table computed by Henning [1]). This addition may be useful, although it must not be forgotten, that exactly in the range below 80° K. the platinum-thermometer gives rise to special difficulties [2]).

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[1]) F. Henning Ann. d. Phys 40, p. 635, 1913.

[2]) Comp. Comm. Leiden 141*a* § 6.

TABLE 1 (continued).

Resistance of the platinum-thermometer Pt'_1 by KAMERLINGH ONNES c.s.

T abs. scale	$\frac{W}{W_0}$	diff.	T abs. scale	$\frac{W}{W_0}$	diff.
90° K.	0.25123	429.8	185° K.	0.64776	405.6
95	27272	428.8	190	66804	404.4
100	29416	427.2	195	68826	403.4
105	31552	425.6	200	70843	402.8
110	33680	423.8	205	72857	402.2
115	35799	422.2	210	74868	401.8
120	37910	420.8	215	76877	401.4
125	40014	419.4	220	78884	401.0
130	42111	418.0	225	80889	400.6
135	44201	416.6	230	82892	400.0
140	46284	415.2	235	84892	399.2
145	48360	413.8	240	86888	398.4
150	50429	412.6	245	88880	397.8
155	52492	411.6	250	90869	397.0
160	54550	411.0	255	92854	396.2
165	56605	410.4	260	94835	395.4
170	58656	409.2	265	96812	394.4
175	60702	408.0	270	98784	393.4
180	62742	406.8	273.09	1.——	

The temperatures given in Table 1 are those read on the hydrogen-thermometer and corrected to the absolute scale, for the latter purpose the corrections as determined by KAMERLINGH ONNES and BRAAK [1]) being used.

In order to be able to form an opinion of the accuracy of this table I have calculated for all four calibrations the temperature corresponding to $\frac{W}{W_0}$ according to the table, and the deviations from the temperatures, as observed.

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[1]) Comm. Leiden 101*b*.

TABLE II.

Comparison of different calibrations of Pt'_1.

$\frac{W}{W_0}$	T_{table}	$T_{\text{obs. and corr. to abs. scale.}}$	$T_{\text{observ.} - \text{calc.}}$
	Calibration 1905 1906. Comm. 95*c* p. 44.		
1.	273.09° K.	273.09° K.	0.
0.88180	243.24	243.29	+ 0.05
76515	214.35	214.34	— 0.01
64749	184.93	184.96	+ 0.03
58345	169.24	169.28	+ 0.04
43450	133.20	133.25	+ 0.05
35486	114.26	114.30	+ 0.04
25280	90.36^5	90.36	— 0.00^5
20013	78.12	77.97	— 0.15
15969	68.61	68.47	— 0.14
12539	60.36	60.34	— 0.02
10709	55.72	55.76	+ 0.04
	Calibration 1907. Comm. 101*a* p. 105.		
0.58426	169.44	169.44	0.00
51825	153.38^5	153.38	— 0.00^5
33265	109.02^5	109.02	— 0.00^5
25467	90.80	90.80	0.00
11028	56.57	56.56	— 0.01

As will be seen the first calibration shows pretty considerable deviations, whereas the others are in very good agreement with each other. Only at one point a deviation of 0.03 of a degree occurs, which is not more than might be expected considering that the accuracy of the hydrogen-thermometer is not much greater than 0.02 of a degree.

TABLE II (continued).

Comparison of different calibrations of Pt'_1.

$\frac{W}{W_0}$	T table	T obc. and corr. to abs. scale	T obs.- calc.
	Calibration 1907—1908. Comm. 107*a* p. 6.		
0.25369	90.57	90.55	— 0.02
23647	86.57	86.55	— 0.02
22395	83.66	83.65	— 0.01
10945	56.35	56.33	— 0.02
25294	90.40	90.41	+ 0.01
25044	89.82	89.85	+ 0.03
	Calibration 1913. Comm. 141*a* p. 7.		
0.90523	249.13° K.	249.13° K.	0.00
82893	230.00	230.00	0.00
75511	211.60	211.60	0.00
68233	193.53	193.53	0.00
58820	170.40	170.39	— 0.01
54359	159.53^5	159.53	— 0.00^5
47389	142.66	142.66	0.00
25234	90.26	90.27	+ 0.01
23554	86.36	86.36	0.00
19925	77.91	77.91	0.00
15866	68.38	68.38	0.00
12622	60.57	60.57	0.00
11162	56.93	56.93	0.00

§ 3. *Comparison of Pt'_1, with P_{32} of* HENNING [1]).

We will now compare the scale as laid down in our table with that determined by HENNING for his platinum-thermometer P_{32}; for this purpose HENNING's values were first reduced to the absolute scale according to KAMERLINGH ONNES and BRAAK's corrections [2]).

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[1]) F. HENNING. Ann. d. Phys. (40), 635, 1913.

[2]) Comm. Leiden 101*b*.

TABLE III.

Comparison of the platinum-thermometer of Kamerlingh Onnes c.s. (Pt'_1) with that of Henning Pt_{32}.

T	$\left(\frac{W}{W_0}\right)_{Pt'_1}$	$\left(\frac{W}{W_0}\right)_{P_{32}}$	Δ
80° K.	0.20819	0.20241	0.00578
100	29416	28881	535
120	37910	37432	478
140	46284	45874	410
160	54550	54200	350
180	62742	62448	294
200	70843	70624	219
220	78884	78737	147
240	86888	86787	101
260	94835	94786	049
273.09	1.—	1.—	0.—

We shall first try to reduce the two scales to each other by means of Nernst's linear formula. For this purpose we can utilize the fact, that on both thermometers the boiling point of oxygen was measured; at this point Pt'_1 gave $\frac{W}{W_0} = 0.25176$, and P_{32} $\frac{W}{W_0} = 0.24631$[1], so that in the formula

$$\Delta\left(\frac{W}{W_0}\right) = \alpha\left(1 - \left(\frac{W}{W_0}\right)_{Pt'_1}\right)$$

$\alpha = 0.007284$.

If we do not want to go beyond an accuracy of $\frac{1}{20}$ of a degree, we may use this linear relation[2]. A much closer correspondence is obtained, however, if with Henning[3]) we use a quadratic relation.

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[1]) F. Henning. Ann. d. Phys. (43), 282, 1914.

[2]) H. Schimank. (Ann. d. Phys. (45), 706, 1914) states, that, for $\alpha = 0{,}03$, a difference of 0,1—0,2 of a degree is to be expected, which agrees with the difference found here of $\frac{1}{20}$ of a degree for $\alpha = 0{,}0073$.

[3]) F. Henning. Ann. d. Phys (40), 635, 1913.

Even then, however, real deviations remain in the range 200° K. - 240° K. showing that the Leiden-temperature-scale lies here somewhat above that of the Phys. Techn. Reichsanstalt.

TABLE IV.

Comparison of the linear and the quadratic deviation-formulae.

T	$\Delta W_{\text{obs.}}$	$\Delta W_{\text{calc.}}$ NERNST	$\Delta T_{Pt'_1-Pt_{32}}$	$\Delta W_{\text{calc.}}$ quadr. form.	$\Delta T_{Pt'_1-Pt_{32}}$
80° K.	0.00578	0.00576	-0.00^5	0.00578	0.00
100	535	514	-0.05	525	-0.02
120	478	452	-0.06	470	-0.02
140	410	391	-0.04^5	408	0.00
160	350	331	-0.04^5	355	$+0.01$
180	294	271	-0.06	296	0.00
200	219	212	-0.02	235	$+0.04$
220	147	154	$+0.02$	173	$+0.06$
240	101	096	-0.01	108	$+0.02$
260	049	038	-0.03	044	-0.01
273.09	0	0	0	0	0

A good correspondence at the lower temperatures is obtained with the following formula

$$\Delta\left(\frac{W}{W_0}\right) = 0.00850\left(1-\frac{W}{W_0}\right) - 0.001515\left(1-\frac{W}{W_0}\right)^2.$$

The greatest deviation amounts to 0.06 of a degree at 220° K. It would seem to me, that this formula cannot be far wrong, and for the following reasons. Looking at fig. 2 on page 653 in HENNING's paper, we see that the curve $T - T_C$ as a function of the temperature, in the temperature region under consideration, allows a small shift upwards, without the agreement with the observations becoming much impaired, which shows, that the deviation from CALLENDAR's formula begins even at a somewhat higher temperature.

In the range in question we can further utilize the freezing point of mercury. HENNING¹) has made a very accurate measurement of this

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¹) F. HENNING. Ann. d. Phys. (43), 282, 1914.

point, from which may be inferred that $\frac{W}{W_0} = 0.84465$ at this point. According to the quadratic formula we should then have for $Pt_1' \frac{W}{W_0} = 0.84593$ corresponding to $-38°.84$ C., whereas the temperature-scale of the P. T. R. gives $-38°.89$. Borrowing from Henning's paper the results of other observers:

Stewart	-38.85
Chappuis	-38.80 ± 0.02
Chree	-38.86

we see that the freezing point as determined by Henning, when reduced to the Leiden scale, coincides exactly with the mean of the other observers. Although this must, of course, not form the basis of a final judgment on the difference of the two temperature-scales, still we may see in it an indication of the cause of the deviation, viz. too great a value having been attributed to Callendar's formula at temperatures below — 20° C.

Each fresh direct determination of the freezing point of mercury may, moreover, lead to a decision in favour of one or the other of the two temperature-scales.

Apart from the deviation just discussed, the agreement is a very good one, no greater deviations occurring than of 0.02 of a degree. It remains a matter for regret, however, that for Pt_1' the constants of Callendar's formula were not determined, before proceeding to use the thermometer at low temperatures, which would have made a more direct comparison possible. With a view to the great importance of Pt_1' for low temperature-thermometry it was not deemed advisable to carry out the determination in question now.[1])

§ 4. *The vapour-pressure of oxygen.*

Kamerlingh Onnes and Braak have determined the vapour-pressure of oxygen at four different temperatures. As the resistance of Pt_1' was measured at the same time, these vapour-pressures may be reduced to the temperature-scale as laid down in the above table.

We find, that the temperature corresponding to a given vapour-pressure may be represented by the following formula which is of the form as proposed by August—Rankine—van der Waals.

$$T = \frac{369.83}{6.98460 - \log p}$$

Henning also gives the vapour-pressure at a few temperatures in

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[1]) Comp Comm. Leiden N⁰. 141*a*

the neighbourhood of the boiling point. Calculating according to the above formula the temperatures corresponding to these vapour-pressures we do not find greater deviations than of 0.02 of a degree, so that the temperature belonging to a given vapour-pressure is pretty sure to be accurate to 0.02 of a degree.

TABLE V.

Vapour-pressures of oxygen according to Kamerlingh Onnes and Braak.

$\frac{W}{W_0}$	$p^{\text{mm.}}$	T_{table}	$T_{\text{K.O. and B.}}$	T_{formula}
0.25424	807.18	90.70° K.	90.68° K.	90.70° K.
25176	760.16	90.12	90.10	90.12
23647	516.19	86.57	86.55	86.57
22395	366.24	83.66	83.65	83.66

TABLE VI.

Vapour-pressures of oxygen according to Henning.

$T_{\text{reduced to abs. scale}}$	p	T_{formula}	ΔT
88.305° K.	626.7	88.31^5° K.	$-$ 0.01
88.805	659.8	88.79	$+$ 0.01^5
90.115	758.0	90.09^5	$+$ 0.02
90.114	758.7	90.10^5	$+$ 0.01
90.171	764.0	90.17	0.00

By means of the formula given above the vapour-pressure measurements by Siemens may now be recalculated. Siemens gives the resistance of his thermometer at an oxygen-pressure of 766.8 mm., where according to the formula $T = 90°,21$ K. According to the table at this point the resistance-ratio for Pt'_1 is 0.25211, whereas for Siemens' thermometer it is 0.25923, so that α in Nernst's linear formula is equal to 0.00961; with this constant the thermometer may be reduced to Pt'_1 and the temperatures may be calculated.

It follows from the value of α, in connection with what was found above in the comparison between Pt'_1 and P_{32}, that no greater

TABLE VII.

Vapour-pressures of oxygen.
Pressures by SIEMENS, temperature by KAMERLINGH ONNES c.s., as calculated by HOLST.

W	$\frac{W}{W_0}$	$\left(\frac{W}{W_0}\right)_{Pt_1'}$	$T_{\text{abs. scale}}$	$p_{\text{mm.}}$
32.597	0.25924	0.25212	90.21° K.	766.8
30.083	0.23924	23193	85.52	457.6
27.341	0.21743	20991	80.40	239.5
25.068	0.19936	19167	76.14	129.5
23.262	0.18500	17717	72.74	75.7
20.400	0.16224	15419	67.31	28.07
18.244	0.14509	13687	63.16	11.52
16.648	0.13240	12406	60.04	5.49
16.253	0.12926	12089	59.26	4.40
15.327	0.12189	11345	57.40	2.68

accuracy may be expected than to about 0.05 of a degree. The corrections for STOCK's thermometer also undergo a change and become as given in Table VIII.

TABLE VIII.

Corrections for STOCK's thermometer according to Table VII.

$t_{\text{obs.}}$	$t_{\text{corr.}}$	$t_{\text{obs.}}$	$t_{\text{corr.}}$
— 183	— 183.96° C.	— 192	— 192.44° C.
— 184	— 184.90	— 193	— 193.41
— 185	— 185.83	— 194	— 194.44
— 186	— 186.79	— 195	— 195.42
— 187	— 187.76	— 196	— 196.39
— 188	— 188.68	— 197	— 197.33
— 189	— 189.62	— 198	— 198.34
— 190	— 190.54	— 199	— 199.37
— 191	— 191.50	— 200	— 200.40

§ 5. *The vapour-pressures of nitrogen.*

The deviations of the scale used by VON SIEMENS from the Leiden scale having been computed in the case of oxygen, SIEMENS' temperatures for nitrogen can be corrected directly. Table IX gives the results.

TABLE IX.

Vapour-pressures of nitrogen.
Pressure by SIEMENS, temperature by K. ONNES C.S., as calculated by HOLST.

T abs. scale	p m.m.
80.48° K.	1086.0
79.82	1009.4
75.86	631.3
72.85	428.6
70.97	329.4
67.89	206.9
66.93	117.6
63.25	93.5
63.25	93.5
62.87	86.1
62.02	71.9
60.83	55.3
60.01	45.8
58.76	34.1
57.73	26.4
57.00	21.8

Physics. — "*The viscosity of liquefied gases. I. The rotational oscillations of a sphere in a viscous liquid.*" By Prof. J. E. Verschaffelt. Comm. N°. 148*b* from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes).

(Communicated in the meeting of October 30, 1915).

1. With a view to an investigation of the viscosity of liquefied gases at low temperatures, especially in the case of hydrogen, which on the invitation of Professor Kamerlingh Onnes I hope to undertake, in conjunction with Mr. Ch. Nicaise, by the method of damped rotational oscillations of a sphere suspended in the liquids in question, I shall here give the theory of the method. The problem has been dealt with before by a number of writers[1]) and the formulae which embody the results of their calculations have also found application in the discussion of different experiments; still I do not consider it superfluous to publish my method of dealing with the problem, because in my opinion it is simpler and less involved than the one followed by previous writers, while the formulae which I have arrived at are much better adopted to numerical calculations.

The sphere will be supposed to swing freely about a diameter under the action of a couple of forces (the torsional moment of the suspension) the moment of which $M\alpha$ is proportional to the angle of deflection α. In the absence of friction the sphere would perform a harmonic oscillation with a time of swing given by:

$$T_0 = 2\pi \sqrt{\frac{K}{M}}\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

K being the moment of inertia of the sphere about a diameter (or more correctly the moment of inertia of the vibrating system of which the sphere forms parts), M the angular moment per unit of angle. If the sphere swings in a viscous liquid, the motion is damped and it appears (although properly speaking an experimental confirmation is lacking), that when the friction is not too strong the sphere executes a damped harmonic vibration, according to the formula:

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[1]) C. J. H. Lampe, Programm des städt. Gymn. zu Danzig, 1866.
G. Kirchhoff, Vorlesungen über mathematische Physik, No. 26, 1877.
Ig. Klemencic, Wien Ber. II. 84, 146, 1882.
G. G. Stokes, Math. and Phys. Papers. Vol. V, p 207.
W. König, Wied. Ann. 32, 193, 1887.
H. Lamb. Hydrodynamics, 1906, p. 571, 599, 581.
G. Zemplén, Ann. d. Phys. 19, 783, 1906; 29, 899, 1909.
M. Brillouin. Leçons sur la viscosité des liquides et des gaz, 1907; 1ère partie p. 96.

$$\alpha = a\, e^{-\delta \frac{t}{T}} \cos 2\pi \frac{t}{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where T is the new time of vibration and δ the logarithmic decrement of the elongations for one vibration.[1]) The problem before us is, how δ and T depend upon the specific properties of the liquid, in particular on the viscosity η, and how η may be calculated from observations on the two quantities in question.

