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THE
SCIENTIFIC PROCEEDINGS
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I.

CORALLORHIZA INNATA R. BR., AND ITS MYCORHIZA.

By A. VAUGHAN JENNINGS, F.L.S., F.G.S., AND HENRY HANNA, M.A., B.Sc. (PLATES I. AND II.)

[Read JUNE 22; Received for Publication JUNE 28; Published OCTOBER 22, 1898.]

THE orchid genus *Corallorhiza* has long been of interest to botanists on account of the peculiar rhizome from which it derives its name, the absence of roots, and the want of chlorophyll usually associated with a saprophytic habit which it shares with such forms as Epipogon and Neottia.[1]

Any additional information bearing on the nutrition of such a specialised type as *Corallorhiza* must be of interest, as we have reason to believe that in this case the relationship which obtains between the mycorhiza and the host plant is of a very complex nature, and not at present thoroughly understood.

Of late years new light has been thrown on the question of the nutrition of saprophytes and certain other plants, owing to the frequency with which fungoid elements are found in association with their roots or rhizomes.

Thus, if we take up a young beech plant and carefully wash the roots with water, we observe numerous fine root fibres to which there cling small portions of humus; no root hairs are

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[1] Chlorophyll is not entirely absent. The flowers and upper part of the scape are of a faint yellow-green colour, but the leaves are reduced to colourless sheathing scales.

present, but instead we find that the entire surface of the fibres is covered over with a web of fungal hyphæ. We are here dealing with a "mycorhiza"; that is, the association of root fibres and fungal hyphæ living in intimate physiological connexion with them.

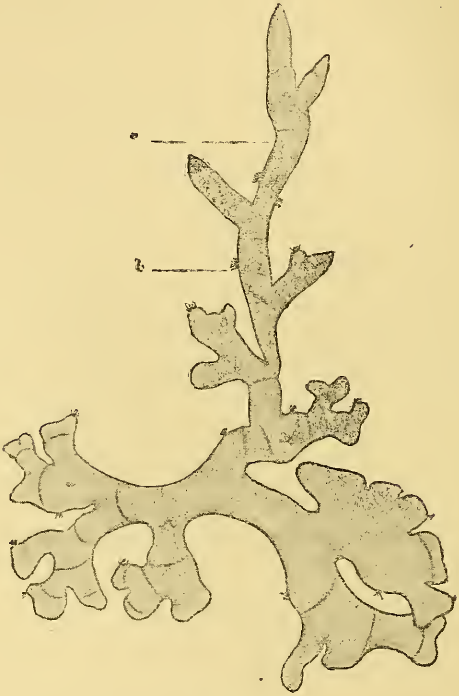

Fig. 1.

Rhizome, with young aerial shoot (*a*) nat. size, showing numerous tufts of hairs (*b*).

There may be advantages accruing both to the fungus and to the beech plant from such a union; the former may help the green flowering plant to obtain water and salts from the soil, while in return it may receive from its host some of the organic compounds manufactured in the green leaves.

So essential to the well-being of the host plant is the presence of the mycorhiza, that if the development of the latter is prevented, the normal development of the beech plant does not take place; and the relationship may perhaps be regarded as a true *symbiosis*.

Frank,[1] who has conducted many experiments in this direction, also concludes, from growing spruce fir seedlings in sterilized and unsterilized soil that the mycorhiza is of service to the plant in enabling it to make use of the nitrogen compounds present in the humus.

Although it is possible that there are advantages accruing to a mycorhiza from such a symbiotic union with the roots or rhizomes of a green flowering plant, one does not see so clearly what benefits accompany the union of a fungus mycelium with similar organs of a plant devoid of chlorophyll. Thomas[2], in his observations on Corallorhiza in America, is of opinion that the fungus supplies food to the host from the decaying vegetable matter of the surrounding soil.

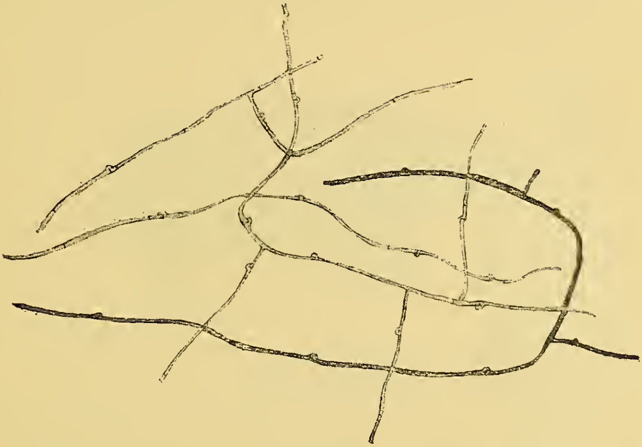

FIG. 2.

Portion of the mycelium of the mycorhiza, showing the "clamp-connexions."

The genus *Corallorhiza*, containing some twelve well-defined species, is of wide distribution, extending throughout the northern hemispheres of the Old and New Worlds, and in the latter ranging as far south as Mexico.

In the British Islands this genus is represented by one species, *C. innata* R. Br.

According to Babington and Hooker it is found only in East Scotland, from Ross to Berwick, living in boggy woods, but it is

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[1] Ber. d. Deutsch. Bot. Gesell. Bd. x., p. 577.

[2] Botanical Gazette, vol. xviii.

very rare. In the high pine woods of Central Europe it is local but not uncommon, and the present observations were made on specimens from the Eastern Alps. The coralloid rhizome differs markedly from the usual type of underground stem met with in Monocotyledons, except that of Epipogon, which is on the whole similar. It grows embedded in a soil unusually rich in humus compounds.

Chlorophyll is often stated to be entirely absent, or present only in the ovary (Warming); but, as above noted, it may be slightly developed in the flowers and top of the scape. The aerial portion of the plant is a simple scape, bearing only colourless leaf-sheaths, and at the top a raceme of small pale flowers.

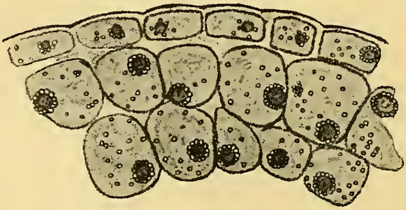

Fig. 3.

Transverse section through the outer layers of the rhizome.

The fungal hyphæ constituting the mycorhiza (when examined microscopically) are seen to have the following characters (fig. 2). They are distinctly septate and repeatedly branched, of a yellow, white, or brownish colour. They possess numerous "clamp-connexions," indicating that the mycelium belongs to one of the higher fungi, a conclusion which is supported by the fact, that young agaricoid sporophores have been, in one instance, found growing from the mycelium round the rhizome. These refused to develop further on cultivation, but comparison with the early stages of *Clitocybe infundibuliformis* Sch., found a few feet distant, indicates that this is the species to which they, in that case, belonged (Plate I.).

Attempts to determine whether the mycelium could be referred to any one species of fungus have been made in the pine woods of Davos Platz by one of us,[1] who has had plants under observation

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[1] A. Vaughan Jennings.

during three summers, and these experiments tend to show that so far as this district is concerned the mycorhiza of *Corallorhiza* is a hymenomycete and commonly an agaric.

In addition to the agaric referred to above, there are others which have been found in very close proximity to the *Corallorhiza*; for instance, species of *Tricholoma* (*T. ionides*, Bull?), *Mycena* (*M. umbellifera*, Sch. ?), and *Cortinarius* (*C. subferrugineus*, Batsch.). It is also interesting to note that one of the subterranean hymenomycetes, evidently the *Hysterangium stoloniferum* of Tulasne, has been found in several instances among the rhizomes. None of the cases observed showed any special hyphal characteristics to absolutely identify them with the mycorhiza, but their mode of occurrence leaves little doubt as to the existence of a real connexion between the mycelium of these fungi and the symbiote or victim of the Corallorhiza.

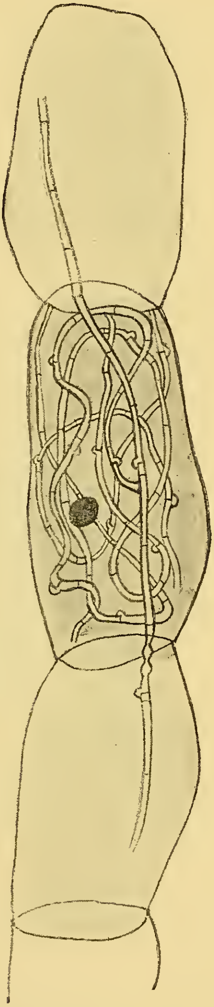

Fig. 4.

Three cells from the outer layers of the cortex, showing hyphæ piercing the cell-walls.

The rhizome when carefully removed from the soil and gently washed, shows, scattered over the surface of the growing shoots, numerous papillæ, from which tufts of hairs arise (fig. 1, *b*). These hairs are, on an average, ·810 mm. to ·432 mm. in length, and ·054 to ·027 mm. in breadth: some have rounded apices, others appear abruptly truncated; and intermediate stages exist which are of great interest. At the tips of the hairs changes evidently of a chemical nature can be seen in progress; the apices lose their definite outline, the walls break down and appear mucilaginous and granular as if ferment-action was going on. The walls of some seem to become weakened along a spiral line (as in Plate II.) apparently corresponding to the course of intrusive hyphæ.

The hyphæ outside the rhizome can be traced inside the hairs; passing down, singly and spirally, or in bundles, to the cortical tissues of the rhizome (Plate II.).[1]

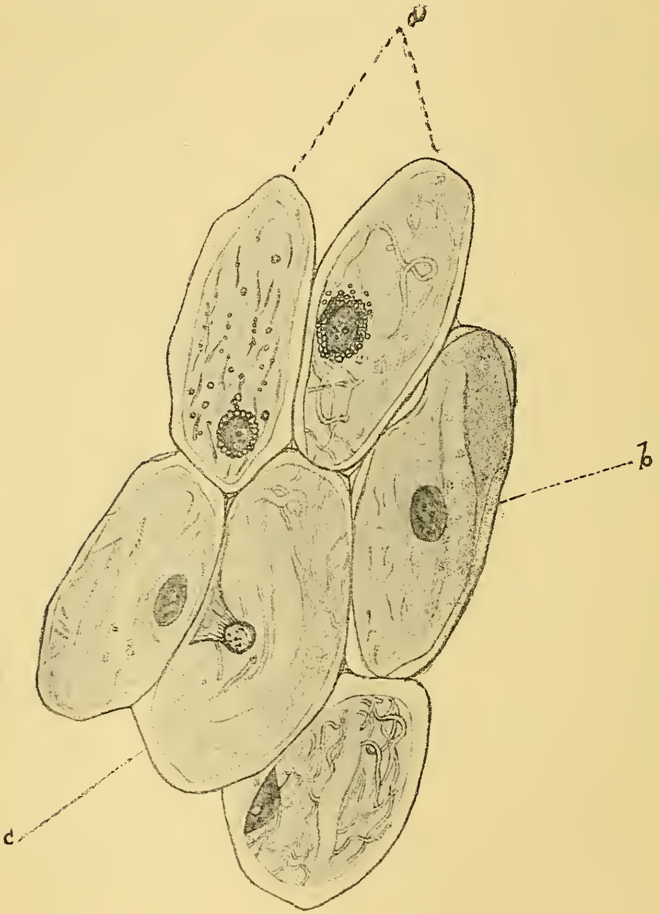

Fig. 5.

Cells from the mediocortex, showing hyphæ in various stages of absorption, and starch grains making their appearance.

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[1] It seems evident, therefore, that these hairs are specialised structures for the attraction and capture of the mycorhiza, and if a special name is needed they might be termed "mykokleptic" hairs.

The hyphæ in the soil outside the plant and those inside the hairs and cortical tissues are similar and continuous, and have the structure shown in fig. 2.

Thomas[1] observed the presence of the papillæ over the surface of the rhizome and also the presence of hairs. He failed, however, to demonstrate the connexion between the hairs and the mycelium in the surrounding soil, considering that the probable function of the former was the purely mechanical one of anchoring the plant to any substance with which it might happen to come into contact, a purpose for which they are evidently inadequate.

The axis of the aerial shoot which arises from the rhizome grows by means of a stratified apical growing point, on the sides of which scale leaves arise in acropetal succession, covering up the growing point (fig. 1).

FIGS. 6 and 7.

Cells from the mediocortex, showing hyphæ in various stages of absorption, and starch grains making their appearance.

Taking sections through the rhizome the following structure is noted:—

1. *Outer layers.*—There is a definite superficial layer of cells, elongated longitudinally; and at irregular intervals, where sections of papillæ are to be seen, the hairs arise as outgrowths at right angles to the surface (Plate II.). On the outer wall of the superficial layer of cells there is a thin cuticle; below it two or three layers of thin parenchymatous, isodiametric cells with small intercellular spaces occur (fig. 3). These cells have large nuclei and protoplasmic contents and small starch grains; the nuclei are

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[1] *Loc. cit. sup.*

surrounded by the starch grains, some of which also lie scattered through the protoplasm. Numerous fungal hyphæ are observed passing more or less directly through these outer layers.. This is an important fact, and is especially obvious in transverse sections of the rhizome in the neighbourhood of a papilla.

2. Internal to the cells constituting these outer tissues there occur one or more layers of cells, usually three, which have thin cellulose walls, and contents markedly different from those of the outer layers ; each cell is filled with a coiled mycelium ; the cell sap is scanty, and the hyphæ may be observed piercing the cell walls.

Fig. 8.

Surface of a nearly median section through lobes of the rhizome, showing the distribution of the mycorhiza in the tissues, as indicated by the light bands. (× 25.)

Where the hyphæ pass straight through from one cell to another, there is a paucity or a marked absence of starch grains (fig. 4).

3. More internally we come to cells which have a very different appearance; these cells are large, thin-walled, and provided with abundant protoplasm; starch grains are numerous. The latter seem to increase in the cells in proportion as the hyphæ disappear (fig. 5, *a*). The hyphæ in no instance were observed to swell into bladder-like bodies in the neighbourhood of the nuclei, the filaments being practically of the same width in all parts of the coil. The mycelium may be observed in all stages of degeneration in the

cells of this region. Minute bodies in groups make their appearance along the course of these degenerating hyphæ; the nucleus is in a state of great activity, becoming larger, and containing a number of bodies which stain deeply with Hoffmann's blue. This is an indication of the increase of materials in the substance of the nucleus, a fact of some significance when we recall the fate of the hyphæ in the cells; their walls collapse and become shrunken, and finally the contents of the cells become one homogeneous mass. Following Groom's[1] terminology we may name the region the *mediocortex* as characterised by the presence of these degenerating fungal masses. Inside this mediocortex there are usually two layers of parenchymatous cells with walls of cellulose, containing abundant starch but no hyphæ.

In the centre of the rhizome there is a simple vascular cylinder of somewhat modified collateral bundles, composed of small and usually quite rudimentary elements, the phlœm in each case being confined to the periphery.

The hyphæ, after passing into the hairs, are distributed in the deeper tissues in a definite and regular manner. They do not appear to pass from the underground portions of the plant into the young aerial shoots. Above the line marked *a* in fig. 1 no hyphæ were present in any of the cells, nor were they present anywhere in the cells of the flower stalk.

If we take a longitudinal section through a small portion of the rhizome, such as that seen on the right hand in fig. 1, a little to one side of the median plane, a very peculiar appearance is seen of alternating bands of light and shade on the surface of the section. On closer examination the light coloured bands are found to be due to the presence of the endotrophic hyphæ forming dense coils in the cells.

SUMMARY AND CONCLUSIONS.

From a consideration of the facts observed there can be very little doubt that ultimately the hyphæ present in the cells are absorbed and made use of in forming food materials for the host plant.

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[1] Ann. Bot. 1895.

The tufts of hairs on the numerous papillæ covering the rhizome appear to act as traps for the mycorhizal hyphæ, the latter being attracted by the presence of some chemotaxic substance formed as a result of the changes going on in the walls of the hairs especially at their tips, which seem to make suitable growing places for fungoid hyphæ. The hyphæ pass down the hairs and through the outer layers of the rhizome without forming coils in the cells; enter the deeper lying cells and form coils there, and then pass on to the mediocortex where they are ultimately absorbed and converted into food materials for the host plant.

This tends to strengthen Frank's view that the fungus is a living organism captured for the benefit of the host plant.

An important point bearing on his comparison of such a "host" to a carnivorous plant is the behaviour of the hyphæ towards the nuclei of the cells.

In no case could we make out an enlargement of the hyphæ in the neighbourhood of the nucleus in cells outside the mediocortex; the nucleus was not perceptibly larger in the cells containing coils of mycelium than in those towards the epidermal layers in which such coils were absent. No bladder-like swellings were observed similar to those described by Groom,[1] in *Thismia Aseroœ* (Ber.), a saprophytic monocotyledon belonging to the order Burmanniaceæ. In some cells of the mediocortex a peculiar semblance to swollen ends of hyphæ has been observed near the nucleus, but this appearance was found to be brought about by the shrunken protoplasm becoming cup-shaped, with one rim very much thickened.

Starch is most abundant in cells in which the hyphæ are in a state of decomposition. In the mediocortex little granules in groups occur along the strands of hyphæ, and increase in proportion as the absorption of the hyphæ in the cells proceeds. This makes it doubtful if the hyphæ obtain any food matter from the host after they have once been attracted into the tissues (fig. 5, *b*).