2. We shall confine our investigation to the two cases in which the liquid is either externally unlimited (i.e. practically speaking, fills a space the dimensions of which are very large compared with the radius of the sphere) or is limited by a stationary spherical surface which is concentric with the oscillating sphere; in these cases we may naturally assume, that the motion in the liquid is such, that it divides itself into spherical, concentric layers, which each separately oscillates as a solid shell about the same axis as the sphere, with the same periodic time and the same logarithmic decrement; it will be shown further down that this assumed state of motion is actually a possible one, at least when the motion is very slow[2]). In that case it is only the amplitude and the phase of the motion which differ from one shell to another, and for a shell of radius r we may therefore put:

$$\alpha_r = a_r\, e^{-\delta \frac{t}{T}} \cos 2\pi \left(\frac{t}{T} - \varphi_r\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where δ_r and φ_r are functions of r. If we further assume that the liquid layer which is contiguous to the sphere, adheres to it, as is well known to be generally the case, expression (3) must become identical with (2) for $r = R$, thus $\alpha_R = \alpha$ and $\varphi_R = 0$.

3. In order to find the functions α_R and φ_R we proceed to establish the equation of motion for a spherical liquid shell. For this purpose we shall consider the ring whose section is $ABCD = r.d\varepsilon.dr$ (comp. adjoining figure) and whose radius is $\varrho = r \cos \varepsilon$. On its side-faces AB and CD this ring according to our assumption does not experience any friction; on the inner surface AB, owing to friction against a shell closer to the centre, it experiences a tangential force F per unit area in the direction of its motion, and on the outer surface BC similarly a force $-\left(F + \frac{\partial F}{\partial r} dr\right)$; writing down the

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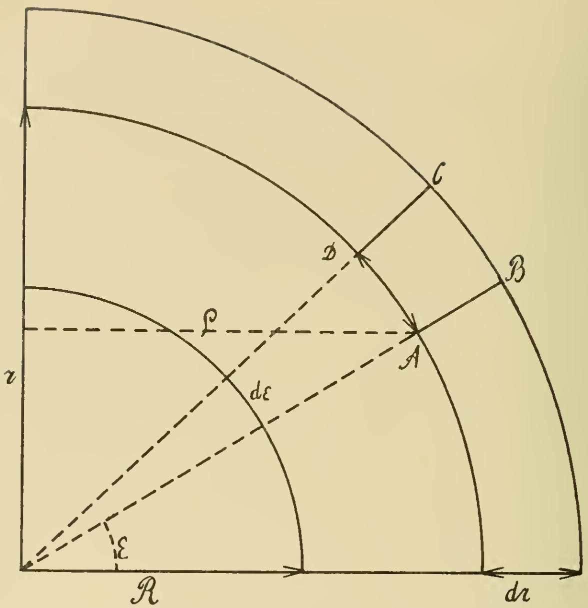
[1]) If the motion of the sphere without friction were a compound harmonic motion, as would be the case, if the sphere were coupled to other oscillating systems, the motion with friction would be compounded of damped harmonic vibrations.

[2]) For the necessary condition of slowness of the motion see note in Comm. N⁰. 148*d*.



condition, that the work of these forces during a small angular displacement equals the increase of the kinetic energy $\frac{1}{2} m v_r^2$ of the ring, we find, when the density of the liquid is μ,

$$F \, . \, 2\pi r \cos\varepsilon \, . \, r d\varepsilon \, . \, r \cos\varepsilon \frac{\partial \alpha_r}{\partial t} - \left(F + \frac{\partial F}{\partial r} dr \right) 2\pi \, (r + dr)^3 \cos^2\varepsilon \, . \, d\varepsilon \, . \, \frac{\partial \alpha r}{\partial t} =$$

$$= \frac{\partial}{\partial t} \left(\tfrac{1}{2} m v_r^2\right) = 2\pi r \cos\varepsilon \, . \, r \, d\varepsilon \, . \, dr \, . \, \mu \, . \, v_r \frac{\partial v_r}{\partial t}$$

or

$$- \frac{\partial F}{\partial r} - \frac{3F}{r} = \mu \frac{\partial v_r}{\partial t} = \mu \, r \cos\varepsilon \frac{\partial^2 \alpha_r}{\partial t^2}.$$

According to the elementary laws of internal friction the force F is proportional to the velocity-gradient in the direction of the radius; in determining this slope we must only take into account the gradient which is due to the change of the angular velocity with r[1]). The velocity-gradient thus becomes equal to $r \cos\varepsilon \frac{\partial}{\partial r} \left(\frac{\partial \alpha_r}{\partial t} \right)$, and therefore

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[1]) The gradient of velocity which is the consequence of a uniform rotation of the liquid does not produce any friction. In the classical hydrodynamical theory this results from the circumstance that in a uniform rotation there is no deformation and consequently no stress. (Note added in the translation).

$$F = -\eta\, r \cos \varepsilon \frac{\partial \omega}{\partial r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

when $\omega = \frac{\partial a_r}{\partial t}$ represents the angular velocity of the shell under consideration and η the viscosity of the liquid. The equation of motion of the sphericall shell may now be written in the form

$$\frac{\partial^2 \omega}{\partial r^2} + \frac{4}{r} \frac{\partial \omega}{\partial r} = \frac{\mu}{\eta} \frac{\partial \omega}{\partial t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

4. This equation determines how ω depends on r; as it does not contain the angle ε, it is in accordance with our assumption, that the individual shells oscillate to and fro as solid bodies[1]). As regards the law of dependence of ω on t, which we have already presupposed in equation (3), it appears that it also is compatible with (5); substituting (3) in (5) and expressing the condition, that equation (5) must be fulfilled at all times (by putting the coefficients of *cos* and *sin* equal to zero), two differential equations are obtained, which do not contain the time and which determine the functions a_r and φ_r.

This method is, however, very cumbrous. It is much simpler first to reduce (3) to the form

$$a_r = e^{-\delta \frac{t}{T}} \left(x \cos 2\pi \frac{t}{T} + y \sin 2\pi \frac{t}{T} \right), \quad . \quad . \quad . \quad . \quad (6)$$

where x and y are new functions which for $r = R$ become equal to a and 0 respectively and are determined by the two differential equations:

$$\left.\begin{aligned} \frac{d^2 x}{dr^2} + \frac{4}{r}\frac{dx}{dr} + \frac{\mu}{\eta T}(\delta x - 2\pi y) = 0 \\ \frac{d^2 y}{dr^2} + \frac{4}{r}\frac{dy}{dr} + \frac{\mu}{\eta T}(\delta y + 2\pi x) = 0 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The simplest method of all is to consider (6) as the real part of an exponential function

$$a_r = u\, e^{kt} \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where u and k are in general complex quantities; in that case (2) is the real part of

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[1]) It should not be overlooked that in this manner the possibility of the aforesaid assumption has been proved, not its necessity (for this proof, see Lamb, loc. cit.). It is moreover easily seen, that with a different law of friction, e g. in which $\varkappa$ would also depend on the velocity itself, the assumption would become unallowable.

$$\alpha = a\, e^{kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8')$$

and u is a function of r only, which for $r = R$ obtains the value a. Putting

$$k = k' + k'' i \quad (i = \sqrt{-1}) \, , \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

it follows by equating (6) to the real part of (8) that

$$k' = -\frac{\delta}{T} \quad \text{and} \quad k'' = \frac{2\pi}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9')$$

The real angular velocity ω is the real part of the complex quantity

$$\omega = k\, u\, e^{kt} \, , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

the function u satisfying the equation

$$\frac{d^2 u}{dr^2} + \frac{4}{r} \frac{du}{dr} = \frac{\mu}{\eta} k\, u \, , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which is obtained by substituting (10) in (5).[1]

5. The general solution of (11) is well known to be

$$u = \frac{1}{r^3} \left[A e^{-br} (br + 1) + B e^{br} (br - 1) \right] ,$$

or

$$u = \frac{1}{r^3} \left[P e^{-b\,r-R} (br + 1) + Q e^{b\,r-R} (br - 1) \right] , \quad . \quad . \quad (12)$$

where

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[1] Equation (10) is a particular solution of equation (5). The mode of motion which it represents is, therefore, a possible one but not necessarily the actually existing one. The reason why we only consider this solution is that we suppose the sphere not to perform forced vibrations. In the case of a compound harmonic motion ω would consist of a number of terms, each with its own k, the u's of which would satisfy as many equations (11).

It is also obvious, that the condition of motion considered cannot exist from the beginning, but can only be reached after a theoretically infinite period, so that the motion of the sphere cannot correspond either to equation (2) from the moment at which the motion begins. The experiments show, however, that the final condition is practically reached after a comparatively short time (a few minutes), i. e. very soon T and δ have become constant; this may be expressed mathematically by saying, that the assumed condition of motion is the limiting condition to which the real motion approaches asymptotically and this approach is in general so rapid, that even after a comparatively short time the deviations of the actual motion from the final limit are within the limits of the errors of observation. The question as to the real motion during the said period of approach is one which would have to be settled by a separate theoretical and experimental investigation, but is of no importance for our present purpose.

$$b = \sqrt{\frac{\mu}{\eta} k}\,; \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

A, B, P and Q are complex constants which are determined by the conditions at the boundaries.

In the first place we have $u = a$ for $r = R$, so that

$$P(bR + 1) + Q(bR - 1) = aR^3 \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

If the liquid is unlimited or at any rate may practically be considered as unlimited, $u = 0$ for $r = \infty$; this leads to the condition $Q = 0$ (unless b were a pure imaginary quantity, i. e. k were real, in which case the motion would be aperiodic, a case which we do not consider here), and therefore

$$u = a \frac{R^3}{r^3} \frac{br+1}{bR+1} e^{-b(r-R)} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

On the other hand, if the liquid is bounded by a stationary spherical surface of radius R', the condition is that $u = 0$ for $r = R'$ at all times (again in the supposition that the liquid adheres to the surface of the sphere) so that

$$Pe^{-b(R'-R)}(bR' + 1) + Qe^{b(R'-R)}(bR' - 1) = 0\,; \quad . \quad . \qquad (16)$$

in that case

$$P = \frac{aR^3(bR'-1)e^{b(R'-R)}}{D} \quad , \quad Q = -\frac{aR^3(bR'+1)e^{-b(R'-R)}}{D}, \qquad (17)$$

where

$$D = (bR + 1)(bR' - 1)\,e^{b(R'-R)} - (bR - 1)(bR' + 1)\,e^{-b(R'-R)}, \qquad (17')$$

so that

$$u = \frac{aR^3}{Dr^3}\left[(br + 1)(bR' - 1)\,e^{b(R'-r)} - (br - 1)(bR' + 1)\,e^{-b(R'-r)}\right] \qquad (17'')$$

6. If we put

$$\sqrt{k} = \pm(\gamma' + \gamma'' i)$$

it follows that

$$\gamma'^2 - \gamma''^2 = k' \quad \text{and} \quad 2\,\gamma'\gamma'' = k'',$$

and therefore, seeing that γ' and γ'' from their nature represent real quantities:

$$\left.\begin{aligned} \gamma' &= \sqrt{\tfrac{1}{2}k' + \tfrac{1}{2}\sqrt{k'^2 + k''^2}} = \sqrt{\frac{-\delta + \sqrt{\delta^2 + 4\pi^2}}{2T}} \\ \gamma'' &= \sqrt{-\tfrac{1}{2}k' + \tfrac{1}{2}\sqrt{k'^2 + k''^2}} = \sqrt{\frac{\delta + \sqrt{\delta^2 + 4\pi^2}}{2T}} \end{aligned}\right\} \quad . \quad (18)$$

As a rule the circumstances under which the experiments are conducted are such, that δ is a small number, of the order of magnitude 0,1; in that case the expressions (18) can be developed into series progressing according to the ascending powers of $\chi = \frac{\delta}{2\pi}$, which leads to:

$$\left.\begin{aligned} \gamma' &= \sqrt{\frac{\pi}{T}}\left(1 - \tfrac{1}{2}\chi + \tfrac{1}{8}\chi^2 + \ldots\right) \\ \gamma'' &= \sqrt{\frac{\pi}{T}}\left(1 + \tfrac{1}{2}\chi + \tfrac{1}{8}\chi^2 + \ldots\right) \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad (19)$$

so that

$$b = \sqrt{\frac{\pi\mu}{\eta T}}\left[(1+i) - (1-i)\frac{\chi}{2} + (1+i)\frac{\chi^2}{8} + \ldots\right]. \qquad (20)$$

7. As mentioned above in section 1, the real part of (8) may in general be written in the form

$$\begin{aligned} a_r = {} & e^{k't-b'r}\left[X_1 \cos(k''t-b''r) + Y_1 \sin(k't-b''r)\right] \\ & + e^{k't+b'r}\left[X_2 \cos(k''t+b''r) + Y_2 \sin(k''t+b''r)\right], \quad . \quad . \quad (21) \end{aligned}$$

where X_1, X_2, Y_1 and Y_2 are again functions of r, but now real quantities. This form shows, that the motion of the liquid is the result of the propagation of two waves, the one moving away from the oscillating sphere, the other moving towards the sphere; writing $k''t \pm b''r$ in the form $\frac{2\pi}{T}\left(t \pm \frac{r}{V}\right)$, the speed of propagation appears to be

$$V = \frac{k''}{b''} = \frac{2\pi}{b''T}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

this velocity therefore depends not on the specific properties of the liquid only, but in addition on the time of swing of the sphere. The wave-length is $\lambda = \frac{2\pi}{b''}$.

For δ very small we have by (19'),

$$V = 2\sqrt{\frac{\pi\eta}{\mu T}} \text{ and } \lambda = 2\sqrt{\frac{\pi\eta T}{\mu}}. \quad . \quad . \quad . \quad (22')$$

When the liquid extends to infinity (practically), we have only to deal with the former of the two waves: but when the liquid is bounded, the wave which is emitted by the oscillating sphere is reflected on the fixed wall, in such a manner that the phase is reversed, and thereby the amplitude u becomes zero at the wall.

In addition the waves undergo a damping effect during propagation, in such a manner that, independently of the algebraic dependence on r, the amplitude is reduced in the ratio $\Delta : 1$ over a distance 1, where $\Delta = e^{-b'}$.

With a small value of δ according to (20) the damping increases as T becomes smaller and with a sufficiently small value of T it may happen, that even a comparatively narrowly bounded liquid is practically unbounded, because the motion which starts from the sphere is practically completely damped, before it reaches the external boundary; to this point we shall return later on (§ 12).

8. We can now proceed to calculate the time of swing and the logarithmic decrement of the damped oscillations of the sphere from the specific constants of the liquid (viz. the viscosity η and the density μ). The equation of motion of the oscillating sphere is

$$K\frac{d^2\alpha}{dt^2} - C + M\alpha = 0\,,^{1)} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where C, the moment of the frictional forces, is given by (comp. § 3)

$$C = -\int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} F \,.\, 2\pi R^3 \cos^2 \varepsilon \, d\varepsilon = \tfrac{8}{3}\,\pi R^4 \eta \left(\frac{\partial\omega}{\partial r}\right)_{R'} \quad . \quad . \quad (23')$$

According to (10) and (12) we may write

$$\frac{\partial\omega}{\partial r} = -\frac{ke^{kt}}{R^4}\left[P\,(b^2r^2+3br+3)\,e^{-b(r-R)} - Q\,(b^2r^2-3br+3)\,e^{b(r-R)}\right],$$

and therefore

$$\left(\frac{\partial\omega}{\partial r}\right)_R = -\frac{ke^{kt}}{R^4}\left[P\,(b^2R^2+3bR+3) - Q\,(b^2R^2-3bR+3)\right] =$$

$$= -\frac{1}{aR^4}\left[P\,(b^2R^2+3bR+3) - Q\,(b^2R^2-3bR+3)\right]\frac{d\alpha}{dt}\,,$$

so that for the case of a damped harmonic motion we may write

$$K\frac{d^2\alpha}{dt^2} + L\frac{d\alpha}{dt} + M\alpha = 0,^{2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where

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1) The equation once more expresses the fact that the sphere oscillates freely.

2) In the case of a not purely harmonic damped motion the proportionality of C with $\frac{d\alpha}{dt}$ no longer exists. As far as I can see, it is in that case impossible to say, how in general C depends on the motion, so that it will then probably be impossible to establish a general differential equation for α.

$$L=\tfrac{8}{3}\frac{\pi R^3\eta}{D}\left[(b^2R^2+3bR+3)(bR'-1)e^{b(R'-R)}+(b^2R^2-3bR+3)(bR'+1)e^{-b(R'-R)}\right]. \quad (24')$$

D being the form given in (17'). L is again a complex quantity.[1]

When the liquid is (practically) unbounded and the motion periodic (i.e. $Q=0$), we have simply:

$$L=\tfrac{8}{3}\pi R^3\eta\,\frac{b^2R^2+3bR+3}{bR+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

9. The expression (8') actually satisfies the equation (24), when k satisfies the equation

$$Kk^2+Lk+M=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

If we put again $L=L'+L''i$, we find:

$$K(k'^2-k''^2)+L'k'-L''k''+M=0 \text{ and } 2Kk'k''+L'k''+L''k'=0, \quad (26')$$

or according to (9') and (1),

$$\delta^2-4\pi^2-\delta\frac{L'T}{K}-2\pi\frac{L''T}{K}+4\pi^2\frac{T^2}{T_0^2}=0 \text{ and } 4\pi\delta=2\pi\frac{L'T}{K}-\delta\frac{L''T}{K} \quad (27)$$

These are therefore the equations which determine k' and k'', and thus also δ and T, under the given experimental conditions; conversely they enable us to compute L' and L'' from the experimental values of T and δ and thereby by the aid of (24') to calculate η.

From (27) it follows that:

$$\frac{L'}{K}=\frac{\delta}{T}\left[\frac{T^2}{T_0^2}\frac{4\pi^2}{4\pi^2+\delta^2}+1\right], \quad \frac{L''}{K}=\frac{2\pi}{T}\left[\frac{T^2}{T_0^2}\frac{4\pi^2}{4\pi^2+\delta^2}-1\right]. \quad (28)$$

When δ is a small number, as also $\psi=\dfrac{T-T_0}{T_0}$ (as is usually the case), we may write:

$$\left.\begin{aligned}\frac{L'}{K}&=\frac{2\delta}{T}\left[1+\psi+\tfrac{1}{2}(\psi^2-\chi^2)+\ldots\right]=\frac{2\delta}{T_0}\left[1+\tfrac{1}{2}(\psi^2-\chi^2)+\ldots\right]\\ \frac{L''}{K}&=\frac{4\pi}{T}y\left[1+\frac{\psi^2-\chi^2}{\psi}+\ldots\right]=\frac{4\pi}{T_0}\psi\left[1-\frac{\psi^2+\chi^2}{2\psi}+\ldots\right]\end{aligned}\right\} \quad . \quad (28')$$

10. As we have been using complex quantities all along, we

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[1] The meaning of this is as follows: the real angle α satisfies equation (23), where everything is real, even C, the moment of the frictional forces, which is determined by (23') with α still real. If, however, a complex angle α is introduced, the real part of which is the real α, C will be the real part of (23'), where α must be taken as a complex quantity, and this is at the same time the real part of an expression of the form $I\dfrac{d\alpha}{dt}$, where L is then similarly a complex quantity.

have not come across the fictitious addition to the moment of inertia which usually occurs in problems of this kind. This addition does not show itself, until the real part is extracted from equation (24).

This real part is equal to

$$K\frac{d^2a'}{dt^2}+L'\frac{da'}{dt}-L''\frac{da''}{dt}+Ma'=0\ , \qquad . \quad . \quad (29)$$

having put $a=a'+a''i$; and as is easily found from (8′)

$$\frac{da''}{dt}=-\frac{1}{k''}\frac{d^2a'}{dt^2}+\frac{k'}{k''}\frac{da'}{dt},$$

so that

$$\left(K+\frac{L''}{k''}\right)\frac{d^2a'}{dt^2}+\left(L'-L''\frac{k'}{k''}\right)\frac{da'}{dt}+Ma'=0, \quad . \quad . \quad . \quad (29')$$

which means an apparent increase of the moment of inertia by the amount $K'=\frac{L''}{k''}$.[1])

Substituting the expression (2) in (29) and again expressing the fact that for all values of t the equation must be satisfied, by equating to zero the coefficients of *cos* and *sin*, the same equations (26′) are arrived at.

11. The separation of the general expression (24′) into its real and imaginary parts is a troublesome performance, which is of no practical value; the general expressions for L' and L'' are so involved, that they are practically useless for the computation of η from the observed values of T and δ by means of the equations (28). As a matter of fact it is only under simplified conditions, that the determination of η by observation of the oscillations of a sphere is practically possible. Now the whole problem becomes most simple, when the liquid may be considered as unbounded; in that case it follows from (25) which may also be written as

$$L=\tfrac{8}{3}\pi R^3\eta\left(bR+2+\frac{1}{bR+1}\right),$$

---

[1]) From (29′) it also follows, that even in the case of friction in a liquid the well-known equation

$$\frac{T^2-T_0^{\,2}}{T_0^{\,2}}=\frac{\delta^2}{4\pi^2}$$

still holds, on condition that for T_0 is taken the fictitious periodic time T_0 given by

$$T_0=2\pi\sqrt{\frac{K+K'}{M}}.$$

that

$$\left.\begin{aligned} L' &= \tfrac{8}{3}\,\pi R^3 \eta \left(b'R + 2 + \frac{b'R+1}{(b'R+1)^2 + b''^2 R^2} \right) \\ L'' &= \tfrac{8}{3}\,\pi R^4 b'' \eta \left(1 - \frac{1}{(b'R+1)^2 + b''^2 R^2} \right) \end{aligned}\right| \text{1)} \quad . \quad . \quad (30)$$

For a further approximation in the case, that the liquid may by approximation be considered as unbounded, (24′) can be developed in the form of a series. For this purpose we write first:

$$L = \tfrac{8}{3}\pi R^3 \eta \,.\, \frac{b^2R^2 + 3bR + 3}{bR+1} \,.\, \frac{1 + \dfrac{b^2R^2 - 3bR + 3}{b^2R^2 + 3bR + 3} \cdot \dfrac{bR'+1}{bR'-1} \cdot e^{-2b(R'-R)}}{1 - \dfrac{bR-1}{bR+1} \cdot \dfrac{bR'+1}{bR'-1} \cdot e^{-2b(R'-R)}} \qquad (24'')$$

when $e^{-2b(R'-R)}$ is sufficiently small 2), formula (25) will hold as a first approximation; if necessary a first correction-term may be added of the form

$$L_1 = \tfrac{16}{3}\,\pi R^6 b^3 \eta \frac{bR'-1}{(bR'+1)(bR+1)^2}\, e^{-2b(R'-R)}, \quad . \quad . \quad . \quad (31)$$

the value of which can be computed fairly easily, when an approximate value has been found for η.

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1) If $k\,(k_1)$ is replaced by the conjugate imaginary quantity k_2, it is clear, that the real part of α and also of α_r do not undergo any change (b_1 and b_2 are similarly conjugate), so that exactly the same results must be obtained, in particular the same equations (30). That this is actually true may be easily seen from the fact that L_1 and L_2 according to (24′) are also conjugate imaginary.

We might even, in general, have represented the damped harmonic oscillation by the real part of

$$\alpha = \alpha_1 + \alpha_2 = a_1 e^{k_1 t} + a_2 e^{k_2 t}.$$

We should then have obtained

$$\omega = k_1 u_1 e^{k_1 t} + k_2 u_2 e^{k_2 t},$$

and have found, that α must satisfy the equation

$$K \frac{d^2\alpha}{dt^2} + L_1 \frac{d\alpha_1}{dt} + L_2 \frac{d\alpha_2}{dt} + M\alpha = 0,$$

which, owing to $L'_2 = L'_1$ and $L''_2 = -L''_1$ may also be written as:

$$K \frac{d^2\alpha'}{dt^2} + L'_1 \frac{d\alpha'}{dt} - L''_1 \frac{d\,(\alpha''_1 - \alpha''_2)}{dt} + M\alpha' = 0.$$

By putting $a_1 = a_2$ α may then be real (form. (2)).

2) The coefficients of this factor in (24″) cannot become infinite in this case, on the contrary they do not differ much from unity.

12. In our experiments we intend to choose the conditions such that the liquid may, at least approximately, be considered as unbounded; moreover we shall arrange to make δ small. It is easily found, what conditions these simplifications are subject to.

Clearly it is necessary that the factor $e^{b'(R'-R)}$ obtains so high a value, that the terms containing this factor are sufficiently preponderant; this condition does not necessarily involve a specially high value of b', for if e.g. $R'-R=1$ i.e. if the distance of the two spherical surfaces is only 1 cm. (and this will be about the case in our experiments) still even for $b'=10$, the value of $e^{b'(R'-R)}$ will be as high as 10000 about. For water in C. G. S. units $\eta=0{,}01$ and $\mu=1$, so that even with $T=3$, i.e. a time of swing of 3 second, b' will reach the value 10, so that even in that case the desired condition will be fulfilled of the wave-motion, which starts from the oscillating sphere, when arriving at the external sphere, being practically completely damped out (§7). If it is further taken into account, that the oscillating sphere can only undergo an influence from the bounding wall by the waves reflected on the wall returning to the sphere and that the returning waves again undergo a damping process, it becomes clear, that the damping on the way from the inner sphere to the outer wall does not need to be so very complete, in order to be able to consider the liquid as being practically unbounded.

This fact is also expressed in our equations (24'') and (31). Practically (24'') is identical with (25), or $L_1=0$, when $e^{-2b'(R'-R)}$ is sufficiently small, i.e. when the damping over a distance $2(R'-R)$ is sufficiently strong; in order that $e^{-2b'(R'-R)}$ may be say $\frac{1}{1000}$ with $R'-R=1$, even $b'=3$ would be sufficient and this would still be the case for water with T as high as 30. A somewhat large time of swing of about that magnitude is favourable to the readings from which the logarithmic decrement must be determined and it is accordingly intended in our experiments to make the periodic time about that size.

With $R'-R=1$ and $T=30$ even when working with water the liquid can thus approximately be considered as unbounded. But, moreover, it appears from (20) that with a given time of swing b' and b'' become greater, and therefore the conditions more favourable, according as the ratio $\frac{\eta}{\mu}$ is smaller; for very mobile liquids, like ether and benzene, they would therefore be even more favourable than with water, and, as the available data show, most favourable of all for liquified gases. The oscillation-method appears thus a particularly suitable one for liquid gases (1).

13. With a view to our experiments it appeared to us desirable to have a rough idea as to the value of the viscosity for liquid hydrogen, say at the boiling point; an estimate may be obtained by the application of the law of corresponding states. KAMERLINGH ONNES (2) has shown that for two different substances obeying this law the expressions

$$\eta \sqrt[6]{\frac{T_k}{p_k^4 M^3}},$$

must have the same value at corresponding temperatures, where T_k and p_k are the critical temperature and pressure and M the molecular weight. It is therefore possible by the application of this rule, which will be at least approximately valid, to calculate η for hydrogen by comparison with a substance whose viscosity is known over a somewhat wide range of temperatures, such as methyl-chloride according to measurements by DE HAAS (3). For methyl-chloride $T_k=416$, $p_k = 66$ (atm.), $M = 50$, and therefore $\sqrt[6]{\frac{T_k}{p_k^4 M^3}} = 0{,}024$; for hydrogen similarly $T_k=31$, $p_k=11$, $M=2$, so that $\sqrt[6]{\frac{T_k}{p_k^4 M^3}} = 0{,}40$. The boiling point of hydrogen is 20° K. and the corresponding temperature for methyl chloride is $20 \times \frac{416}{31} = 268°$ K., or about 0° C., at which temperature η for methyl chloride is 0,0022; it follows that for hydrogen at 20° K. $0{,}40\, \eta = 0{,}024 . 0{,}0022$, which gives $\eta = 0{,}00013$. As at this temperature the density of liquid hydrogen is about 0,071 (4), we have $\frac{\eta}{\mu} = 0{,}0018$.

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(1) On the other hand, in ZEMPLÉN's experiments (Ann. d. Phys., 19, 783, 1906) on the viscosity of air in which concentric spheres were used of 5 and 6 cms. radius the condition of nearly complete damping of the reflected wave is not satisfied by a long way; with $\nu = 0{,}0002$, $\mu = 0{,}00012$ and $T = 30$, $b' = 0{,}8$ i.e. $e^{-2b'(R'-R)} = \frac{1}{4}$ about. The damping is thus so weak in this case that the first correction-term (31) is not sufficient: we have therefore been obliged to abandon our intention originally formed, of recalculating ZEMPLÉN's experiments by means of our formulae.

(2) Comm. phys. Lab. Leiden, n°. 12, p. 9.

(3) Comm. phys. Lab. Leiden, n°. 12, p. 1

(4) Comm. phys. Lab. Leiden, n°. 137*d*.

14. In all the above calculations it is assumed that the oscillations of the sphere are only weakly damped; this condition can in any case be satisfied, independently of the specific properties of the liquid. For, even when L' obtains a high value, the logarithmic decrement, by formula (28) can be made as small as desired by giving the oscillating system a high moment of inertia; this does not necessarily involve a corresponding increase of the time of swing, because the rotational moment M may still be chosen at will.

It is, moreover, easily seen, that for substances with a small value of $\frac{\eta}{\mu}$ the circumstances must again be the most favourable: according to (28) and (30) it is exactly for these substances, that under otherwise equal circumstances the oscillations of the sphere will be least damped.

15. When equation (25) holds, the calculation of η, the quantities μ, R, K, T_0, T and δ being known from the experiment, can be made in a fairly simple manner. First L' and L'' are calculated with the aid of equations (28) or, as the case may be, (28'). An approximate value of η having been found, b' and b'' can be obtained in first approximation by means of (20) and using these values a sufficiently accurate value can in general be calculated from the terms $p = \frac{b'R+1}{(b'R+1)^2+b''^2R^2}$ and $q = \frac{1}{(b'R+1)^2+b''^2R^2}$ in equations (30). Finally it only remains to solve the following quadratic equation in $\sqrt{\eta}$:

$$(2+p)\eta + \gamma' R \sqrt{\mu\eta} = \frac{3L'}{8\pi R^3} \quad . \quad . \quad . \quad . \quad . \quad (a)$$

An alternative method of calculation would be from

$$\sqrt{\eta} = \frac{3L''}{8\pi R^4 \gamma' \sqrt{\mu(1-q)}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

but in general this will yield a much less accurate value owing to the smaller accuracy with which $\vartheta = \frac{T-T_0}{T_0}$ is determined as compared with δ. Equation (b) ought rather to be looked upon as a kind of check on the result obtained; but it may also render excellent service for the purpose of obtaining an approximate value for η, if this should not be known; in that case it is even sufficient to neglect q with respect to 1.

16. As an example of a calculation the results of a preliminary experiment made by Mr. Ch. Nicaise in water of 20° C. may be given here. A brass sphere of 1,927 cm. radius and weighing 250,8 grms. was suspended from a wire of phosphorbronze, such that in air the time of swing was 12,05 sec.; immersed in a large vessel with pure water the sphere had a periodic time of 12,24 sec. the amplitude of the oscillations diminishing per time of swing in a constant ratio, the natural logarithm of which was 0,1148 (it was found that this did not increase appreciably, until much narrower vessels were used, which shows that the liquid could be considered as being practically unbounded). For this experiment we have therefore $R = 1,927$, $K = 372,5$, $T_0 = 12,05$ (properly speaking the time of swing ought to have been measured in vacuo, but this would not have made a difference within the limits of accuracy of the observation) $T = 12,24$, $\delta = 0,1145$ (freed from the internal friction of the wire) [1]) and $\mu = 0,998$.

This gives $\frac{\delta}{4\pi} = 0,0091$ and $\psi = \frac{T - T_0}{T_0} = 0,016$, and therefore within the limits of accuracy of the observation

$$L' = \frac{2\delta K}{T_0} = 7,08 \quad , \quad L'' = \frac{4\pi\psi K}{T_0} = 6\,.$$

A first approximation with $\eta = 0,01$, gives $b' = b'' = \sqrt{\frac{\pi\mu}{\eta T}} = 5$, therefore $b'R = b''R = 10$, so that $p = 0,05$, $q = 0,004$. The viscosity is now given by

$$2,05\eta + 0,966\sqrt{\eta} = 0,1181.$$

hence:

$$\eta_{20} = 0,01014,$$

a value which agrees very well with the known data. The equation with L'' gives as a very rough verification $\eta = 0,010$.