The peculiar characters of the hairs in this instance, and the histological features of the infected cells point to the host

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[1] Ann. Bot. 1895.

plant as being at least by far the larger shareholder in the symbiotic relationship, if it can be regarded as such. More probable seems the view that there is no symbiosis, but that the fungus is captured and utilised by the orchid without any compensating benefit to itself.

EXPLANATION OF PLATES I. AND II.

PLATE I.—Fig. 1.—A plant of *Corallorhiza innata*, R. Br. (natural size) showing (*a*) aerial shoot with terminal raceme of flowers; (*b*) coralloid rhizome; (*c*) fungus mycelium; (*d*) young sporophores of *Clitocybe infundibuliformis.* Figs. 2 and 4.—Aerial branch of the rhizome; surface view and section, showing the buds sheathed in brown scales, the scars of older, fallen scales, and the tufts of fungus catching ("mykokleptic") hairs. Figs. 3 and 5.—Similar views of the termination of subterranean lobes of the rhizome.

PLATE II.—Transverse section through portion of the rhizome, showing a group of the hairs which collect and transmit the hyphæ of the mycorhiza.

II.

MINING AND MINERALS IN THE TRANSVAAL AND SWAZIELAND. By E. St. JOHN LYBURN, M.E., A.R.C.Sc.I., F.G.S. (Plate III.)

[Read June 22; Received for Publication October 7; Published November 30, 1898.]

Introduction.—The object of this communication is to afford some information on the reality and extent of the mineral wealth of the Transvaal and Swazieland, from data acquired in the course of the last two years, during which I held the position of consulting Mining Engineer to Mr. E. F. Bourke, a gentleman largely interested in the mining industry. Exceptional opportunities have thus been afforded me of studying the geology and mineralogy of these countries.

Prior to my engagement with Mr. Bourke I held the position of assayer and surveyor to several gold mining companies on the Witwatersrandt.

Geology.—The elevation of the Witwatersrandt (White watershed) varies from 5500 to 6000 feet above sea-level). The Witwatersrandt forms the water-shed of the principal rivers of the Transvaal, which is drained by the Orange River and its tributaries to the South Atlantic Ocean on the south-west, and the Limpopo, or Crocodile River and its tributaries into the Indian Ocean, on the south-east.

To illustrate better the relations of the strata in the Witwatersrandt I have prepared a diagrammatic section (Plate iii.). On the working out of this strata I was engaged during many months of actual survey in the field; it shows three distinct systems.

1st. The primary, represented by the granitic rocks north of Rietfontein, north of Johannesburg.

2nd. The Cape System, containing the famous Randt deposits, divisible into five series:—

I.—Hospital Hill series, consisting of quartzites sand-stones, and ferruginous shales, the latter banded, and containing magnetite and titanite. They are regarded by the prospector as the guides to the location of the Main-reef series, prospectors maintaining that the Main-reef lies at a distance varying from 1¼ to 1½ miles south of these shales. Many similar beds are to be met with west of Johannesburg.

II.—The Banket (= puddingstone in Dutch) series, embracing the sandstones, quartzites, and conglomerate beds of the Witwatersrandt, may be sub-divided into—1, the Main-reef series; 2, the Bird-reef series; 3, the Kimberley series; 4, the Elsburg series.

III.—The Black-reef series.

IV.—The Dolomitic Limestone.

V.—The Magaliesburg series.

1. *Main-reef series.*—The main-reef series mostly strike east and west, with southerly dip, and can be traced for about twenty-eight miles. At Boksburg, east of Johannesburg, the beds disappear under the coal, or Karoo formation, and reappear in the vicinity of Benoni, and can be followed for a distance of about six miles, disappearing again under the Coal-measures. Following the outcrop of the series where observable, the general formation is found to strike in the extreme east of the district north and south, with westerly dip. The series are seen at Heidelburg striking east and west, with northerly dip, thus completing a syncline.

To the west of Johannesburg in the Krugersdorp district, the series are much faulted and other conglomerate beds are met with. The Main series consist of three productive reefs, namely, the Main-reef, the Main-reef leader, and the south reef, and are separated by sandstones of variable thickness, the distance from the Main-reef to the Main-reef leader varying from a few inches to 7 feet, and from the latter to the South reef from 30 feet to 110 feet. Other reefs are known to exist, but are of no commercial value at present.

The thickness of the Main-reef ranges from 3 feet to 12 feet. The Main-reef leader from 1 inch to 3 feet, and the South reef from a single pebble to 5 feet 6 inches.

The South reef is the richest; the Main-reef the poorest.

The conglomerates are composed of white and smoky pebbles presenting a waterworn appearance and are cemented by silica, impregnated with iron pyrites, the gold being obtained from the cementing matter. The pebbles vary greatly in size, ranging from the size of a small marble to that of a turkey's egg.

2. *Bird-reef series.*—These consist of eight beds of conglomerate. In some places gold is found in paying quantity, but the series has not yet been fully prospected.

3. *Kimberley series.*—These consist of a large number of conglomerate beds varying in thickness.

South of Florida, the Kimberley-reef proper is about 100 feet thick, gold in paying quantities not having hitherto been discovered in it.

4. *Elsburg series.*—These consist of a large number of beds of considerable thickness, and here, too, gold in paying quantities has not been met with.

Each and all of these series are accompanied by their own particular characteristic pebbles, by which they are easily recognized.

Overlying the Elsburg series, an extensive sheet of amygdaloidal diabase is found, forming the Klipriviersburg, the Black reef resting on this formation, with the dolomitic limestone superimposed. In succession appears the Magaliesburg quartzite sandstone. North of the Main-reef series, in the vicinity of Rietfontein, a thin bed of conglomerate is encountered, called Du Preez reef, on which successful work is being carried on.

The Black reef series.—This consists of quartzites which lie unconformably on the Banket series, the angle of dip ranging from 5° to 15° from the horizon. Taken as a whole, this reef is remarkably "patchy," and varies in thickness from that of a single pebble to 5 feet. In some places the reef is absent. The pebbles are cemented with the sulphides and oxides of iron.

The Dolomitic Limestone.—This overlies unconformably the Black reef. In appearance it is bluish grey, and contains a large percentage of magnesia. Numerous siliceous beds occur, running through it, conformably with the stratification. Quartz veins destitute of gold are also found, cutting through the strata. Underground cavities also form a characteristic of the group. The thickness of this dolomitic limestone may be set down at about 10,000 feet.

The Magaliesburg series.—This consists of quartzites, sandstones, and shales, which form the hills known as the Magaliesburg range.

Numerous sheets of igneous rock are interbedded with the quartzites. The series is devoid of fossils. To the north of Pretoria the shales contain galena.

The Karoo System.—This system comprises the sandstones, shales, and Coal-measures. The sandstones are arkose in character. Red sandstone predominates at the surface, and is characteristic of the coal-bearing deposit. It is hard and compact where exposed. Shales are found underlying the sandstones. The formation may be divided into the Upper and Lower Karoo. I shall only refer to the Molteno beds, which are coal-bearing. The distribution of these beds has hitherto been imperfectly worked out; they are met with in the Cape Colony, extending into the Middleburg district of the Transvaal, and are traceable into Orange Free State, Natal, Zululand, Pondoland, and the Portuguese territory; they mostly lie in a horizontal position; their age is an open question. The fossils so far obtained are *Sigillaria* and *Glossopteris* (the latter is also met with in the Indian Trias). From my own observation, I estimate the coal area of South Africa to be about 175,000 square miles, or, say, about 400 miles by 440.

Recently a coal seam of the abnormal thickness of 211 feet has been discovered to the east of Johannesburg, on the farm Zuurbekom. I consider this to be one of the greatest coal discoveries of recent times. The sandstones and shales overlying the coal, totaling 320 feet. As to the quality of South African coal, it may be stated that its average calorific value is about 1 lb. for 7 lbs. of steam compared with Welsh coal, 1 lb. of which gives 11 or 12lbs. of steam.

Mining.—The underground development is performed by means of rock-drills driven by compressed air, white miners operating the machines. "Stopping," or breaking down the ore, is done by hand, and the work alloted to Kafirs, supervised by white miners, who charge and fire the blasts. Machine stopping is replacing the hand method.

The deposits of the Witwatersrandt are at present worked by rectangular shafts, both vertical and inclined. In the early days of the industry, vertical shafts were much preferred, cross-cuts being driven to intersect the reef. At the present time the outcrop properties are being worked by inclined shafts, or, in other words, shafts sunk on the reef. Inclined shafts are preferred on account of the sinking being made in the reef proper, thus always being in touch with the reef, giving all necessary data as to value per ton thickness of reef. The ore won in sinking on the incline is afterwards profitably treated by the "reduction plant," whereas in the vertical system, the rock taken out consists only of the country quartzite, which is valueless. The cost in either case is practically about the same. It is now the rule to sink the inclined shaft in the Main-reef leader or middle reef, *i.e.* in the body of the series.