17. The formulae become even simpler, if $b'R$ and $b''R$ are large numbers (say of the order 1000); in that case we have:

$$u = a\frac{R^2}{r^2}e^{-b'(r-R)} \quad , \quad \ldots\ldots\ldots \quad (32)$$

$$L' = \tfrac{8}{3}\pi R^4 b'\eta \quad , \quad L'' = \tfrac{8}{3}\pi R^4 b''\eta. \quad \ldots\ldots \quad (33)$$

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[1]) Observation gave $\delta = 0,1148$; in air $\delta = 0,0011$, of which, according to a calculation of L' with $\eta = 0,0002$ and $\mu = 0,0012$, the fraction 0,0008 is due to the friction of the air, so that 0,0003 is left for the internal friction of the suspension.

If δ is small at the same time, we have in first approximation

$$L' - L'' = \tfrac{8}{3}\,\pi R^4 \sqrt{\frac{\pi\mu\eta}{T}}\,, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (34)$$

from which, by (28')

$$\delta = \tfrac{4}{3}\,\frac{\pi R^4}{K}\sqrt{\pi\mu\eta T_0}\quad , \qquad \frac{T-T_0}{T_0} = \frac{\delta}{2\pi}\,. \quad . \quad . \quad . \quad . \qquad (35)$$

This extreme case is discussed by KIRCHHOFF in his Vorlesungen über mathematische Physik, N°. 26; it occurs when $\frac{\eta T}{\mu R^2}$ is a very small number[1]). This case would be realized, if in a liquid with small $\frac{\eta}{\mu}$ (say a liquid gas) a large sphere was made to swing quickly; taking say $\frac{\eta}{\mu} = 0{,}001$, in order to have $b'R = 1000$ with $R = 10$, it would be necessary for T to be 0,3. Apart from the not very practical nature of these conditions, it may be considered very doubtful, whether with the comparatively high velocities, involved in a rapid vibration of that kind the preceding theory would still hold. It seems to me, therefore, that the extreme case in question has no experimental physical importance.

When $b'R$ and $b''R$ are only moderately large L' and L'' may be developed according tot ascending powers of $\frac{1}{b'R}$ and $\frac{1}{b''R}$; if in addition the series (20) and (28'), are introduced, and the development is stopped at a definite point, formulae such as those of LAMPE[1]), KLEMENCIC[2]), BOLTZMANN[3]) and KÖNIG[2]) are obtained.

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[1]) KIRCHHOFF assumes $\varkappa$ to be very small, which must of course be taken to mean: under otherwise normal circumstances, for, taken absolutely, it has no sense to suppose a quantity which is not dimensionless to be very small, seeing that the value depends on the choice of units. For the rest, the liquid need not necessarily have a very small viscosity in order to obtain the simple case in question; a small friction would even be a disadvantage, if combined with a small density, as in the case of gases. For air for instance $\frac{\eta}{\mu}$ is about 0,2, and thus much larger than for water, notwithstanding the much smaller value of $\varkappa$ (comp. 12 note).

[2]) loc. cit.

[3]) Vid. LAMPE, Wien Ber. II. 93, 291, 1886. These formulae are as a rule not very suitable for accurate calculations, because a sufficient accuracy cannot be obtained with only a few terms; as an instance, KÖNIG's experiments can be calculated much more simply and accurately in the manner of section 15 of this paper, than by KÖNIG's own method. From one of KÖNIG's experiments (the last

18. The opposite extreme case is that, in which bR and $b(R'-R)$ are very small numbers; in that case R' cannot of course be infinite, i. e. the liquid must be bounded. With normal dimensions of the spheres and usual times of swing this case might be realized with liquids of very high viscosity; for ordinary liquids the time of swing would have to be much greater than practice allows.

In that case (24′) leads to:

$$L = L' = 8\pi R^3 \eta \frac{R'^3}{R'^3 - R^3} \quad \text{and} \quad L'' = 0 \;, \quad . \quad . \quad . \quad (36)$$

therefore
$$\delta = \frac{4\pi}{K} \frac{R'^3 R^3}{R'^3 - R^3} \eta T \quad \text{and} \quad \frac{T^2 - T_0^{\,2}}{T_0^{\,2}} = \frac{\delta^2}{4\pi^2}. \quad . \quad . \quad . \quad (37)$$

Seeing that by (22)

$$b''R = \frac{2\pi R}{VT} = \frac{2\pi R}{\lambda} \;, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

λ being the wave-length in the liquid, the physical meaning of the given simplifying condition is thus, that the radii R and R' are small as compared to the wavelength. In that case all the spherical shells in the liquid swing practically in the same phase [1] (q_r and y are nearly zero, so that u becomes real; in that case $u = x$ (sect. 4) and equation (11) reduces to the first equation (7)); at the same time approximately $e^{-b'(R'-R)} = e^{b'(R'-R)} = 1$, i.e. the waves are propagated without being appreciably damped, as they move forward. The resulting equation is this time:

$$u = a \frac{R^3}{r^3} \frac{R'^3 - r^3}{R'^3 - R^3} \,{}^{2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

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with sphere 3) I find for water of 15° $\nu = 0{,}01103$, whereas König himself found 0,01140.

[1] This is the simplifying condition used by Zemplén (Ann. d. Phys. (4) 19, 783, 1906) as the basis in the deduction of the formulae which served for the calculation of the results of his experiments; thereby he overlooked the fact, that in that case his coefficient m (our factor b') is very small, so that $\cos m\,(R-r')$ and $\sin m\,(R-r')$ ought to have been developed according to powers of $m\,(R-r')$; carrying out this development, his equation (14) leads to our equation (39) (it may be noted here, thot a small error has crept into his equation (14); the terms m^2Rr^2 and $m^2Rr_2^{\,2}$ should be m^2Rr and m^2Rr_2 respectively). As a matter of fact in Zemplén's experiments the assumed approximation is not applicable, for in his case $\lambda = 9$, and thus not large as compared to the radii of the spheres($R = 5$, $R' = 6$); his result is, therefore, very doubtful. Later on (Ann. d. Physik. 29, 899, 1909) he discovered this himsolf and gave a more accurate treatment of the problem; but owing to the very complicated nature of the correct formulae he did not submit his experiments to a new calculation.

2) This distribution of velocities is the same as the one found for uniform rotation (comp. for instance Brillouin l.c. p. 89); this explains itself by the consi-

When bR and bR' are only moderately small numbers, L' and L'' can be developed according to powers of those quantities; the equations (36) are the first terms of the series which are obtained in that manner. Probably η might be found by that method for ordinary liquids at low temperature.

19. The formulae become also very simple, when $R'-R$ is small with respect to R, a case which may possibly be of some importance experimentally. In that case:

$$u = a\frac{R'-r}{R'-R} \text{ [1]}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

$$L = \pi R^3 \eta \cdot \frac{R}{R'-R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

20. Although probably not of any practical utility I will for the sake of completeness discuss the case, in which the oscillating sphere is hollow, contains the liquid and swings about a smaller fixed sphere. Seeing that our general discussion of the state of motion in the liquid is not altered thereby, the preceding treatment retains in general its validity; the boundary-conditions also remain the same, so that equations (17) and (17′) remain valid. Only owing to the fact that $R > r > R'$, it is now more logical to write

$$u = \frac{1}{r^3}\left[P' e^{-b(R-r)}(br-1) + Q' e^{b(R-r)}(br+1)\right], \quad . \quad . \quad (42)$$

and the conditions at the boundaries now give

$$P' = \frac{aR^3(bR'+1)e^{b(R-R')}}{D}, \qquad Q' = -\frac{aR^3(bR'-1)e^{-b(R-R')}}{D} \quad (43)$$

where

$$D = (bR-1)(bR'+1)e^{b(R-R')} - (bR+1)(bR'-1)e^{-b(R-R')}, \quad (44)$$

As regards L, the expression given in (24′) still holds for it, except that it has to be provided with the negative sign, because now that the sphere undergoes friction on the inside, the tangential force is not F but $-F$ (comp. sect. 3 and 8); we thus have [2]:

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deration that, when the wave-length is large as compared to the radii of the spheres, the condition may at any moment be considered as stationary.

[1] This distribution of velocities agrees with that between two parallel planes, which move with respect to each other at constant speed; this result could have been expected.

[2] All the formulae for this case are obtained from the corresponding ones in 5 and 8 by giving R, R' and r everywhere the opposite sign; this is quite intelligible from a mathematical point of view.

$$L=\tfrac{8}{3}\frac{\pi R^3\eta}{D}[(b^2R^2-3bR+3)(bR'+1)e^{b\,R-R'}+(b^2R^2+3bR+3)(bR'-1)e^{-b\,R-R'}]\quad(45)$$

For the rest no alterations have to be made to section 9 and the calculation of η would proceed in the same manner as with an internal oscillating sphere.

21. Another case which is of practical importance and has found experimental application [1]), is that of a hollow sphere completely filled with liquid which is made to swing. It may be expected that this case can be derived as a special case from our general formulae by putting $R'=0$. In that case according to (53):

$$P'e^{-bR}=Q'e^{bR}=\frac{aR^3}{(bR-1)e^{bR}+(bR+1)e^{-bR}}\quad .\ .\ .\ (46)$$

and

$$u=a\frac{R^3}{r^3}\frac{(br-1)e^{br}+(br+1)e^{-br}}{(bR-1)e^{bR}+(bR+1)e^{-bR}}\quad .\ .\ .\ .\ .\ (47)$$

Physically, however, this is only possible, if for $r=0$, u does not become infinite and, as a matter of fact, it does not, for with $r=0$, u becomes

$$u_0=\tfrac{2}{3}ab^3\frac{R^3}{(bR-1)\,e^{bR}+(bR+1)\,e^{-bR}}\quad .\ .\ .\ .\ .\ (48)$$

In the general case the liquid cannot be at rest at the centre: the wave-motion starting from the oscillating sphere passes through the centre and expands again beyond it; this may also be formulated by saying, that the waves are reflected at the centre, this time as upon a free boundary, i. e. without reversal of phase. Only when bR is so large, that the motion is damped out before reaching the centre, $v_0=0$ practically and further

$$u=a\frac{R^3}{r^3}\frac{br-1}{bR-1}e^{-b(R-r)}\quad .\ .\ .\ .\ .\ .\ .\ (49)$$

22. In the case of a sphere filled with a liquid we have further (by putting $R'=0$ in (45)):

$$L=\tfrac{8}{3}\pi R^3\eta\frac{(b^2R^2-3bR+3)\,e^{bR}-(b^2R^2+3bR+3)\,e^{-bR}}{(bR-1)\,e^{bR}+(bR+1)\,e^{-bR}}\quad .\ (50)$$

If the wave-motion is damped out when arriving at the centre, i. e. if e^{-bR} may be put very small, the value of λ is given by

$$L=\tfrac{8}{3}\pi R^3\eta\frac{b^2R^2-3bR+3}{bR-1}\quad ,\ .\ .\ .\ .\ (51)$$

which is obtained from (25) by reversing the sign of R; in the same

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1) H. v. Helmholtz und G. v. Piotrowski, Wien. Ber. 40 (2), 607, 1860. H. v. Helmholtz, Wissensch. Abh., 1, p. 172.

G Zemplén, Ann. d. Phys., 19, 791, 1906; 29, 902, 1909.

Vid. also Lamb, Hydrodynamics, p. 578.

manner (30) will then give:

$$L' = \tfrac{8}{3}\pi R^3 \eta \left(b'R - 2 + \frac{b'R-1}{(b'R-1)^2 + b''^2 R^2} \right),$$

$$L'' = \tfrac{8}{3}\pi R^4 b'' \eta \left(1 - \frac{1}{(b'R-1)^2 + b''^2 R^2} \right) \quad . \quad . \quad . \quad . \quad (52)$$

The calculations are to be carried out as in § 15.

When $b'R$ and $b''R$ are very large, the same formulae (33) are arrived at as before, which means that, when the motion is completely extinguished at a very short distance from the oscillating sphere, it makes no difference whether the friction is internal or external; this might of course have been foreseen. [1])

23. When bR, and therefore also br, are very small, that is: when the wavelength is very large compared to the radius of the sphere, as would probably be the case with very viscous liquids (comp. § 18), it follows from (49) that $u = \alpha$, i. e. the sphere swings as a completely solid mass, as might have been expected a priori. There will thus be no damping and the time of swing must be that of a system the moment of inertia of which is equal to K with the addition of the moment of inertia of the liquid.

This actually follows from the above formulae, for (50) then reduces to

$$L = \tfrac{8}{15}\pi\, b^2 R^5 \eta = \tfrac{8}{15}\pi \mu R^5 k,$$

and introducing this into (26'), we find that

$$k' = 0 \quad \text{and} \quad \frac{1}{k''^2} = \frac{T^2}{4\pi^2} = \frac{1}{M}(K + K'),$$

where $K' = \tfrac{8}{15}\pi\mu R^5$, the moment of inertia of the liquid. [2])

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[1]) In PIOTROWSKI's experiments the aforesaid condition was not fulfilled, no more than in KÖNIG's experiments; R was $= 12{,}5$, $T = 30$, and hence $b'R = 7{,}5$ about. Still this value is sufficiently large to make the application of (51) allowable, and as in KÖNIG's experiments, this leads without difficulty to the value of ν. Similarly in ZEMPLÉN's experiments with air equation (51) is applicable to the inside-friction on the oscillating sphere, for with $\mu = 0{,}0012$, $\nu = 0{,}0002$, $T = 30$ and $R = 5$ one finds $b' = \sqrt{\dfrac{\pi\mu}{\eta T}} = 0{,}8$, hence $e^{-2b'R} = e^{-8} = \dfrac{1}{2000}$ about.

[2]) This result may be expressed as follows; L is imaginary in this case and

$$L' = 0 \quad \text{and} \quad L'' = \tfrac{8}{15}\pi\mu R^5 k'',$$

showing that the addition to the moment of inertia (comp § 10), is here equal to the actual moment of inertia of the liquid, and the equation of motion of the sphere becomes (29'):

$$(K + K')\frac{d^2\alpha'}{dt^2} + M\alpha' = 0.$$

Physics. — "*The viscosity of liquefied gases* II. *On the similarity of the oscillations of spheres in viscous liquids.*" By Prof. J. E. VERSCHAFFELT. Comm. N°. 148*c* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of October 30, 1915).

1. When two different spheres are swinging in two different liquids, the question may be raised, whether the one movement might be a conform representation of the second, that is to say, whether it is possible in each of the two cases to choose the units of length, mass and time such that, quantitatively, the two systems become identical. It is easily seen, that in general this is not possible.

Indeed it is clear, that the numerical values of quantities of dimension 0, such as: logarithmic decrements per time of swing of the oscillations of the spheres, are not changed by a change of the units. For two states of motion to be "similar", the logarithmic decrements have thus to be equal, which would naturally not be the case in general. Similarly in order that there may be correspondence in the two states of motion, the damping of the waves over corresponding distances must be the same in both systems; as the radii of the spheres are corresponding lengths, the quantity $b'R$, according to the previous communication, would have to be numerically equal in the two systems; this again would not necessarily be the case. In general therefore the two states of motion would not be similar.

On the other hand, when a definite state of motion is given, it is possible to produce a similar motion in a different liquid, and we shall now inquire, to what conditions this similarity is subjected.

2. In the first place there must be similarity in the motions of the spheres. These motions are represented by equation (2) of the previous paper: we may also write this formula as follows

$$\alpha = ae^{-\delta\tau}\cos 2\pi\tau = ae^{(-\delta+2\pi i)\tau} \text{ (real part)},$$

where $\tau = \frac{t}{T}$ i.e. the time measured in the time of swing as unit; if we take the time of swing in both cases as the unit of time, the expression no longer contains anything specific, if at a given moment α has the same value in both cases and δ is also equal in the two cases. We can of course arrange the experiments in such a manner, that the first condition is satisfied; we shall see immediately, how the second condition may be fulfilled.