Deep-level Shafts.—It may be advisable to define the term "deep-level." The reefs dip in a southerly direction. The outcrop, as the word implies, is that part of the ore-body which is exposed at the surface, the ore-body being inclined and dipping to the south; the further south claims are held, the greater vertical sinking is needed to strike the reef. Data regarding the depth at which the reef should be struck depend upon the dip of the reef and the extent of the claims held by the outcrop Company south of the outcrop.

A claim consists of 60,000 square (Cape) feet,[1] equal to 400 (Cape) feet measured along the outcrop, by 150 (Cape) feet at right angles to the same. The diagram on Plate III. shows four claims on the dip, equal to 600 (Cape) feet measured at right angles to the outcrop. The deep-level shaft would be sunk on claim No. 5.

The vertical shaft is used to reach the reef in depth. When the reef is intersected, the shaft is continued on the inclination of the reef. It is a very open question whether the shaft should be continued on the vertical, or follow the dip of the reef. In sinking on the reef as mentioned in the cases of outcrop properties, all data are obtained as to the value and thickness of the reef, which could not be furnished by a vertical shaft in barren ground. On the other hand, the wear and tear on the vertical system is much less than that on the inclined. The turning point (that is to say, the point where the vertical branches into the incline) is a source of trouble and loss of time, as it becomes necessary to slow down the hauling engines, on arrival at the point mentioned. The dip of the deep levels varies from 20° to 30° from the horizontal.

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[1] 1033 English feet equal 1000 Cape feet.

The question of maximum workable depth arises in connexion with the deep levels of the Randt. In connexion with this question it may be learned from the State Reports that experiments have been made on the property of the Robinson Deep-Level Gold Mining Company. The observations were made in a shaft 2067 feet deep, which was not connected with any other shaft on the estate. The result gave a rise of 1° C. in temperature for every 492 feet, say (1° C. for 150 metres), the ordinary rate of increase being in Europe and America 1° C. for 30 to 31 metres.

Experiments were also carried out on the Langlaagte Company's property, the depth of the shaft being 1083 feet, resulting in demonstrating a rise of 1° C. for each 300 feet (or 1° C. for 92).

Taking 5000 feet as a limit to which working can actually be pushed, and considering it, in view of the less favourable of the above-mentioned experiments, viz. that of the Langlaagte Deep, it would appear that the total increase of temperature to be expected would not exceed 17° C. at 5000 feet, which, added to the temperature at the top of the shaft, in this case 20° C., would bring the temperature, which the worker would be exposed to, up to 37° C., equivalent to 98° F., a temperature which would in no practical way impede mining operations. The fact is to be borne in mind that these tests were carried out in shafts, entirely disconnected from any other.

The result of connecting shafts would undoubtedly be a lowering of temperature in both.

Judging by the above data it will be reasonable to infer that mining operations can be carried on, in these countries, to a very great depth. As bearing on the geology of the country and the working of the reefs, attention should be called to the faults occurring in the Randt which are either of the ordinary class or of the class of fault known as the "overthrust fault," and called in Europe "reversed fault." The existence of these faults will largely influence enterprise in the future, in deep levels (Plate iii.).

On the property of the Witwatersrandt Gold Mining Company, two outcrops of the Main-reef series are known to exist. The reef series has been thrown up by an overthrust fault, the fault-plane being filled up by dyke matter, viz. dolerite. This at first gave rise to considerable speculation, many mining men believing it to consist of two independent reef series; however, shaft-sinking has proved it to be a case of overthrust faulting. Similar faulting may also be encountered at the Robinson and the Langlaagte Royal, establishing the same deduction. I could multiply instances, all pointing to the same conclusion.

Treatment of the Ore.—The ore having been brought to the surface in the "skip" is sent to the sorting machinery. Circular sorting tables are mostly in use. Kafirs stand around these tables and reject all country rock, quartzite, &c. The reef matter is thrown into the crushing machinery, which reduces the ore to fragments representing about 2-inch cubes.

This product is carried forward in trucks driven by wire-haulage to the "stamp-battery," where it undergoes crushing to about "four hundred mesh," the standard of fineness of the mesh differing in many mines.

The crushed material passes over copper plates amalgamated with mercury, which seizes the free gold. The residue (or "tailings"), which contains about 33 per cent. of the total gold, is then subjected to the cyanide treatment, by being pumped (or elevated by a wheel) into the Spitzlutzen or hydraulic classifiers, which separate the coarser sands and pyrites from the finer sands, or slimes, the latter flowing away into the slimes-dam, to undergo further operation, whilst the coarser sands are dealt with in the cyanide tanks, which consist of wooden structure, as in the older establishments, but which are being discarded by the more modern undertakings in favour of iron tanks.

In these tanks the material is treated with cyanide of potassium solution for a few days, after which it is drawn off and passes through wooden boxes charged with zinc shavings, resulting in the precipitation of the gold in the form of fine black slime, which, having been dried and calcined, is smelted in graphite crucibles, yielding "cyanide gold," containing an average of 750 "fine," in which form it is exported to the English refiners.

In many mines electrical precipitation by the aid of lead plates is rapidly becoming availed of, which effects a saving of the cyanide. The gold is deposited on lead plates, which are afterwards subjected to cupellation.

The Occurrence of Gold in the Transvaal and Swazieland.—In the first portion of this communication I dealt with the occurrence of gold in the beds of the Witwatersrandt; I now propose to give a succinct account of other localities in which gold has been proved to exist.

Gold was first discovered in 1869, in the North-Eastern Transvaal, in a district embracing the Zoutpansburg, Houtboschburg, Murchison, and Letaba goldfields. The gold occurs in quartz reefs, which are mostly of the bedded-vein type, true fissure veins being rarely encountered. The reefs are interstratified with schistose rocks. Mining at present is at a standstill in this district. Auriferous stibnite has been discovered in the Murchison district.

Gold in the De Kaap or Lydenburg Districts.—The Lydenburg district consists of an extensive plateau, dipping about eight degrees to the west; the strata lie partly unconformably on the Swazieland schists, and partly on the rocks forming the low country. It may be divided into four systems :—

1. The underlying schists.
2. The Drakensburg sandstones and quartzite.
3. The dolomitic limestones.
4. The upper schists and sandstones.

The gold-bearing beds are found in the Drakensburg system, in the dolomite beds, and in the upper schists and sandstones. The conglomerate bed of the Kaapsche Hoop, or Devils' kantoor, contains gold, but up to the present in unremunerative quantity. This conglomerate is highly mineralized with iron pyrites, the pebbles ranging from a smoky quartz to white. The cement is coarser than that of the Witwatersrandt.

The Dolomite beds.—The auriferous reefs found in these beds consist of quartz and pyrites, with occasional bands of chert, containing manganese. The gold occurs in the cavities left vacant by the chemical decomposition of the iron pyrites. Diorite sheets always accompany the reef, and range from the "hanging-wall" to the "foot-wall."

On the property of the Barrett Gold Mining Company, sheets of a highly felspathic igneous rock occur. They are much decomposed, and intersected by quartz veins, which however seldom carry gold, which only occurs in the igneous sheets.

Gold in the Barberton District.—The Swazieland schists mostly predominate here, quartz-bedded veins generally carrying the gold. In the Steynsdorp district, gold has been discovered in a lode, associated with copper pyrites and carbonate of iron. On the Piggspeak, in Swazieland, the white sandstones and quartzite contain gold.

Swazieland.—This country lies to the east of the Transvaal. It is practically unexplored. Gold, tin, and other metals undoubtedly exist there, but capital is not forthcoming to carry out the necessary exploration.

On the Occurrence of other Metals.—At present there are no mines in operation for the production of the following metals, although they exist, viz.:—iron, lead, copper, tin, antimony, silver, and mercury.

Iron.—Large deposits of magnetite and hæmatite are found in the Pretoria and Middleburg districts, but remain unproductive.

Lead.—Galena is found in the Machadadorp district, in the Pretoria and Delagoa Bay railway country; it contains a large percentage of silver, the ore body consisting of quartz impregnated with galena. Galena also occurs in the Pretoria and Malmani districts.

Copper.—Copper is now being prospected for in the Bronkhorstspruit district, and several leads of chalco-pyrite have been discovered.

Tin.—Alluvial cassiterite occurs in the Embabaam, Swazieland. The mother lode has not yet been discovered.

Antimony.—Antimony ore, occurring as stibnite, is found on the Murchison, north-east Transvaal.

Silver.—Silver is found, combined with bornite copper ore, in the Pretoria district, in addition to that already mentioned.