In the second place the spherical shells, at corresponding distances, must perform the same motion, reduced to the time of swing as unit, that is in

$$a_r = ue^{kt} = ue^{(-\delta+2\pi i)\tau}$$

u must have the same value for corresponding values of r in the two systems. Seeing that the radii of the spheres are corresponding values of r, we shall find all corresponding values of r by taking equal multiples of R. Calling $\rho = \frac{r}{R}$ the reduced distance from the centre, the function u, reduced to the time of swing, must be the same for reduced distances. For an unbounded liquid we have according to (15)

$$u = a \frac{1}{\rho^3} \frac{\beta\rho + 1}{\beta + 1} e^{-\beta(\rho-1)},$$

where $\beta = bR$; it appears, therefore, in order that this expression may not contain any specific quantity, that the quantities b must be such in the two cases that $b_1 R_1 = b_2 R_2$. As $b = \sqrt{\frac{\mu}{\eta}}\, k$, it follows that $\frac{\mu R^2}{\eta T}(-\delta + 2\pi i)$ must have the same value in both cases, in other words $\frac{\mu R^2}{\eta T}$ must have the same numerical value.

In order therefore that similarity may exist between the two states of motion, R and T cannot be chosen at will: the radii of the spheres being given, at least one of the spheres must have a prescribed time of swing and in order to obtain this value the moment of inertia of the sphere and the rotational moment are at our disposal. As we shall see, both these quantities are thereby completely determined.

3. The motion of the sphere is determined by equation (26), which we may write in the form

$$k^2 T^2 + \frac{LT}{K} kT + \frac{M}{K} T^2 = 0.$$

If $kT = -\delta + 2\pi$ is to have the same value in both cases, the quantities $\frac{LT}{K}$ and $\frac{M}{K} T^2$ or $\frac{T^2}{T_0^2}$ have to be equal. Owing to the equality of bR, the equality of $\frac{LT}{K}$ involves on account of (25) that of $\frac{R^3 \eta T}{K}$; according to (28) the condition of the equality of $\frac{T^2}{T_0^2}$ is then satisfied at the same time and the periodic time of the damped vibrations is in both cases the same multiple of the periodic time of the undamped motion, or differently expressed: the reduced periodic time is the same.

Then it appears that for the similarity of the two motions it is necessary and sufficient that the expressions:

$$C_1 = \frac{\mu R^2}{\eta T_0} \text{ and } C_2 = \frac{R^3 \eta T_0}{K} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

have the same value in both cases; for given R, η and μ these equalities determine for one of the systems K and T_0 and therefore also M, since:

$$K = C_3 \mu R^5 \text{ and } T_0 = \frac{1}{C_1} \frac{\mu R^2}{\eta}, \text{ therefore } M = 4\pi \frac{K}{T_0^2} = C_4 \frac{\eta^2 R}{\mu}, \quad (II)$$

where C_3 and C_4 again stand for equal values in both cases. Each system of values of C_3 and C_4 defines a state of motion, of which there is thus a doubly infinite series.

If the oscillating system consisted of nothing but the sphere, we should have $K = \frac{8}{15} \pi \mu' R^5$, μ' being the density of the sphere, and in that case it follows from the required proportionality of K to μR^5, that μ' must be proportional to μ, i.e. the density of the sphere would have to be the same multiple of the density of the liquid in both cases. Seeing that the oscillating system can be more complicated, the latter condition does not need to be fulfilled, if only K has the required value.

4. We may conclude therefore that it is possible to obtain a conform representation of the oscillating movement of a sphere in a liquid, by taking a different sphere in a second liquid; the radius of the second sphere may even be chosen arbitrarily, but the moment of inertia of the vibrating system and the rotational moment are then completely determined. That there is no similarity in general, is due to the fact, that the motion depends upon five quantities: η μ, R,K and M, which can all be changed independently, whereas by making a suitable choice of the fundamental units for each case only three of these quantities can be made to assume equal values. If in each case a system of units is chosen such that $\eta = 1, \mu = 1$ and $R = 1$ it does not follow that K and M have the same value in both systems; the equality of the values of K and M expressed in the special units in the two systems is thus the condition to which similarity is tied down.

5. In the above discussion we assumed the liquid to be unbounded, but it is evident, that everything remains valid, when the liquid is externally bounded by a sphere; the only additional condition is that R' must have the same reduced value in both systems. By varying the ratio $\frac{R'}{R}$ in all possible ways (from 0 to ∞) an infinite series of similar cases is again obtained.

It is obvious that similarity may still exist, if the bounding surfaces were arbitrary, if only similar; the vibrating body would not even have to be a sphere[1]). For this reason it would be possible to make relative measurements of viscosities with "similar" apparatus (in the simplest case with one apparatus); this might be done by first determining the undamped time of vibration and the decrement in a standard liquid (e. g. water), then for the experiment in the liquid which is to be examined first modifying the moment of inertia of the vibrating system until condition (II) is satisfied, that is: for the same apparatus increasing or diminishing K proportionally to μ and finally changing the rotational couple until the logarithmic decrement becomes the same as in the first liquid: according to (I) the times of vibration of the undamped oscillations for one and the same apparatus would then be proportional to $\frac{\mu}{\eta}$ and in this manner it would be possible to calculate η.

It is obvious, however, that relative measurements of that nature would be much more elaborate than absolute measurements by direct calculation of η from experimental data obtained in the simple cases, which were dealt with in the previous paper.

6. Returning to the case of a sphere oscillating in an externally unbounded liquid, it was shown that all possible cases which can occur can be realized by giving K and M, or K and T_0 all possible values between 0 and ∞. In order to give a general survey of the different cases I have calculated for special values of μ, η and R a few systems of values of K and T_0 (or K and M) corresponding to definite values of δ and T. To simplify the calculations I have taken $\mu = 1$, $\eta = 1$ and $R = 1$ (C. G. S. units), representing a fictitious liquid which might, however, be realized at a special temperature by mixing special real liquids. In that case, δ and T being given, K and T_0 are determined by the equations (comp. equations 18, 28 and 30)

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[1]) This, of course, does not follow from the foregoing discussion but may be proved in a more general way. (Note added in the translation.)

$T = 10\pi$

$\delta =$	$T_0 =$	$\frac{T}{T_0} =$	$K =$	$M =$	$b' =$	$b'' =$	$V =$	$\lambda =$	$\Delta =$
0	10π	1	∞	∞	0.32	0.32	0.63	20	0.73
5π	2.75π	3.6	16.2	8.5	0.14	0.72	0.28	8.7	0.87
8π	1.10π	9.1	4.4	14.5	0.11	0.90	0.22	7.0	0.90
9π	0.65π	15	1.8	18	0.10	0.95	0.21	6.6	0.91
9.9π	0	∞	0	22	0.10	1.00	0.20	6.3	0.91

$T = 100\pi$

$\delta =$	$T_0 =$	$\frac{T}{T_0} =$	$K =$	$M =$	$b' =$	$b'' =$	$V =$	$=$	$\Delta =$
0	100π	1	∞	∞	0.10	0.10	0.20	63	0.91
10π	18.1π	5.5	106	1.29	0.03	0.32	0.06	20	0.97
20π	7.3π	13.7	39	2.95	0.02	0.45	0.04	14	0.98
25π	4.70π	21	23.5	4.3	0.02	0.50	0.03	13	0.98
30π	2.90π	34	12.0	5.9	0.02	0.55	0.03	11	0.99
35	1.05π	95	2.0	8.0	0.02	0.59	0.03	11	0.99
36	0	∞	0	9.1	0.02	0.60	0.03	11	0.99

$T = 1000\pi$

$\delta =$	$T_0 =$	$\frac{T}{T_0} =$	$K =$	$M =$	$b' =$	$b'' =$	$V =$	$\lambda =$	$\Delta =$
0	1000π	1	∞	∞	0.03	0.03	0.06	200	0.97
80π	18.8π	53	104	1.18	0.00	0.28	0.01	22	1.00
100π	11.4π	88	61	1.9	0.00	0.32	0.01	20	1.00
120π	5.8π	170	22.5	2.6	0.00	0.35	0.01	18	1.00
130π	3.0π	330	6.6	2.9	0.00	0.36	0.01	18	1.00
135π	0	∞	0	3.2	0.00	0.37	0.01	18	1.00

$T=\pi.$

$\delta=$	$T_0=$	$\frac{T}{T_0}=$	$K=$	$M=$	$b'=$	$b''=$	$V=$	$\lambda=$	$\Delta=$
0	π	1	∞	∞	1.00	1.00	2	6.3	0.37
π	0.75π	1.3	10.8	77	0.79	1.27	1.58	4.9	0.45
2π	0.45π	2.2	3.5	69	0.64	1.55	1.29	4.0	0.53
3π	0.20π	5	0.8	80	0.55	1.82	1.10	3.4	0.58
3.4π	0	∞	0	100	0.52	1.92	1.04	3.2	0.60

$T=2\pi$

$\delta=$	$T_0=$	$\frac{T}{T_0}=$	$K=$	$M=$	$b'=$	$b''=$	$V=$	$\lambda=$	$\Delta=$
0	2π	1	∞	∞	0.71	0.71	1.41	8.8	0.49
π	1.65π	1.2	23.1	34	0.56	0.90	1.11	7.0	0.57
2π	1.10π	1.8	8.6	29	0.46	1.10	0.90	5.8	0.63
3π	0.65π	3.8	3.8	36	0.39	1.29	0.77	4.9	0.68
4π	0.30π	6.7	1.1	45	0.35	1.46	0.68	4.2	0.70
4.5π	0	∞	0	51	0.33	1.53	0.66	3.9	0.71

$T=4\pi$

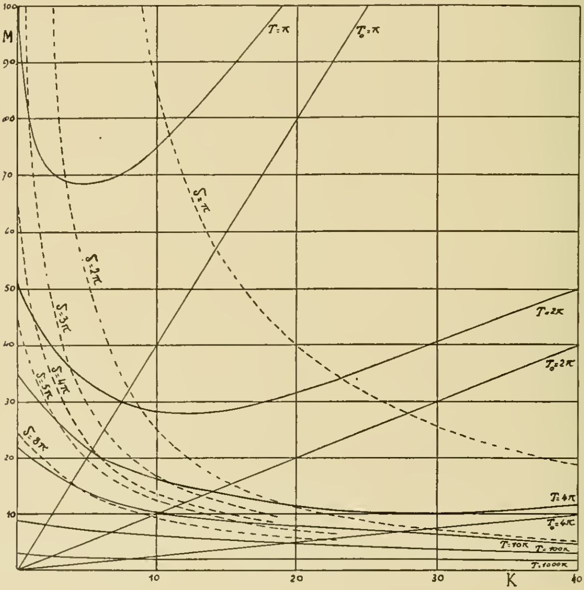
$\delta=$	$T_0=$	$\frac{T}{T_0}=$	$K=$	$M=$	$b'=$	$b''=$	$V=$	$\lambda=$	$\Delta=$
0	4π	1	∞	∞	0.50	0.50	1.00	12.6	0.61
2π	2.45π	1.6	19.2	12.8	0.32	0.78	0.64	8.1	0.73
3π	1.65π	2.4	10.8	16	0.28	0.91	0.54	6.9	0.76
4π	1.10π	3.6	6.0	20	0.25	1.03	0.48	6.1	0.78
5π	0.60π	6.7	2.7	27	0.22	1.14	0.43	5.5	0.80
6π	0.20π	8	0.4	34	0.20	1.24	0.40	5.1	0.82
6.2π	0	∞	0	35	0.20	1.26	0.39	5.0	0.82

$$\frac{8\,\pi}{3\,K}\left(b'+2+\frac{b'+1}{(b'+1)^2+b''^2}\right)=\frac{\delta}{T}\left[\frac{T^2}{T_0^{\,2}}\frac{4\pi^2}{4\pi^2+\delta^2}+1\right]$$

$$\frac{8\,\pi}{3\,K}\left(1-\frac{1}{(b'+1)^2+b''^2}\right)b''=\frac{2\pi}{T}\left[\frac{T^2}{T_0^{\,2}}\frac{4\pi^2}{4\pi^2+\delta^2}-1\right]$$

$$b'=\sqrt{\frac{-\delta+\sqrt{\delta^2+4\pi^2}}{2T}}\ ,\qquad b''=\sqrt{\frac{\delta+\sqrt{\delta^2+4\pi^2}}{2T}}.$$

By means of these relations the tables of page 864 and 865 have been obtained, which also contain the values of $\frac{T}{T_0}$, the quantities b' and b'', the velocity of propagation of the waves V, the wavelength λ and the damping-factor $\Delta = e^{-b'}$, i.e. the ratio in which the amplitude of the oscillation is reduced in a distance of 1 cm.



7. It appears from these tables that not every system of values of T and δ gives a possible system of values for K and T_0 or of K and M. For δ very small K and M are very large and in that case $T_0 = T$; as δ diminishes, K, T_0 and also M decrease, but,

whereas K and T_0 approach a final value of 0, M goes through a minimum and then rises once more to a limiting value. Similarly there is a maximum-value for δ, above which with a given T it cannot rise; for higher values of δ K would become negative and T_0 imaginary; the limit lies at a higher value, as T itself is larger, but compared to T it becomes smaller and smaller, so that $\frac{\delta}{T}$ becomes itself zero for $T = \infty$.

On the other hand to every finite system of values of K and M corresponds a finite set of values for δ and T. In order to make this clearer a graphical representation of the Tables may be given in a K, M-diagram. Here the drawn-out curves are those along which T is constant, the dotted curves those for $\delta =$ constant. A few T_0 curves are also given $\left(\frac{K}{M} = Const.\right)$ to which the corresponding T curves approach asymptotically.

8. The Tables and corresponding diagram can also be utilised in a more general case; K must then be replaced by the characteristic constant $C_3 = \frac{K}{\mu R^5}$ and M by the characteristic constant $C^4 = \frac{\mu M}{R\eta^2}$. The values given in the Tables for T, b, V, λ and $\Delta = e^{-b'}$ are then in general those of $\frac{\eta T}{\mu R^2}$, bR, $\frac{\mu R V}{\eta}$, $\frac{\lambda}{R}$ and $e^{-b'R}$, corresponding to a set of values of C_3 and C_4; from those values it is thus possible to calculate T, b, V, λ and Δ under other more general circumstances. The value of δ as well as that of $\frac{T}{T_0}$ naturally remain unaltered.

The above results can also be used to derive what happens when one of the quantities is gradually altered, the others remaining the same. As an example, without making any change in the adjustment of the apparatus, liquids can be taken of increasing viscosity; in that case C_3 does not change, whereas C_4 diminishes continually; δ and T are then found to increase gradually, V diminishes, λ increases and Δ approaches the value 1.

Physics. — "*Two theorems concerning the second virial coefficient for rigid spherical molecules which besides collisional forces only exert* Coulomb-*forces and for which the total charge of the active agent is zero*". By Dr. W. H. Keesom. Supplement No. 39*b* to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes).

(Communicated in the meeting of October 29).

§ 1. In calculating the second virial coefficient B in the equation of state written in the form:

$$pv = RT\left(1 + \frac{B}{v} + \frac{C}{v^2} + \ldots\right) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for a system of rigid spherical molecules, which carry a doublet at the centre (Suppl. No. 24*b*, June 1912), the second term in the development according to inverse powers of the temperature:

$$B = B_\infty\left(1 + \frac{b_1}{T} + \frac{b_2}{T^2} \ldots\right) . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

did not occur. This was also the case as regards all the higher odd powers.

In treating rigid spherical molecules which carry a quadruplet of revolution-type in Suppl. No. 39*a* (see p. 636), the second term in (2) was again found to be absent, but in this case the higher terms with b_3 etc. were present.

The question now arises whether general conditions can be given for the structure of the molecules under which the second term in (2) does not occur.

If, as will appear to be the case, such conditions can be given, the next question is: can still further conditions be given under which, if also satisfied by the molecules, no one of the odd powers of T^{-1} occurs in (2)?

In discussing these questions we shall place ourselves completely on the basis of classical mechanics.

In that case the following theorems can be proved:

1. In the development of B the term with T^{-1} does not occur if the following conditions are fulfilled:

(*A*). *a*. the molecules behave at their collisions as rigid spheres,
b. the attractive or repulsive forces[1]), which the molecules exert on each other, originate from fixed points in the molecule, and can be derived from a Coulomb law of force (inversely proportional to

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[1]) Not including the collisional forces.

the second power of the distance between the attracting or repulsing points), so that these forces might be ascribed to an electric agent.[1]) possibly with multiple points[2]),

c. the total quantity of the agent in each molecule $= 0$ (the molecules behave as electrically neutral).