Mercury.—This metal has been discovered on the Portuguese border.

Diamonds.—The recent discovery of diamonds in the Transvaal has induced me to give a short description of the diamond deposits of South Africa. The existence of a pipe or chimney is characteristic of all the diamond deposits of South Africa. The yellow ground in which they were first found passes, at a deeper level, into what is termed hard blue, or "kimberlite." At first the appearance of the blue ground caused much excitement, the general opinion being that the yellow ground had become exhausted; the yellow ground is, however, neither more nor less than decomposed blue ground.

The diamond-pipes contain a large quantity of foreign material, in the shape of shale, sandstones, dolerite, and granite. The sandstones and shales, have evidently fallen in from the sides, the granite having been carried up in the ascent of the molten material.

The diamond matrix (kimberlite) consists of garnets (pyrope), ilmenite, mica (vaalite), and olivine crystals, constituting a serpentine breccia. The rock in a state of decomposition has a greasy feel.

In the river diggings, crystals of ilmenite, pyrope, and olivine, accompanied by agates and zeolites, are found. Recently, in the neighbourhood of Pretoria, a pipe containing kimberlite (?) has been discovered. Alluvial diamonds are also being found in the south-western border of the Transvaal, in the vicinity of Christiana. I may here add that diamonds occur in the strata of all the different geological periods of South Africa.

III.

A LIST OF IRISH CORALLINACEÆ.

By T. JOHNSON, D.Sc., (Lond.), F.L.S., Professor of Botany, Royal College of Science, and Keeper of the Botanical Collections, Science and Art Museum, Dublin; and MISS R. HENSMAN.

[Read April 20; Received for Publication[1] November 26;
Published January 4, 1899.]

The Corallinaceæ form a well-defined group of marine red algæ, characterised by the presence of carbonate of lime, the plant-body having a pink, brittle, chalky, or even stony consistence. The group is represented on the coast of Ireland by the genera Schmitziella, Choreonema, Melobesia, Lithothamnion (including Lithophyllum), and Corallina (including Jania).

Until fifty years ago these sea-weeds were regarded as animals associated with the corals, and known as Nullipores.

Schmitziella has a peculiar habitat, growing in the thick cell-wall of a green alga, *Cladophora pellucida*, Kütz. Choreonema forms wartlike projections on the joints of various species of Corallina. Melobesia occurs as an epiphyte in colonies of usually minute thin discs on Zostera and various sea-weeds.

Lithothamnion and Lithophyllum have a more or less stony aspect, unbranched, or with small warty, or clumsy-looking, or delicate, or even ribbon-like branches. Rockpools—floors and sides—are often completely covered with Lithothamnion species.

Corallina is, in some of its species, very common and widely distributed. It has a jointed, branched plant-body. At one time several of the genera were supposed to be the early

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[1] The publication of this Paper was delayed in the hope that the nomenclature of the Corallinaceæ, on which discussion is proceeding, would have become more stable.

stages of Corallina, and to be indicated in it by its disc of attachment.

Reproduction takes place vegetatively by the usual Floridean tetrasporangia which, in the Corallinaceæ, show zonately arranged tetraspores. These asexual organs are like the male organs (antheridia) and female organs (procarps), arranged in groups in small hemispherical, conical, or depressed conceptacles, which open, in some cases, by a single pore; in others, in a sieve-like manner. The cystocarp, or fruit of sexually formed carpospores, is peculiar in its mode of formation, to the group. We obtained confirmation[1] of the views expressed by Solms Laubach and others as to the mode, in the examination of the cystocarps of *Melobesia Corallinæ*, Crn. We had hoped to give an account of our examination of the anatomy of different members of the group, but various duties have compelled us to postpone the matter for the present. The list embodies the result of collections made during the past seven or eight years at different points of the coast. One of us (T. J.), in April, 1891, spent a fortnight on the Fishery Survey boat, S.S. *Harlequin*, with the Rev. W. S. Green, F.R.G.S., and made such collections, as opportunity afforded, between Galway Bay and Belmullet. It was during an enforced stay of several hours in Frenchport, to allow the Race round Erris Head to lose some of its force, that the species *Melobesia confinis*, Crn., a French weed, new to the United Kingdom, was collected.

The late Professor W. H. Harvey wrote, fifty years ago, of the economic value of the Corallinaceæ of Bantry Bay—the "coral sand"—as a manure.[2] This coral sand, chiefly composed of *Lithothamnion coralloides*, is now largely dredged and used in county Cork as a top-dressing for lime for potatoes. In Connemara and other parts of the Irish coast similar coralline beds occur. We are not aware of their being utilized elsewhere than in Bantry district. We are indebted to R. J. Moss, F.C.S., F.I.C., the Registrar and Consulting Chemist of the Royal Dublin Society and to T. S. Porter, Agricultural Superintendent, Irish Land

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[1] The importance of this confirmation is increased by the just-published discovery of Oltmanns that in *Dudresnaya*, etc., a second act of fertilisation does not take place.

[2] A specimen is to be seen in the Botanical Collections of the Science and Art Museum, presented by W. M. Murphy, J.P. The same species occurs on the west coast of France, and is used there also as a manure.

Commission, for the permission to publish the following analysis of the "coral sand":—

"*October 21st, 1895.*

"Analysis of sand from Knockboy, county Galway, received August 1st.

"Analysis of 'coral' from Bantry, received August 6th.

"100 parts, air-dried, contain:—

—	KNOCKBOY.	BANTRY.
Moisture, ...	0·70	1·38
Iron and Aluminium Oxides, ..	·55	·94
Lime, ...	33·26	44·63
Magnesia, ...	·28	3·40
Soda, ...	1·53	·92
Potash, ...	1·54	·36
Silica, ...	—	·23
Carbonic acid, ...	28·65	37·50
Phosphoric acid, ...	trace.	·06
Sulphuric acid, ...	trace.	·61
Chlorine, ...	0·18	·76
Organic and Volatile matter* by difference,	4·49	5·50
Sand, insoluble matter, ...	28·82	3·71
	100·00	100·00

* Containing Nitrogen, ..	0·056	0·073

"The Knockboy sample contains 59·4 per cent. of carbonate of lime, and the Bantry sample 79·72 per cent. of carbonate of lime. In the former sample the carbonate of lime is in the form of the *débris* of sea-shells, and in the latter it is in the form of fragments of corallines. In both samples I have represented the alkalies as oxides, though doubtless they are present to some extent as chlorides. It should be noted, too, that the total alkalies, including those in the insoluble sand, are given in each case. This introduces an error which falls upon the organic and volatile matter; it is inappreciable in the Bantry sand, but may amount to about 2 per cent. in the Knockboy.

"In both samples the efficacy of the sand as a fertilizing agent must be attributed mainly to the carbonate of lime; phosphoric acid and nitrogen are not present in sufficient quantity to produce much effect. The Knockboy sand, however, contains a notable quantity of potash in addition to carbonate of lime. This potash would render the sand a valuable fertilizing agent in potato cultivation.

"(Sgd.) "RICHARD J. MOSS, F.C.S., F.I.C.,
"*Chemical Analyst, Royal Dublin Society.*

"THE SECRETARY,
"AGRICULTURAL DEPARTMENT,
"IRISH LAND COMMISSION."

The number of species recorded as Irish in Harvey's *Phycologia Britannica* (1846–1851) is 13.

The useful "Revised List of British Marine Algæ," contributed by Holmes and Batters to the Annals of Botany, 1891, adds nothing to Harvey's records of the group. This list contains some 30–35 Irish species, of which those marked * are additions to the list. There are several forms, not in the list, awaiting more complete material, or comparison with specimens from different seas, for their satisfactory identification.

Our work has been materially aided by the Royal Dublin Society, as already mentioned, by the Fauna and Flora Committee of the Royal Irish Academy, as well as by the Royal Society.

Our thanks are due to Dr. M. Foslie, through whose hands the Lithothamnion specimens have passed, and from whom the Museum has received a fine set of Norwegian Corallinaceæ.

CORALLINACEÆ.

*SCHMITZIELLA, Born. et Batt.

S. endophlœa, Born. et Batt.

Farrihy Bay, county Clare, 1891; Calf Island, county Cork; Dalkey, county Dublin.

*CHOREONEMA, Schmitz.

Ch. Thureti, Schmitz. (*Melobesia Thureti*, Born.)

Common all round the coast, growing on *Corallina officinalis*, *C. squamata*, *C. rubens*. This species was for a long time regarded as an abnormal fruit of *C. officinalis*.

MELOBESIA, Lamx.

M. confervoides (*Lithocystis Allmanni*, Phyc. Brit.)

Malahide, county Dublin (Phyc. Brit.); Farrihy Bay, county Clare; Helvick Point, county Waterford.[1]

We are not altogether satisfied as to the independence of this species, in the absence of reproductive organs.