2. No odd power of T^{-1} occurs, if the following conditions are fulfilled:

(B): *a*, *b* and *c* as above, and besides:

d. the molecule possesses, as regards its attractive and repulsive forces, at least one axis of "inverse symmetry", by which expression we mean, that each volume element contains a quantity of the agent (as indicated under *b*) equal and opposite to that of the volume element with which it coincides after a revolution about that axis through an angle of $2\pi/k$, k being a whole and necessarily even number[3]).

In this case B is an even function of the temperature.

The proof of these two theorems follows below in § 3 and 4.

If in the development of B according to (2) the second term does not occur, the series for B reduces for high temperatures to:

$$B = B_{\infty}\left(1 + \frac{b_2}{T^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This dependence of B on the temperature is the same as that which follows from VAN DER WAALS' equation by putting $b_W =$ constant, and assuming for a_W with CLAUSIUS and D. BERTHELOT: $a_W \backsim T^{-1}$ (cf. Suppl. N°. 39*a*). Hence if the molecules satisfy the conditions (A), then for high temperatures and at densities for which only encounters of two molecules at a time have to be considered, the equation of state in the form accepted by D. BERTHELOT would hold.

If the conditions (B) are fulfilled the agreement with BERTHELOT's equation of state is still closer in consequence of the absence of the term b_3/T^3.

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[1]) On the supposition that electrodynamic forces (other than magnetic) need not be considered.

[2]) In this, if need be, a magnetic agent may be included.

[3]) As examples of this we mention the cases, that a molecule contains two positive and two negative charges situated at the corners of a square, the centre of which coincides with that of the molecule. If the homonymous charges lie diametrically opposite to each other, the molecule has one quadruple and two double axes of inverse symmetry. in the other case it has two double axes of inverse symmetry. We have another example, where the charges form a figure of revolution about an axis through the centre of the molecule, and the part on one side of the equatorial plane is the "inverse image" of the part on the other side.

§ 2. The second virial coefficient for a gas the molecules of which fulfil the conditions (A) can be deduced by the method given in Suppl. N°. 24, for which method BOLTZMANN's entropy principle serves as basis. This deduction follows more particularly the lines of the treatment in § § 4 and 6 of that paper; it differs, however, from that treatment in the following points:

1st. The three principal moments of inertia are now supposed to be unequal. In this case also in determining micro-elements of equal probability the expression $d\varphi d\theta d\chi d\bar{\varphi} d\bar{\theta} d\bar{\chi}$, φ, θ and χ being the angles which determine the position of the principal axes of inertia relative to a fixed system of coordinates, and $\bar{\varphi}$, $\bar{\theta}$ and $\bar{\chi}$ being the corresponding moments of momentum, may be replaced by $dod\chi dp_2 dq_2 dr_2$, where do represents a surface element of the sphere of unit radius, which serves for marking the position of one of the principal axes of inertia, and p_2, q_2 and r_2 represent the velocities of rotation about the principal axes of inertia.

2nd. For determining the relative position of the two members of a pair of molecules, we now need, besides the coordinates r, θ_1, θ_2, φ, which as in Suppl. N°. 24b § 6 and recently N°. 39a fix the distance of the centres and the relative orientation of a definite arbitrarily chosen principal axis of inertia of one molecule relative to the corresponding axis of inertia of the other molecule, two more angles, which for each molecule specify the azimuth of the plane going through the principal axis of inertia mentioned above and a second principal axis of inertia. As such we may choose the angle χ_1 between that plane and the plane which contains the first principal axis of inertia and the line joining the centres . χ , and similarly χ_2, for the second molecule, are counted from 0 to 2π.

Quite analagously to Suppl. N°. 24b § 6 the following result is obtained:

$$B = \tfrac{1}{2}\, n \left(\tfrac{4}{3}\, \pi\sigma^3 - P'\right) \quad . \; . \; . \; . \; . \; . \; . \; . \qquad (4)$$

where now [1]:

$$P' = \frac{1}{8\pi^2} \int_\sigma^\infty \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \left(e^{-hu_{b1}} - 1\right) r^2 \sin\theta_1 \sin\theta_2\, dr\, d\theta_1\, d\theta_2\, d\chi_1\, d\chi_2\, d\varphi \; . \qquad (5)$$

In this formula u_{b1} is again the potential energy of a pair of molecules in the position indicated by definite values of $r \ldots \varphi$, the

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[1] As in P' the manner in which the density is distributed over the spherical molecule does not occur, it appears that the limitation to molecules of spherical symmetry observed in Suppl. N°. 24b § 6, can be omitted (cf Suppl. N°. 39a § 2 note).

potential energy for $r = \infty$ being chosen as zero. Further $h = \frac{1}{kT}$, k being PLANCK's constant. Finally the attraction is supposed to decrease sufficiently rapidly with increasing r, for the integral in (5) to be convergent.

§ 3. For the proof of the first of the theorems mentioned in § 1 we develop P' according to ascending powers of h. The first term becomes:

$$-\frac{1}{8\pi^2}\; h \int_0^\infty\int_0^\pi\int_0^\pi\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} u_{b1} r^2 \sin\theta_1 \sin\theta_2 \, dr d\theta_1 d\theta_2 d\chi_1 d\chi_2 d\varphi \,. \quad . \qquad (6)$$

The integration according to θ_2, χ_2 and φ, the coordinates r_1, θ_1 and χ_1 being kept constant, must necessarily give 0, if the conditions (A) are fulfilled. In fact the result of this integration can be represented as the potential energy of a molecule 1 relative to a great number of superposed molecules 2, all with the same centre, but further as regards their orientations uniformly distributed over all the possible positions. By this superposition at the limit a sphere is obtained in which the agent is uniformly distributed over concentric shells. According to a well known theorem of the theory of potential, the potential outside such a sphere is constant if the total quantity of the agent acting according to COULOMB's law of the inverse square of the distance equals 0; from this, together with the assumption mentioned above about u_{b1} becoming 0 for $r = \infty$, follows the above result; the theorem in question is hereby proved.

§ 4. The odd powers of h in the development of P' (§ 3) occur in the following form:

$$-\frac{1}{8\pi^2}\cdot\frac{1}{(2q+1)!}\cdot h^{2q+1} \int_0^\infty\int_0^\pi\int_0^\pi\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} u_{b1}{}^{2q+1} r^2 \sin\theta_1 \sin\theta_2 \, dr d\theta_1 d\theta_2 d\chi_1 d\chi_2 d\varphi \qquad (7)$$

q is here a whole positive number.

If the conditions (B) are fulfilled, the integration of this integral according to θ_2, χ_2 and φ, the coordinates r, θ_1 and χ_1 being kept constant, will again necessarily give 0. This results from the fact that each contribution to the integral, obtained from positions of the second molecule indicated by definite values of θ_2, χ_2 and φ, with the ranges $d\theta_2$, $d\chi_2$, $d\varphi$, is neutralized by the contribution obtained from positions, which can be derived from the first by a revolution through an angle of $2\pi/k$ about one of the axes of inverse symmetry. With this the second theorem mentioned in § 1 is proved also.

Physics. — "*Investigation of the equilibrium liquid—vapour of the system argon—nitrogen*". By G. Holst and L. Hamburger. (Communicated by Professor H. Kamerlingh Onnes.)

(Communicated in the Meeting of October 30, 1915).

Summary: I *Introduction*. II. *Preparation and analysis of the gases*. 1. Preparation. 2. Test of purity. 3. Methods of analysis. III. *Temperature measurement*. IV *Determination of the end-points of condensation*. 1. Apparatus. 2 Vapourpressures of oxygen, nitrogen and argon. 3. Mixtures. V. *Determination of the points of beginning cond nsation*. 1. Apparatus. 2. Measurements. 3. Equation of state of the mixtures. VI. *Tx- and px-diagrams*. VII. *Resumé*.

I. *Introduction*.

Owing to the development in recent years of the incandescent-lamp industry the problem of the technical preparation of argon has come to the front. For this purpose it was natural that beside chemical methods the cryogenic method should draw the attention. As it is a simple matter to obtain mixtures of argon and nitrogen by chemically removing the oxygen from oxygen-nitrogen mixtures which are rich in argon, an investigation became desirable of the behaviour of argon-nitrogen mixtures at low temperature with a view to collecting useful data for a possible argon-nitrogen rectification. This investigation has been carried out by us and we have determined the composition of the liquid and vapour phase as a function of temperature and pressure in the corresponding range of temperatures.

II. *Preparation and analysis of the gases*.

1. *Preparation*.

The preparation of the gases was in general carried out in glass apparatus which had been previously exhausted with a mercury pump and liquid air to a pressure of 0.0003 to 0.001 mm. and subsequently washed out with pure gas. For the calibration of our thermometer the vapour-pressure of pure oxygen was used.

a. *Oxygen*.

This gas we prepared from recrystallised, dry potassium permanganate; the first portion of the gas evolved was drawn away and the rest of the oxygen formed was condensed; the middle fraction of the condensed gas was used.

b. *Nitrogen*.

This gas we prepared from ammonium sulphate, potassium chromate and sodium nitrite; in the purification special attention was given to the removal of nitric oxide (glowing copper); for further details we refer to a paper which will appear elsewhere.

In this case, as well as in that of oxygen, the purity of the gas was proved inter alia by the equality of the vapour-pressures obtained at the beginning and at the end of condensation.

c. *Argon.*

For this gas we could start from the strongly argonous gas-mixtures which the firm of LINDE has recently brought into the market The final purification was effected by means of HEMPEL's mixture [1]) in a manner similar to that given by CROMMELIN [2]). The only modification which we applied in our apparatus consisted in each tube containing chemical substances which might develop impurities, such as water-vapour etc., or conversely might react with them, being flanked at each end by cooling tubes immersed in liquid oxygen. Care was taken, moreover, that during the complete circulation-process the gas should be at a higher pressure than the atmosphere throughout the whole apparatus.

Again in this case the final product was found to satisfy the test of equal pressures at the beginning and the end of condensation.

d. *The mixtures.*

The mixtures were prepared by adding nitrogen to LINDE's argon-nitrogen mixtures after these had been freed from oxygen by means of glowing copper. The nitrogen had been obtained from air by liberation from oxygen. We gladly acknowledge our indebtedness to Mr. H. FILIPPO JZN. for his kind collaboration in this part of our work. In a few cases use was made of the method of diminishing the percentage of nitrogen of LINDE's mixtures (down to about 5°/₀) by means of a fraction-apparatus constructed by Mr. FILIPPO.

2. *Test of purity.*

The gases and mixtures were tested for the following impurities or, if necessary, simultaneously freed from them.

a. *Water-vapour* and *carbon dioxide* were removed from the gases which were kept above water, freed from air by boiling, by passing them previously to the measurements through a couple of cooling tubes immersed in liquid oxygen.

b. *Hydrocarbons.* It was found that these were not present: a thin spiral wire of tungsten which was made to glow in the gas mixture was found not to change in resistance [3]).

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[1]) W. M. HEMPEL. Gasanal. Methoden, 3nd edition p. 151.

[2]) C. A. CROMMELIN. Dissert. Leiden 1910.

[3]) Comp. L. HAMBURGER, Chem. Weekbl. 12, (1915) 62.

c. *Oxygen* was completely removed with yellow phosphorus.

d. *Carbon monoxide.* The gas was tested for this by means of I_2O_5[1]: it was found not to contain more than $^1/_{50}$ %.

e. *Hydrogen.* In testing for this gas we used the method given by PHILLIPS[2]. The gas contained less than 0.01 % of hydrogen. We may add, that the gases were always condensed before they were used in the measurements and that the liquefied gases were then made to boil under reduced pressure; the vapour that was drawn off must have contained the last traces of hydrogen present and the small admixture of neon must also have been for the greater part removed in this way.

Finally we may give the following data as providing a measure of the purity of the gases.

A. Oxygen. The gas was analysed by means of copper (immersed in an ammoniacal solution of ammonium carbonate), later on with sodium hydrosulphite. It was found to contain more than 99.9 % of oxygen.

B. Nitrogen. Observations were made with nitrogen, obtained from air by removal of oxygen, which corresponded completely to those made with chemically prepared nitrogen, taking into account the percentage of argon in air nitrogen.

This correspondence, with such widely different methods of preparation, may give us additional confidence that our gases were satisfactorily free from impurities.

C. Argon. This substance was tested for absence of nitrogen indirectly by means of the determination of the pressure at the beginning and the end of condensation, but also more directly by means of glow-discharges in potassium vapour (comp. 3) in which no diminution of volume could be detected. (Comp. also the determination of specific gravity § 3*c*).

3. *Methods of analysis.* It follows from the above that the only gas besides argon which could be present in the mixtures which were intended for the measurements was nitrogen. This fact made it possible to determine the percentage of nitrogen by means of a baroscope. It appeared, however, that the sensitivity of the available balance was not so high as we should have wished, in consequence of which these determinations, at least in the most unfavourable

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[1] Comp. DENNIS, Gas analysis (1913) p. 231 and 235.

[2] Am. Chem. J. **16** 259 (1894).

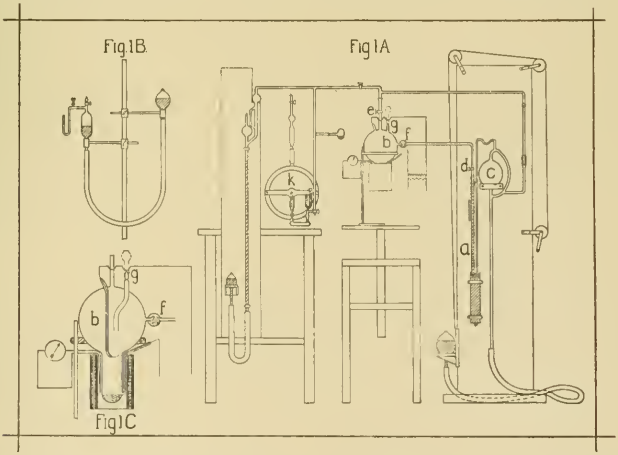
case, are not more accurate than to about 0.2 %. Fortunately we were able to carry out the analysis more accurately by a chemical method, which enabled us to attain an accuracy of 0.1 %.[1] We shall begin by a description of the latter method.

A. *Determination of the percentage of nitrogen in Ar—N mixtures by means of glow discharges in potassium vapour.*

It has been long known[2], that in electric discharges through gases such as nitrogen, hydrogen etc. a chemical reaction may occur, especially between the material of the cathode and the rarified gas. Mey[3]) pointed out, that this provided a means of liberating rare gases from admixtures. This method was further developed by Gehlhof[4]), who succeeded by means of glow discharges through potassium vapour in preparing spectroscopically pure rare gases comparatively rapidly — although not in large quantities.

In order to adopt this method to a quantitative analysis of *Ar—N* mixtures the following apparatus was constructed by us.

A definite quantity of the gas-sample which is collected above



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[1] The readings might have been further refined by the use of a cathetometer. but we did not adopt this method, as an accuracy of 0,1 % was sufficient for our purpose.

[2] Comp. G. Salet, Pogg. Ann. (158) 332, 1876. L Zehnder, Wied. Ann. (52) 56, 1894.

[3] Mey, Ann. d. Phys. 11 127 (1903). Gehlhoff and Rottgardt, Verh. d. D. phys. Ges. 12 411 (1910).

[4] Gehlhoff, Verh. D. phys. Ges. 13 271 (1911).

mercury (fig. 1B) was drawn into the burette *a* (fig. 1A). Previously the absorption-apparatus *b* and the TÖPLER-pump *c* had been exhausted by means of the mercury pump *k*; tap *e* was then closed and by opening *d* the gas was transferred from the burette into *b* by means of the mercury column in *C*. On the bottom of the absorption-apparatus (fig. 1C) is the potassium, which is now heated to 200°C. by means of a small electric furnace. An induction-coil is used to send a glow-discharge through the evolved potassium-vapour.

After a few hours — the time required depends on the percentage of nitrogen in the mixture — the unabsorbed portion is transferred back to the burette by means of the TÖPLER-pump.

In using the method the question arises, whether the potassium which may be deposited from the vapour on the cooler parts of the absorption-vessel [1]) may possibly absorb argon at its large, freshly formed surface. It is well known, that sublimated metals may absorb at their finely divided surface even the rare gases. Fortunately argon often does not show the phenomenon [2]). It appeared, moreover, that in our case an absorption of this nature was improbable, from the fact that, after the nitrogen had been absorbed, there was always a residue of gas left which did not show any further contraction however long it remained exposed to the glow-discharge. In the mean time the potassium goes on evaporating and depositing on the colder surfaces, so that the metallic surface is constantly being renewed. If an appreciable absorption of argon took place, it would have been impossible to obtain a constant final volume. It may finally be noted, that a sample of the pure argon which we had prepared did not show any contraction in the absorption-apparatus.