**M. corticiformis*, Kütz.

Common all round the coast, on *Furcellaria fastigiata*, Lamx.

M. membranacea, Lamx.

Rosanoff (" Recherches anatomiques s. l. Mélobésiées") states that this species is not at all as common as recorded. There is danger of confusing it with *M. Lejolisii*, Rosan., and *M. farinosa*, Lamx.

In the S.W. on *Cystoseira*. General (?).

M. farinosa, Lamx.

Roundstone, and other points in the West of Ireland; Helvick Point. Probably generally distributed, growing on *Zostera*.

[*M. verrucata*, Lamx.]

In answer to our inquiries, M. le Prof. Le Jolis wrote:—"I do not possess any specimens of the enigmatic *M. verrucata*, Lamx., and my opinion is that such a name should be suppressed. Rosanoff, a very clever and conscientious botanist, who, at my request, undertook here the study of Melobesieæ, went to Caen in order to investigate the type specimens of Lamouroux's herbarium, and ascertained that the specimen labelled *M. verrucata* by Lamouroux, is nothing but *M. pustulata*."

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[1] We have been helped in the examination of the S.-E. Collections by Miss M. C. Knowles.

**M. Lejolisii*, Rosan.

Roundstone; Bear Island, Bantry Bay.

This species is more or less distinguishable, to the naked eye or by the pocket lens, from *M. membranacea*, Lamx., which has larger conceptacles, more sharply marked off from the thallus. Microscopically *M. Lejolisii* is distinguished by its hair-beset conceptacular pore.

M. pustulata, Lamx.

This species occurs all round the coast, especially on *Phyllophora rubens*, Grev.

**M. macrocarpa*, Rosan.

Bear Island.

This species is easily mistaken for *M. pustulata*, being distinguished from it by having bisporous tetrasporangia, not tetrasporous ones, as in *M. pustulata*.

**M. Laminariæ*, Crn.

West of Ireland; Dungarvan.

This species is common on stalks of Laminaria, in Dungarvan Bay, forming thick, brittle, pink incrustations on the stalk, and must add largely to the manurial value of such Laminarias.

**M. Corallinæ*, Crn.

This species has been collected nearly all round the Irish coast (not between Howth and Raven Point, the least examined stretch of coast for marine algæ generally). It forms thick, lumpy expansions on *Corallina officinalis*, with conceptacles not much projecting.

**M. confinis*, Crn.

Frenchport, county Mayo.

Forms small, slightly thickened, hard swellings on *C. officinalis*, and on limpet shells; has vertically elongated thallus-cells and bisporous tetrasporangia.

LITHOTHAMNION, Phil.

Sub-Gen. EULITHOTHAMNION, Fosl.

Section I.—**Innatæ**, Fosl.

**Lithothamnion fruticulosum* (Kütz.), Fosl.

Roundstone, M'Calla; Great Man's Bay.

**L. apiculatum*, Fosl. (?)

Very nearly related to *L. tophiforme*, Unger; needs further examination. Roundstone.

**L. coralloides*, Crn.

f. flabelligera, Fosl.

Dalkey; Belfast.

This Coralline is abundant in Dalkey Sound; was also dredged by us in Belfast Lough, off Carrickfergus; and has been collected by Batters, off Bute, in Scotland.

f. australis, Fosl.

f. subsimplex, Batt.

West of Ireland.

**L. colliculosum*, Fosl.

Roundstone, M'Calla; West of Ireland.

L. polymorphum (L.), Areschg.

Bundoran; Belfast; Ireland's Eye; Dalkey Sound.

This species has given algologists a great deal of trouble, and has been mistaken constantly for *L. incrustans* (Phil.), Fosl.

**L. incrustans* (Phil.), Fosl.

Gola Island, county Donegal; Bundoran; Frenchport; Aranmore; Roundstone, Farrihy Bay; Kilkee, and many other points on the west coast of Ireland; Baltimore; Ballinacourty; Ireland's Eye.

A common species.

L. fasciculatum, Harv.

Roundstone, M'Calla; west of Ireland; dredged off Schull; Ballinacourty.

The locality near Schull was indicated to one of us by a coastguard officer at Baltimore, who had brought up "red clinkers" when oyster-dredging off Schull.

L. calcareum (Harv.), Areschg.

Donegal Bay, off Killybegs; Roundstone, M'Calla; Great Man's Bay; Valencia Island; and many other points on the west coast.

Foslie finds it difficult to determine the exact limits of Harvey's *Melobesia calcarea*, and considers M'Calla's *Nullipora compressa* a variety of the present species.

Our specimens of *L. coralloides*, *f. flabelligera*, agree very well with the figures of *Nullipora compressa* in Johnstone's "British Sponges and Lithophytes," and come from the same locality. The circumstances of the loss of the collection of specimens of *Corallinaceæ* made by M'Calla, and utilized by Harvey for description and illustration in *Phycologia Britannica*, have recently been described by Dr. E. P. Wright ("Notes from the Botanical School of Trinity College, Dublin, 1896"). The M'Calla Collection, in the charge of one of us, had the labels rewritten some time before we saw it, and is unfortunately not now, to this extent, authentic.

**L. dentatum*, Kütz., with **L. Hauckii*, Fosl. (*L. mamillosum*, Hauck), the latter partly covered with *L. incrustans* (Phil.), Fosl.

Roundstone, M'Calla.

L. agariciforme, Areschg.

Roundstone, M'Calla ; Roundstone, 1893.

This interesting and extremely local species is still to be got by dredging on the coral bank in Roundstone Bay.

Section II.—**Evanidæ.**

**L. tophiforme*, Unger (?).

Roundstone, 1893.

**L. Sonderi*, Hauck.

West of Ireland ; Ireland's Eye, 1896.

**L. circumscriptum*, Strömf.

West of Ireland.

**L. laevigatum*, Fosl.

Go Island, county Donegal ; and West of Ireland.

**L. Strömfeltii*, Fosl.

Common in Ireland.

Sub-Gen. LITHOPHYLLUM (Phil.), Fosl.

**L. Lenormandi* (Areschg.), Fosl.

Bundoran; Aranmore; Cave Islands; Bear Island; Baltimore; Dalkey Sound; Balbriggan; generally round the coast.

L. lichenoides (Phil.).

Roundstone; Miltown-Malbay; West of Ireland; Calf Island. Generally round Ireland; common in the west and south-west, as Harvey supposed.

CORALLINA, Lamx.

C. officinalis, L.

Common all round the coast.

C. squamata, Ellis.

Not uncommon all round the coast.

**C. mediterranea*, Areschg.

Ballydonegan Bay, and Baltimore, county Cork.

Distinguished from *C. officinalis*, of which Hauck regards it as a variety, by having one or more—one- to several-jointed, antenna-like outgrowths on the conceptacles.

C. rubens, Ellis et Sol.

Common round the coast, as is *C. rubens f. corniculata*, Hauck.

IV.

NOTES ON A METHOD OF COMPARING THE RELATIVE OPACITIES OF ORGANIC SUBSTANCES TO THE X RAYS.

By ERNEST A. W. HENLEY, B.A.

[COMMUNICATED BY PROFESSOR GEO. FRAS. FITZ GERALD, F.R.S., F.T.C.D.]

[Read December 21 ; Received for Publication, December 23 ;
Published January 21, 1899.]

In the following experiments, the method adopted was one which was suggested to me by Professor Fitz Gerald. A piece of the substance under examination was cut in the form of a right-angled triangular prism, and placed with its base over a photographic plate enclosed in a light-tight bag which was separated from the wedge by a thin sheet of celluloid, so as to prevent any moisture reaching the plate. Beside this wedge-shaped piece, another of the same dimensions, but of different material, was similarly placed, with its thin edge in the same straight line with the edge of the first wedge. The two wedges were then photographed by the X rays. On examining the negative, a gradual increase in the opacity of each wedge from the thin end towards the thick end was observed, as might be expected. Several prints of varying depths of colour were taken from the negative, and then the actual process of measurement commenced. The prints were cut at right angles to the thin edges of the wedges, and part of the photograph of one substance was placed in apposition with that of another substance. Now, if the substances under examination had the same opacity to the X rays, then, for points equally distant from the thin edges of the wedges, equal depths of colour would be observed. If, on the other hand, a certain substance A was more opaque to the X rays than another substance B, then, to obtain equal depths of colouring, it would be necessary to go back farther from the edge of the wedge B than from the edge of A. In the case of wedges of the same dimensions, the thickness at any point is proportional to its distance from the thin end of the wedge, measured along its base line.

The substances examined by this method were bone, muscle, and fat, taken from the sheep. The maximum thickness of the wedges varied from one to two inches. It was necessary to freeze the materials so that the wedges might be accurately cut. No attempt was made to secure a uniform current in the 10-inch Ruhmkorff coil used, as measurements were only made in the case of wedges which had been exposed at the same time and on the same plate. The time of exposure varied from one to three minutes. Only photographs of the central strip of each wedge were used, as shadows of the edges of the upper surface were thrown on the plate, owing to the obliquity of some of the rays. The time of exposure was varied, as well as the depth of colour in the prints, so as to obtain the greatest diversity of conditions. The lighter-coloured prints were found to be the most satisfactory for purposes of comparison.

Some of the wedges compared were of different sizes; and in such cases, a vertical section of each wedge was drawn to scale on paper, and the thicknesses corresponding to different distances along the base line in each wedge were easily obtained.

The first comparison was made between muscle and fat. As the result of seventeen measurements made on different prints from various negatives, the ratio of the opacities of muscle and fat was found to be 2·5 : 1.

The next comparison was made between bone and muscle. In the case of bone, variations occurred according as the specimen contained different proportions of cancellous tissue and of compact tissue. The results given are the mean of all the measurements. The ratio of the opacity of bone to that of muscle was found to be 1·6 : 1, as obtained from eleven measurements. This result, when combined with the previous one, gives the ratio of the opacity of bone to fat as 4 : 1. Hence, the numbers obtained, as representing the relative opacities of bone, muscle, and fat, are 4, 2·5, and 1.

V.

THE KIESELGUHR OF COUNTY ANTRIM. By JAMES HOLMS POLLOK, B. Sc.

[Read, January 18; Received for Publication, January 21; Published, March 13, 1899.]

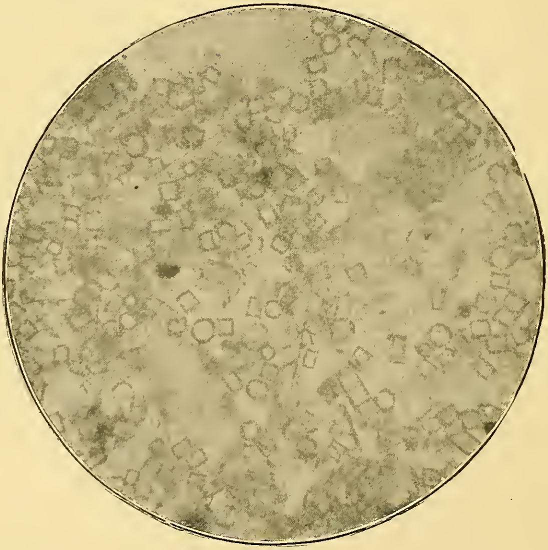
Some considerable time ago I received from Mrs. Hartley a sample of Kieselguhr from county Antrim to exhibit at the Conversazione of the Royal Dublin Society. Afterwards I noticed, in Pliny's "Natural History," the remarkable statement that the Romans were acquainted with a brick that floated. The passage says:—"At Pitane, in Asia, and in the cities of Maxilua and Calentum, in Farther Spain, there are bricks made which float in water when dry, the material being a sort of pumice earth, extremely good for the purpose when it can be made to unite"; and in the Bohn edition there is a footnote saying these bricks have been imitated by Fabroni with a light argillaceous earth found in the territory of Sienna.

It occurred to me that the floating bricks of ancient Rome could probably be reproduced from the county Antrim Kieselguhr, and on trial it made a brick that floated exceedingly well when first placed in the water, but soon absorbed water and sank, exactly in accordance with Pliny's statement. By coating the bricks over with a thin skin of paraffin wax to prevent absorption of water they are rendered permanently buoyant.

An analysis was then made of the specimen I had received, and its composition found to be:—

	Per cent.
Silica, ...	70·9
Alumina, . . .	9·8
Ferric Oxide, . .	5·4
Lime, ...	1·5
Magnesia, . . .	0·1
Water and Organic Matter,	12·0
	99·7

I am indebted to Mr. R. G. Norman for many specimens of Irish and other Kieselguhrs which I have examined. Under the microscope the Kieselguhr from county Antrim presents a very pretty appearance, showing innumerable little cubical box-shaped diatoms, also little tubs or drums in less quantity, and a few elongated and boat-shaped diatoms, apparently of the kind known as pinnulariæ and *Navicula Westii*; there are others of a star or radial shape, but the neatly shaped cubical boxes are the predominating form. A curious fact was noted that in focussing for the boxes the large boat-shaped and radial diatoms almost disappeared, and that when they were brought out clearly the boxes became very indistinct. On measurement the width of the little box-shaped diatoms is found to be about $\frac{1}{200}$ mm.



This illustration shows the highly magnified image of the box and tub-shaped diatoms.

The raw Kieselguhr, as cut from the deposit and sun-dried, has a specific gravity of ·5422; when moulded in a brick, and burned at a very low temperature, it was found to have a density of ·8073. When burned at a somewhat higher temperature it takes a light red colour, and has a density of ·7691.

A piece of burned Kieselguhr of 54·87 grams absorbed on immersion 38 grams of water, having then a weight of 92·87 grams, and its actual volume was 68 cubic centimetres, corresponding to a density of ·8069. If we may take the volume of the water absorbed as a measure of the porosity, we see that every 100 c.c. of Kieselguhr has pores of a total capacity of 55·9 c.c. for absorption of liquids of any kind. It is interesting to note that this would give an absolute density of the solid skeleton of the Kieselguhr of 1·829, the density of solid quartz being 2·6, but we have no right to suppose that the pores when treated as above are fully saturated.

In July of 1898 I visited Toome Bridge, and found that the deposit was being worked on the east bank by Messrs. J. and F. Grant, who gave me every opportunity of examining the character of the deposit, and to whom I am indebted for the following analysis of the deposit at this point.

Analysis of Kieselguhr from Toome Bridge, County Antrim.

Sample from the Middle of the Deposit.

	As Received.		Calcined.	
Silica (soluble),.	57·12	per cent.	66·50	per cent.
Silica (insoluble),	15·89	,,	18·50	,,
Alumina,	8·55	,,	9·95	,,
Oxide of Iron,	2·09	,,	2·43	,,
Lime,	1·14	,,	1·33	,,
Magnesia,	0·83	,,	0·96	,,
Alkalies,	0·28	,,	0·33	,,
Organic Matter and Combined Water,	7·71	,,	—	,,
Moisture,	6·39	,,	—	,,
	100·00	,,	100·00	,,

At Toome Bridge the deposit is some four feet thick; and, after cutting and drying in the sun, the Kieselguhr is of a very white colour, with a few roots through it, but otherwise exceedingly pure and, after drying, of surprising lightness.

The deposit, as it rests on the top of peat, and is covered only by vegetation, is obviously of exceedingly recent formation. It extends all along both banks of the lower Bann, from Toome Bridge, where the river emerges from Loch Neagh, right down to Coleraine. At Toome Bridge the deposit, so far as one can judge by superficial indications, and without actually proving by digging, extends some two miles west of the Bann, then narrows in the form of a great triangle, towards Coleraine. It is absolutely flat, only a few feet above the level of the Bann, and at such a height that it would be covered at times of inundation. Rocks and stones that are covered when the Bann is in flood have on them a thin skin of diatomecious deposit, so that one is irresistibly led to the conclusion that the deposit is laid down when the Bann is flooded, and that the deposition is going on now. That the water, highly charged with silicious skeletons of diatoms, comes pouring out of Loch Neagh, and deposits this infusorial earth in the quiet waters of the flooded portions. The great storehouse of the Kieselguhr is Loch Neagh itself, and the deposit on the banks of the Bann is as nothing to the immense deposit there must be on the bottom of the Loch. Of course this is a point that cannot be finally settled by speculative considerations such as the above, but must be determined by actual dredging, which will mean a certain amount of expense.

The commercial uses of Kieselguhr are numerous, firstly, for dynamite, but the dynamite manufacturer states that the particular forms of the organisms in the county Antrim Kieselguhr are not those best suited for making dynamite, a tubular form giving, I am told, the best explosive effect. Kieselguhr, however, has many other uses for which thousands of tons a year are required, and are now shipped from the Continent to London. It is one of the best non-conductors of heat and sound, and is superior to all other materials for covering boilers and steam-pipes, for lining fireproof walls, floors, safes, and refrigerators, and its extreme lightness should specially recommend it for all such uses on board ship, and especially for lining fireproof bulkheads, for which one would imagine a very ready market would be found at Belfast if it were put in the proper form for consumption.

VI.

ON THE CORRECTION OF ERRORS IN THE DISTRIBUTION OF TIME SIGNALS. BY SIR HOWARD GRUBB, F.R.S., Vice-President, Royal Dublin Society. (PLATES IV. and V.)