We have also tried to utilize for the purpose of analysis the method of binding nitrogen recommended by STARK [3]) (electric discharge through mercury vapour). It was found, however, that for a sufficient rate of absorption we had to work at much lower pressures — even when the electrodes were placed opposite each other in the middle of the vessel. With potassium on the other hand every gas-mixture, however high the percentage of nitrogen might be, could be made to react with the metallic vapour at relatively high pressures. [4])

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[1]) As well as the compound which is formed.

[2]) TRAVERS. Proc. Roy. Soc. 60 449. Comp. also KOHLSCHÜTTER, Jahrb. Radioakt. 9 402. (1912).

[3]) Phys. Zeitschr. 1913 p. 497.

[4]) It is very probable that the reaction is in general started by the splitting of

B. Determination of the percentage of nitrogen by means of a baroscope.

For this purpose use was made of the difference in the upward pressure produced by the gas-mixture on a glass body (volume about 300 c.m.^{3}) which was suspended from one arm of a balance as compared to an open glass vessel of an equal outer surface on the other arm.

The apparatus was arranged in such a manner, that by the turning of a properly shutting glass tap the arresting arrangement of the balance could also be put into action in a high vacuum. The pressures were read by means of a cathetometer.

The following data 1) were used for the baroscope-determinations: density of *air,* free from water-vapour and carbon dioxide, 45° N.L., sea-level, 0° and 76 cm.

air, free from water-vapour and carbon dioxide, 45° N.L., sea-level, 0° and 76 cm.	0.0012928
nitrogen (Rayleigh and Leduc)	12514
argon (Watson)	17809

C. *Results.*

The following table (p. 878) (column 1—6) gives a survey of different determinations by methods A and B.

In deducing the mean (column 6) we have attributed a double weight to the determinations by method A.

When the mean of the results by method A is compared with those by method B, a systematic deviation will be seen to exist which increases with the percentage of argon in the mixture. As the baroscope had been previously calibrated with other gases (carbon dioxide, nitrogen, air) with satisfactory results, we were led to conjecture that the atomic weight of argon, respectively its specific

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the nitrogen molecules by the electric discharge, the atoms which are formed combining with the potassium. Strutt, (Proc. Royal Soc. Serie A **85** 219 and subsequent volumes) found that the re-combination of the N-atoms to molecules (which do not react with the potassium) is much accelerated by an increase of the pressure. This was the main ground, on which we chose the dimensions of the absorption-vessel large as compared with those of the burette. (The low pressure also facilitates the production of the discharge). The fact explains in particular, why the time of absorption in our analyses increases with the percentage of nitrogen in the mixtures. It is also known (Strutt l. c. comp. also Koenig Zeitschr. f. Electroch. 1915. 1 June), that metallic vapours accelerate the molisation of nitrogen atoms. (An afterglow on interrupting the discharge was therefore entirely absent in our apparatus). It is of course possible that mercury has this property to a higher degree than potassium, although a different affinity of mercury towards N may also play a part here; this might be one reason for the stronger reaction of the potassium vapour.

) Landolt-Börnstein Phys. Chem. Tabellen. 4th ed.

gravity, as at present assumed, was probably not entirely accurate, and we made preparations for an accurate determination. A preliminary measurement gave the normal density as 0.001783^4.

TABLE 1.

Number of the gas-mixture.	Method A $^0/_0$ N.			Method B $^0/_0$ N.	Assumed value.	Method B. modified value.	Final value.
	1st determination.	2nd determination.	3rd determination.				
I.	82.6	82.6	—	82.5	82.6	82.6	82.6
II.	65.2	65.3	65.4	65.0	65.2^5	65.2	65.3
III.	31.4	31.6	—	31.3	31.4^5	31.6^5	31.5
IV.	9.9	9.9	—	9.7^6	9.9	10.2^5	10.0
V.	74.2	74.0	—	73.7	74.0	73.8^5	74.0^5
VI.	52.9	52.8	—	52.4	52.7^5	52.7	52.8
VII.	24.4	24.2^5	—	23.8	24.2	24.2	24.3
Pure argon.	0.0	—		−0.5	0.—	0.0	0.0
1.	2.	3.	4.	5.	6.	7.	8.

The account of our investigation had already been written, when a paper appeared by H. Schultze 1) in which the specific gravity of argon is given as 0,00178376. When we use this value, we obtain the results given in columns 7 and 8 of the above table. The mean difference between the determinations with the baroscope and those by method A is now only 0.04$^0/_0$, in other words there is no sign now of a systematic deviation between the two methods. This result proves on the one hand the reliability of method A and may on the other hand be taken to confirm Schultze's result. We hope soon to be able to publish the results of a more accurate direct determination.

III. *The temperature measurement.*

The measurements were made in a bath of liquid oxygen. In the construction of the cryostat as well as of many other parts of our apparatus we could avail ourselves of the experience gained in the cryogenic Laboratory at Leiden, where one of us had the advantage of working for several years under the guidance of

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1) Ann. d. Physik 48 (1915) p. 269. Heft 2 published 14 Oct. '15.

Professor H. Kamerlingh Onnes. The temperatures were measured with the aid of a platinum resistance-thermometer. The wire was about 0,1 mm. in diameter and was wound bifilarly on a small tube of Marquardt-material on which a double spiral groove had been cut. At the ends of the tube stouter platinum wires were autogenically sealed on; to these wires the four copper leads were soldered. Before using the thermometer it had been treated thermally by a tenfold immersion in liquid air, each time followed by glowing at about 700°. By that means a constant zero-point was obtained. On three different days the resistance w_0 was found equal to 18.4695 Ω, 18.4697 Ω and 18.4695 Ω respectively; it was measured with a differential galvanometer by Kohlrausch's method.

The calibration of the thermometer took place by using the vapour-pressures of oxygen as determined by Kamerlingh Onnes and Braak, [1]) in the apparatus in which the end-points of the condensation were determined. If p represents the vapour-pressure in mms., the relation between T and p in the range 83,5° and 90° abs. is: [2])

$$T = \frac{369,83}{6,98460 - log.\, p}.$$

The ratio $\frac{w}{w_0}$ was determined at the same time.

For the Leiden standard platinum thermometer Pt'_1 the ratio $\frac{w}{w_0}$ as a function of the temperature in the range of temperatures in question is accurately known. It is therefore possible to calculate the value of the constant α in the linear relation which according to Nernst holds for different thermometers:

$$\Delta\left(\frac{w}{w_0}\right) = \alpha\left(1 - \frac{w}{w_0}\right).$$

With $\alpha = 0,00121$ our thermometer could be reduced to Pt'_1 and this constant was therefore used in calculating the temperatures.

To test the apparatus which served for the determination of the points of beginning condensation for its utility, the boiling point of oxygen was also determined in it. The pressure was 762.4 mm. According to the vapour-pressure formula this corresponds to a temperature of 90°.15; the ratio $\frac{w}{w_0}$ gave 90°.16, which agrees very closely. As α was comparatively small for our thermometer [3]) and,

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[1]) H. Kamerlingh Onnes en Braak. Comm. Leiden No. 107*a*.

[2]) G. Holst. Comm. Leiden No. 148*a*.

[3]) H. Schimank, (Ann. d. Phys. (45) 706, 1914), gives 0.1–0.2° as the uncertainty for $\alpha = 0.03$.

TABLE 2.

p_{mm}	T	$\left(\frac{W}{W_0}\right)$	$\left(\frac{W}{W_0}\right)_{Pt'_1}$	α
758.1	90.10	0.25258	0.25166	0.00123
757.6	90.09	0.25251	0.25162	0.00119
593.2	87.82	0.24273	0.24184	0.00118
751.2	90.01	0.25220	0.25127	0.00124
			Mean . . .	0.00121

as our platinum was obtained from Heraeus like that of Pt'_1, it is very probable that the temperatures as given by us are correct to about 0,02°.

IV. *Determination of the end-points of condensation.*

1. *The apparatus.* The end-points of condensation were measured by means of a vapour-pressure apparatus provided with a stirrer, as used by Kuenen. The small vessel was placed in a cryostat which contained, beside the resistance-thermometer, a small pump which provided a thorough circulation in the oxygen-bath. The temperature was regulated by an adjustment of the pressure in the cryostat. The constancy of the temperature during the measurements was about 0,01°.

2. *Vapour-pressures of oxygen, nitrogen and argon.*

Beside the measurements which served as a calibration of our thermometer we determined the vapour-pressure of oxygen at two other temperatures.

TABLE 3.

T	p	T calc. from vapour pressure formula
83.49	357.7	83.47
78.42	184.3	78.37

Whereas at 83°.5 the temperature as measured agrees with that calculated from the vapour-pressure to within 0.02°, there is a difference of 0.05° at 78°. It will therefore be advisable as a precaution not to use the formula for T as a function of $\log p$ for purposes of extrapolation.

For nitrogen we found:

TABLE 4.

T	p
80.88	1138.0
78.50	878.1
72.10	396.6
69.29	264.6

For argon:

TABLE 5.

T	p
89.95	1001.0
87.78	801.7
87.76	802.2
84.02	533.9
83.84	522.6
83.78	518.7
83.71	514.1
83.62	509.2

and hence for the triple point $T = 83°,81$ $p = 521,4$ m.m.

We shall compare these figures with some recent ones of other observers.

For oxygen the measurements by HENNING[1]) and by v. SIEMENS[2]) may be used.

For all these measurements we have drawn $log.\, p = f\left(\frac{1}{T}\right)$. The

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[1]) F. HENNING. Ann. d. Phys. (43) 282, 1914.

[2]) H v. SIEMENS. Ann. d. Phys. (42) 882, 1913. Comp. also G. HOLST. Comm. Leiden N⁰. 148*a*.

greatest differences with Henning are about 0.02°, v. Siemens's measurements differing a little more at the lower temperatures, not more than 0.06° however.

For nitrogen we can also compare our measurements with those by v. Siemens; here again the difference is very small at the higher pressures and increases as the temperature falls.

At the higher temperatures our measurements agree but moderately with those of Crommelin 1), even if we discard his lowest point which he himself considers less accurate.

The values which we obtain for the vapour-pressures of pure nitrogen by extrapolating the measurements with the argon-nitrogen mixtures are in good agreement with our direct observations.

Argon has also been investigated by Crommelin 2) in the same temperature-range. His results correspond very well to ours.

There is only a small difference as regards the triple point. As we made a number of observations in the immediate neighbourhood of this point (fig. 2) and as our points fall very accurately on the curve drawn through the other points determined by Crommelin, we think it probable that the triple point as determined by us is to be preferred. The differences are for the rest of the order of magnitude of the errors of observation.

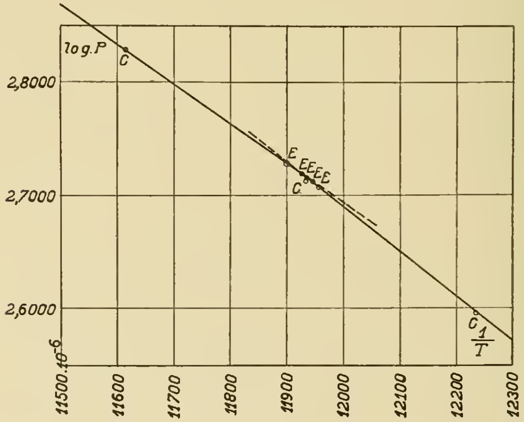

Fig. 2

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1) C. A. Crommelin. Comm. Leiden N⁰. 145*d*.

2) C. A. Crommelin. Comm. Leiden N⁰. 138*b*.

3. *Mixtures.*

For five mixtures the pressure at the end of the condensation was measured at three different temperatures. Not more than $\frac{1}{3}\ {}^0/_0$ of the gas was uncondensed.

The composition of the mixtures was given above.

The results are contained in Table 6:

TABLE 6.

Mixture I. 82.6 ${}^0/_0$. N.		Mixture III. 31.5 ${}^0/_0$ N.	
T	p_{mm}	T	p
82.63	1218.1	86.55	1162.3
78.53	781.5	83.47	852.2
74.02	451.0	78.46	487.8
Mixture II. 65.3 ${}^0/_0$ N.		Mixture IV. 10.0 ${}^0/_0$ N.	
T	p	T	p
83.49	1175.9	89.86	1198.6
78.53	686.5	87.69	972.0
74.53	424.2	83.53	631.2
Mixture VIII (atmospheric nitrogen 99.— ${}^0/_0$ N. (baroscope)).			
T		p	
81.06		1151.6	
78.43^{5}		863.5	
71.29^{5}		350.9	

When *log.* p was drawn as a function of $\frac{1}{T}$ for argon, nitrogen and the mixtures, a set of straight lines was obtained which converge at higher temperatures. The values of p and T which will be used later on for the construction of the px- and Tx-diagrams were taken from this graphic representation.

V. *Determination of the points of beginning condensation.*

1. *Apparatus.*

The apparatus used for this purpose was arranged in the manner of a constant volume gas-thermometer. Its vessel had a volume of about 142 cc. and was provided at the lower end with a small appendix 8 mms. long in which the liquid gas collected. In order to make sure that equilibrium was attained the liquid could be stirred by means of a small steel ball, which on closing a current was drawn up in the field of a small electro-magnet with pole-pieces cut at 45°. In calculating the changes of volume of the vessel the coefficient of expansion was taken as 0.0000212, the mean of the results obtained by TRAVERS, SENTER and JAQUEROD[1]) and by KAMERLINGH ONNES and HEUSE[2]) for Thüringen-glass between 0° and —190°.

The measurement was conducted as follows: a measured quantity of gas was transferred to the vessel and the pressure read at a definite temperature; a second quantity of gas was then measured and transferred to the vessel, and the pressure was read again, etc. etc. until condensation set in. The vapour-pressure was then measured at increasing densities of the vapour.

For a convenient measurement of the quantities of gas which were added, the manometer-tube on the vessel-side was provided with a scale-division and had been accurately calibrated. For the reading of the pressures a cathetometer was sometimes used, sometimes a vertical comparator with steel measuring-rod. In the latter case the accuracy is smaller, but not smaller than about 0,1 mm.

2. *The measurements.*

For each mixture at three different temperatures $\frac{pv}{760}$ was now determined as a function of the pressure, where p is the pressure of the mixture in mms. and v the volume of the gas in the vessel, divided by the theoretical normal volume of the same quantity.[3]) The point, where this curve shows a discontinuity, is the point of beginning condensation in question.

For each quantity of gas which was added the normal volume was each time calculated; this volume was diminished by the quantity contained in the dead space and the capillary in order to obtain the quantity of gas in the vessel.

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[1]) TRAVERS, SENTER and JAQUEROD. Phil. Trans. A 200. p. 138.

[2]) H. KAMERLINGH ONNES and W. HEUSE. Comm. Leiden No. 85.

[3]) H. KAMERLINGH ONNES and W. H. KEESOM. Enc. d. Math. Wiss. Comm. Leiden Suppl. 23.

TABLE 7.

Mixture V. 74.05 % N.

$T = 83.^{\circ}54$		$RT = 0.3059^5$		$T = 78.^{\circ}62$		$RT = 0.2879$	
$v = \frac{v_r}{v_{thn}}$	p	$\frac{pv}{760}$	$-\frac{pv}{760} + RT$	$v = \frac{v_r}{v_{thn}}$	p	$\frac{pv}{760}$	$-\frac{pv}{760} + RT$
0.4424	513.5	0.2991	0.0068^5	0.6956	308.9	0.2829	0.0050
3541	637.7	2973	0.0083^5	0.4421	482.1	0.2806^5	0.0072^5
2853	786.4	2954	0.0105^5	0.3540^5	597.4	0.2785	
2423	920.4	2937	0.0122^5	0.3540^5	597.1	0.2783^5	
2117	1044.9	2913	0.0146^5	0.2849	630.4	0.2365	
1854	1079.8	2635	—	0.2849^5	629.2	0.2360	
1854	1079.0	2633	—	0.2419	650.9	0.2073	
1773	1088.9	2542	—				
1682^5	1099.1	2435	—				

Mixture V. 74.05 % N.				Mixture VI. 52.8 % N.			
$T = 73.^{\circ}78$		$RT = 0.2702$		$T = 85.^{\circ}93$		$RT = 0.3147$	
0.8861	228.6	0.2667	0.0035	1.3663	169.7	0.3123	0.0024
6954	290.0	2655	0.0047	0.6310	373.0	0.3099	0.0048
5657	327.8	2443	—	0.2316	989.0	0.3016	0.0131
4413^5	349.3^5	2031	—	0.2144	1053.9	0.2974^5	—
3530	363.2	1688	—	0.2078	1061.6	0.2905	—
				0.2004	1065.3	0.2811	—

Mixture VI. 52.8 % N.

$T = 80^{\circ}.89$		$RT = 0.2962^5$		$T = 76^{\circ}.22^5$		$RT = 0.2791$	
1.3979	159.8	0.2941	0.0021^5	1.3964	150.6	0.2769	0.0022
0.9459^5	235.5	0.2933	0.0029^5	0.9439	221.7	0.2755	0.0036
0.7125	311.5	0.2923	0.0039^5	0.7122^5	293.0	0.2748	0.0043
0.4697	468.4	0.2897	0.0065^5	0.6303	330.2	0.2741	0.0050
0.4047	541.8	0.2887	0.0075^5	0.5628^5	340.5	0.2523^5	—
0.3742^5	584.1	0.2878	0.0084^5	0.4690	357.5	0.2208	—
0.3465	606.6	0.2767^5	—	0.4038^5	379.8	0.1966	—
0.3069	624.0	0.2521^5	—				
0.2807^5	636.0	0.2351	—				

TABLE 7. (Continued).

Mixture VII. 24.3% N.

$T = 90.11$		$RT = 0.3300$		$T = 85.36$		$RT = 0.3126^5$	
$v = \frac{v_r}{v_{thn}}$	p	$\left(\frac{pv}{760}\right)$	$-\frac{pv}{760}+RT$	$v = \frac{v_r}{v_{thn}}$	p	$\left(\frac{pv}{760}\right)$	$-\frac{pv}{760}+RT$
4.0803	61.1	0.3280	0.0020	4.079	57.7	0.3101	0.0025^5
0.5666	434.7	0.3243	0057	2.073	114.0	3110	0016^5
0.3170	766.0	0.3197	0103	1.0943	215.3	3102	0024^5
0.2959	819.6	0.3191	0109	0.4327	534.3	3044^5	0082
0.2011	1186.7	0.3142	0158	0.3437	669.3	3029	0097^5
0.1928	1228.4	0.3118	—	0.3174	722.8	3021	0105^5
0.1882	1232.7	0.3054	—	0.3108	737.6	3018	0108^5
0.1795	1236.7	0.2923	—	0.3048	752.5	3018	0108^5
				0.2956	756.2	2954	—
				0.2867	758.6	2864	—
				0.2743	762.5	2754	—
$T = 80.53$		$RT = 0.2950$		$T = 80.53$		$RT = 0.2950$	
4.078	54.6	0.2931	0.0019	0.5961^5	368.0	0.2888	0062
2.072	107.6	0.2935	0015	0.4923	429.5	0.2785	—
1.094^2	202.9	0.2923	0027	0.4444	438.7	0.2567	—
0.8446	261.5	0.2908	0042	0.4324	439.3	0.2502	—
0.5961^5	368.0	0.2888	0062	0.4212	439.4^5	0.2437	—

The first column of the above table 7 contains the volume of the vessel v_r, divided by the theoretical normal volume v_{thn} of the quantity of gas which it contains.

For argon we assumed $\frac{v_n}{v_{thn}} = 0{,}9992$ 1)
,, nitrogen ,, ,, ,, $= 0{,}9996$ 2)
for the mixtures intermediate values were taken.

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1) H. Kamerlingh Onnes and C. A. Crommelin, Comm. Leiden 118*b*.

2) Recueil des constantes p. 189.

The second column gives the pressures in mm. mercury, all reduced to the same temperature, the third column gives $\frac{pv}{760}$ and the last $\left(\frac{pv}{760}\right) - RT$ for the gaseous state.

In fig. 3 $\frac{pv}{760}$ is drawn as a function of p for each of the mixtures for the purpose of determining the pressure at which the condensation begins.

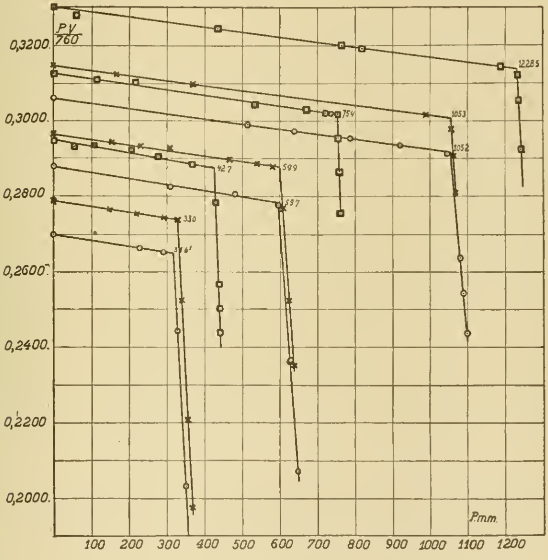

Fig 3.

Table 8 contains these pressures and the corresponding temperatures; it also gives the volumes of the saturated vapour expressed in the theoretical normal volume as unit.

When *log. p* was represented as a function of $f\left(\frac{1}{T}\right)$, a set of straight lines was obtained, in this case also. As before, the values which served for the construction of the final diagrams were derived from these curves.

It may be mentioned, that with the last mixture of 24.3 °/₀ N at a temperature very little below 80°.50 the solid began to separate out.

TABLE 8.

Mixture V. 74.05 % N			
T	p	$\frac{vp}{760}$	v
83.54	1052	0.2918^5	0.2107
78.62	597	0.2787^5	0.355
73.78	316^5	0.2652	0.638

Mixture VI. 52.8 % N			
T	p	$\frac{vp}{760}$	v
85.93	1053	0.3007^5	0.2171
80.89	599	0.2879^5	0.365
76.22^5	330	0.2741^5	0.631

Mixture VII. 24.3 % N			
7	p	$\frac{vp}{760}$	v
90.11	1228.5	0.3138	0.1942
85.36	754	0.3017^5	0.304
80.53	427	0.2878^5	0.512

3. *Equation of state of the mixtures.*

Fig. (3) shows on inspection that $\frac{pv}{760}$ is a linear function of p. It is preferable, however, to choose $\frac{1}{v}$ as the independent variable. The equation of state for the mixtures under investigation in the region

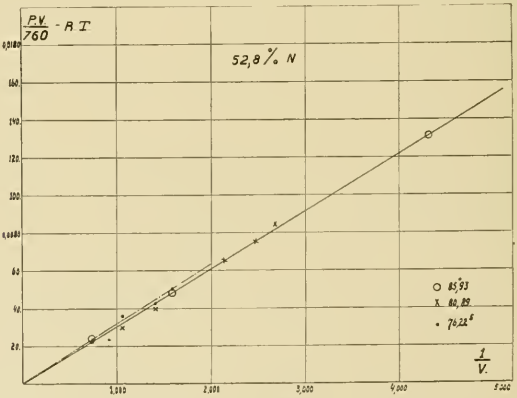

Fig 4

in question can then be represented in the form

$$pv = RT\left(1 + \frac{B}{v}\right)^{1)}.$$

In fig. 4 $pv - RT$ is represented as a function of $\frac{1}{v}$ for mixture VI.

We have computed the values of B in this equation and have obtained the following results

TABLE 9.

Mixture V. 74.05 % N.		Mixture VI. 52.8 % N.	
T	B	T	B
83.54	— 0.0100	85.93	— 0.0096
78.62	— 0.0113	80.89	— 0.0103
73.78	— 0.0118	76.22	— 0.0108

Mixture VII. 24.3 % N.

T	B
90.11	— 0.0100
85.36	— 0.0107
80.53	— 0.0122

Unfortunately so far determinations of B-values for argon at these low temperatures have not been published[2]. For nitrogen measurements by BESTELMEYER and VALENTINER[3]) are available.

These measurements give $B = -0.0116$ at $T = 81.4$ in good agreement with our results as regards the order of magnitude.

The equation of state finally enables us to calculate the volume of the saturated vapour. This calculation we are, however, obliged to defer. Table 8 gives the volumes of the saturated vapour for the points which were experimentally determined.

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1) Comp. H. KAMERLINGH ONNES and W. H. KEESOM Enc. d. Math. Wiss. Comm. Leiden Suppl. 23.

2) We understand that the measurements of B for argon undertaken by KAMERLINGH ONNES and CROMMELIN in the Leiden Laboratory will not be completed for a considerable time.

3) A. BESTELMEYER and S. VALENTINER. Ann. d. Phys. (15) 61, 1904.

VI. *Tx- and px-diagrams.*

The data found above enable us to derive temperature-composition as well as pressure-composition diagrams. The values which we obtained are arranged in Table 10 on page 891; by means of these a few Tx-curves were drawn (fig. 5) and the px-diagram for $T = 85°.11$ (fig. 6)[1]).

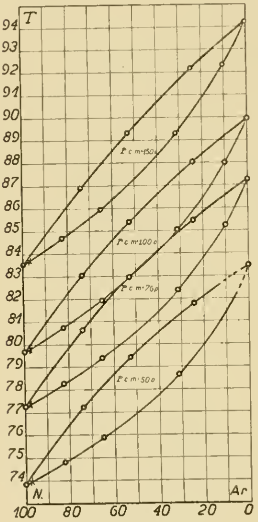

Fig. 5.

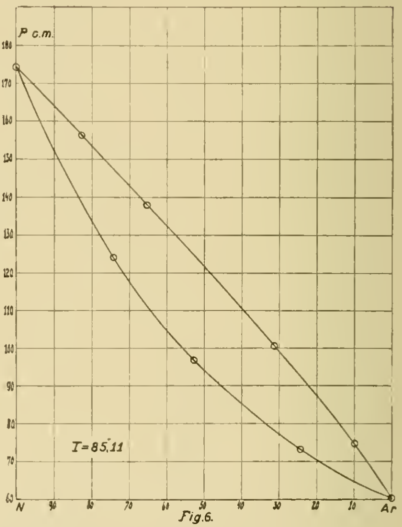

Fig. 6.

It will be seen, that the difference in composition between the liquid- and vapour-phases is a little smaller on the nitrogen- than on the argon-side. A glance at the figure further shows, that in the preparation by means of fractionation of argon from mixtures containing only a few hundredths of argon no great advantage can be gained from raising the pressure, although the advantages of a better exchange of cold at the higher pressures must not be lost sight of, where a technical method is concerned.

The change of the composition of the gas-phase with that of the liquid-phase satisfies the relation[2]):

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[1]) The Tx curves for $p = 50$ have been dotted on the argonside, as the solid makes its appearance here.

[2]) LEHFELDT, Phil. Mag. (5) **40** 397 (1895).

$$\log r' = a + b \log r$$

where r' represents the ratio of the components in the liquid and r the same quantity in the vapour.

TABLE 10. T—x-diagrams.

	x % N.	$T_p = 50.0$ c.m.	$T_p = 76.0$ c.m.	$T_p = 100.0$ c.m.	$T_p = 150.0$ c.m.
End of cond.	0.0	83°.45	87°.26	89°.93	94°.18
	10.0	81.42	85.25	87.98	92.32
	31.5	78.65	82.40	85.05^{5}	89.29
	65.3	75.86	79.41	81.95	85.97
	82.6	74.82	78.30	80.76	84.70
	100.0	73.87	77.28	79.71	83.57
Beginn. of cond.	24.3	81.79	85.46	88.04	92.15
	52.8	79.41	82.97	85.40	89.33
	74.05^{5}	77.21^{5}	80.66	83.08	86.93
End of cond.	99.—	73.94	77.35	79.78	83.64

p-x diagram for $T = 58^\circ 11$

	x %	p. c.m.
End of cond.	0.0	60.28
	10.0	74.75
	31.5	100.5
	65.3	137.9
	82.6	156.2
	100.0	174.3
Beginn. of cond.	24.3	73.18
	52.8	96.78
	74.0^{5}	124.2

TABLE 11.

$p = 50.0$ cm.				$p = 76.0$ cm.			
$a = -0.545$		$b = 1.08$		$a = -0.496$		$b = 1.06$	
T	r'	$r_{calc.}$	r_{found}	T	r'	$r_{calc.}$	r_{found}
76.00	1.74	5.36	5.37	80.00	1.34	3.87	3.85
78.00	0.605	2.01	2.01	82.00	0.534	1.64	1.65
80.00	0.247	0.879	0.869	84.00	0.227	0.725	0.718
82.00	0.0695	0.269	0.270	86.00	0.0593	0.205	0.206
$p = 100.0$ cm.				$p = 150.0$ cm.			
$a = -0.451^5$		$b = 1.04$		$a = -0.396^5$		$b = 1.03^5$	
82.00	1.825	4.82	4.81	86.00	1.85	4.32	4.32
84.00	0.706^5	1.94	1.93	88.00	0.750	1.83	1.84
86.00	0.305^5	0.869	0.872^5	90.00	0.346	0.866	0.866
88.00	0.108^6	0.323	0.324^5	92.00	0.134	0.348	0.348
$T = 85°.11$							
$a = -0.466$		$b = 1.11$					
$p_{cm.}$	r'	$r_{calc.}$	r_{found}				
80.0	0.164	0.516	0.513				
100.0	0.446	1.27	1.26^5				
120.0	0.942	2.49	2.49				
140.0	2.067^5	5.06	5.06				

As appears from the above Table 11, the values of a and b in the several Tx-diagrams change with the pressure. In each diagram taken separately the agreement between the calculated and found values is very good.

The result that the liquid-curve in the px-diagram (especially on the nitrogen side) is only very faintly curved [1]) had been found before in a series of unpublished preliminary determinations and may be looked upon as an indirect confirmation of our observations respecting the vapour-pressures of nitrogen (IV. 2).

The *px*-diagrams shows that especially on the nitrogen-side, the values of the composition of the liquid and vapour phases do not differ much from each other. This would lead to the expectation that the fractionation, especially of the mixtures with little argon, will not be a very easy matter.

When the change with pressure of the composition of the phases is taken into consideration, it follows that the differences in composition increase with diminishing pressure, so that a comparison of the *T-x* diagram for argon-nitrogen at 76.0 cms with BALY's diagram [2]) for the fractionation of air puts the problem of the fractionation of the mixtures in question in a less unfavourable light. At the same time it follows from our results, that the use of mixtures with little argon will give considerable difficulty.

VII. *Resumé.*

1. A method was worked out enabling us to determine the composition of argon-nitrogen mixtures with an accuracy of 0,1 °/₀ or, if need be, higher.

2. A systematic difference was found between the results of the determinations with the baroscope and the method referred to under 1, which led us to the conclusion, independently of SCHULTZE's work (l.c.), that the atomic weight of argon hitherto assumed might not be quite exact. As this systematic difference disappears when SCHULTZE's value is adopted, the latter is thereby rendered highly probable. A preliminary direct determination gave a value in good agreement with SCHULTZE's result.

3. New measurements of vapour-pressures for oxygen, argon and nitrogen are published and critically compared with those of previous observers. The triple point of argon was determined with greater accuracy.

4. The end-points of condensation of the argon-nitrogen mixtures were determined with an accuracy corresponding to 0.02° in the temperature.

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[1]) Pointing to a simple behaviour of argon towards nitrogen.

[2]) Phil. Mag. 49 (1900) p. 517.

5. At the points of beginning condensation the accuracy is about the same. The saturated vapour-volumes are given.

6. The observations with the mixtures are compared with the equation of state in the form $\frac{pv}{760} = RT\left(1 + \frac{B}{v}\right)$. The accuracy in $\frac{pv}{760}$ was found to be about 0,1 %.

7. Within the range of temperatures investigated $\log p$ for the mixtures can be represented as a linear function of $\frac{1}{T}$, both for the points of beginning condensation and for the end-points.

8. The px- and Tx-diagrams are established. As regards the composition of the gas-phase (r) and the liquid-phase (r') they were found to satisfy the relation $\log r' = a + b \log r$.

9. Conclusions were drawn from the shape of the curves in the diagrams in connection with a possible fractional distillation of argon-nitrogen mixtures.

We are glad to be able here to express our sincere thanks to Mr. G. L. F. Philips for the unstinted support afforded to us by which this investigation was made possible.

We also wish to record our cordial thanks to Messrs. W. Koopman and J. Scharp de Visser for their zealous assistance in carrying out the measurements and calculations.

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