[Read NOVEMBER 16; Received for Publication NOVEMBER 21, 1898;
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HAVING had occasion lately to inquire into the merits of the various existing systems of synchronizing clocks, and to report on the best arrangements to be made suitable for a large Municipal Institution in one of the larger English towns, I have thought that it might be interesting to the Royal Dublin Society if I placed before them the results of my inquiries and the conclusions at which I have arrived, more especially as the conditions existing in the Institution referred to are, in many ways, very similar to those in the Royal Dublin Society, though on a larger scale.

It is hardly necessary, at this period of the nineteenth century, to enlarge on the importance of having correct time available; and the Royal Dublin Society recognised this many years ago by establishing a system of synchronized clocks in Dublin, controlled from a central clock in this house, which clock was itself checked by a daily signal from either Greenwich or Dunsink.

The controlling of the outside clocks throughout the town was effected by sympathetic pendulums of the "Ritchie" type, and the system worked well at first; but in time, as the telegraph and telephone wires accumulated in the city, the induction produced in our wires from the strong currents in the adjacent wires caused such serious trouble and irregularities as necessitated the abandonment of the system. This has been the case also in many other towns.

The conditions present in the Institution on which I have lately had to report are, as I said, somewhat similar to that of the Royal Dublin Society (not taking into account any outside clocks); that is to say, it is a building unconnected with any Observatory, and unsuitable for the erection of transit instruments, and therefore has to depend ultimately on a daily signal from Greenwich. It contains some 200 rooms, each requiring a clock face which it is desirable should synchronize with the central or standard clock, and show as nearly as possible the true time.

Under these circumstances I made the following recommendations:—

The installation naturally divided itself under three heads—

(A)—A standard clock, of best procurable make, placed in such a position as would ensure its protection as far as possible from climatic or other changes, and furnished with electrical connexions suitable for the control of—

(B)—A strong piece of uniform motion clockwork automatically controlled at stated intervals (say, every 15 seconds) from A, and further checked and controlled once in every 24 hours by the Greenwich signal received through the Post Office: this piece of mechanism to be enclosed in a glass case exposed in some prominent position (say, in the entrance hall), supplied with dials and hands, and arranged also so as to serve as a distributing clock for driving.

(C)—A series of, say, 200 dials distributed throughout the building, each being furnished with minute and hour hands, and the necessary dial work, actuated once a minute only from the distributing clock B in the entrance hall.

The distributing clock B in the hall, being automatically controlled once in every 15 seconds from the standard clock, may be depended upon to keep as accurate time as the standard clock itself, hour by hour; while, to prevent any accumulation of small errors which might, in the course of some days, reach an inconvenient amount, there is the further check by Greenwich signal at 10 a.m. or 1 p.m. every day. Any error that exists on receipt of this signal is not only wiped out at once automatically, but the amount of this error is registered on a paper tape for after-reference, if desired.

The maximum error that can exist, therefore, cannot be greater than the rate + or − of the standard clock for 24 hours; while, after the receipt of the Greenwich signal, the clock B may be relied on to within a fraction of a second.

I here append details of the construction of the three parts, A, B, and C:—

(A).—Should be the best procurable timekeeper, preferably with a gravity escapement, and furnished with an arrangement which would make a delicate electrical contact once in every 15 seconds.

Such a clock, mounted in the ordinary way, should give an excellent result; but still further to ensure accurate working, I would propose that this clock be enclosed in an air-tight case after the manner adopted by Professor Becker, of Glasgow, by which the pressure is kept constant, and this case placed in another, duly protected by non-conducting material, and the whole mounted within its double chamber in the basement of the Institution, so that it would be practically free from both barometric and thermometric changes.

Such a clock should have very small *errors*, but no clock is without some small *rate*. The rate + or – of a clock must not be confounded with its errors. The very best clock, and that with the smallest error, may have a fairly large rate; that is to say, it may give 86,401, or 86,399 secs. in the 24 hours instead of 86,400, but may preserve that rate steadily, day by day, without any sensible *error* from that rate. This is not serious for one day, but if allowed to accumulate for a week or a month, it is; and it must be remembered that a clock like this standard clock A, being sealed up in a case, cannot be readily got at for re-setting; therefore it is that I propose to depend on this clock, accurate though it may be, for only 24 hours at a time, and have made arrangements in the part B to have this—the distributing clock—checked and automatically corrected by a Greenwich signal, an automatic registration being made each day of the extent of the correction of the standard clock A.

Another trouble with sealed-up clocks has sometimes been experienced—I refer to the gradual oxidation after a lapse of time of the electrical contacts. This will probably not be serious with the very small current necessary; but if desired to ensure against failure in this respect, I would recommend that the air-tight case of the standard clock be enclosed in another larger one, forming a jacket, both the clock case and its jacket being filled with nitrogen gas instead of air ; no oxidation can be possible in the absence of oxygen. The nitrogen in the jacket can be occasionally renewed without affecting the inside chamber, and as the inner chamber is always surrounded, as well as filled, with nitrogen, no evil effects can ensue from diffusion.

(B).—This portion of the apparatus is novel, and I therefore submit a design and detailed description. (See Plate IV.).

It consists essentially of a uniform motion clock somewhat similar to what we use for our astronomical telescopes.

This clock serves to drive two spindles, the first at a rate of once in 15 seconds, and the other once in 60 seconds. On the 15-seconds spindle, there is a controlling apparatus very similar to what we use on our equatorials, by which the rate is checked every turn, *i e.*, every 15 seconds ; and if there be any difference between this clock and the standard clock amounting to even one-tenth of a second, one or other of the correcting differential gears (*b* or *b′*) is brought into action, and this error is wiped out. This spindle (A) may therefore be assumed to revolve exactly in accord with the standard clock A.

On the 60-seconds spindle (B) is a similar correcting arrangement, which, however, only comes into play once in 24 hours, viz., on the arrival of the Greenwich signal, and its duty is to wipe away any difference + or – that may be present between the time as given by Greenwich and that given by the standard clock, and to register this on a paper slip for after-reference.

This corrected 60-seconds spindle (B) is used, first, to show correct time on a suitable dial or set of dials in the hall, and, secondly, to drive or control all the 200 clocks in the various rooms of the building.

(C).—For the distribution of time throughout the building, there is the choice of various systems.

There is the pneumatic system and the electrical system, and the latter can be again divided into a system which regulates or controls clocks possessing a certain motive power in themselves, and that which actually drives the whole series of clocks by electrical impulses.

Any of these systems can be worked from the distributing clock described under head B.

The pneumatic system possesses the great advantage of being quite independent of any electrical currents in adjacent wires, which currents sometimes cause great trouble by producing induced currents in the electrical wires to the clocks.

I was at first inclined to recommend this system, but as the currents in most of the service wires in the new Institution will be, I am informed, constant, and not intermittent, this objection does not apply seriously; besides which, I find, on examination of the pneumatic system, as carried out in Paris, two serious objections—

(*a*). It has apparently been found necessary to transmit the power, not by a sudden pulse of air, but by gradually filling the whole system of tubes with compressed air, the operation taking about 20 seconds, and then allowing this to flow out again during 40 seconds. Consequently the movement of the clock hand may take place anywhere within this 20-seconds period, and this, though accurate enough for domestic purposes, would not suffice for some of the purposes for which these clocks may be used.

(*b*). I find that the air-compressing and distributing apparatus is extensive, complicated, and costly for small installations. Therefore, I do not see my way, at present, to recommend it for this particular case, notwithstanding its obvious advantages in other ways.

As regards the electrical system of distribution:—

There are many excellent systems in the market by which clocks, having motive powers of their own in the form of weights, springs, &c., can be regulated and corrected from a central clock, and almost any of these, except the sympathetic pendulum clocks, would be found suitable. (Fig. 7.) [For figs. 1–6, *see* Plate V.]

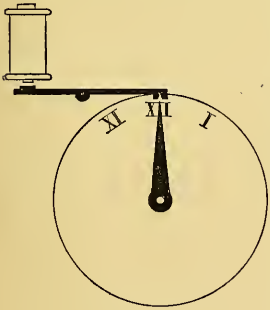

Fig. 7.

That which I would prefer is the clock which is furnished with a forked lever placed over the XII on the dial, which lever is momentarily brought down, at each hour precisely, by a current from the distributing clock, and sets the minute-hand right (if it be wrong) by the impact of the

Λ-shaped fork against a pin on the minute-hand. This is simple, inexpensive, and very reliable.

Any clock of this form, however, requires winding periodically; and if it be desired to avoid this, one or other of the second class of electric clocks which do not require winding must be used.

There are many varieties of these also in the market, but I cannot say that any of them are certain to prove satisfactory. It is much more difficult to keep a clock going correctly when it has no driving power of its own, and when the work of *driving*, as well as *regulating*, has to be done by the electric current.

There are some excellent clocks of this description in the market, but it must be remembered that there is one great difference between the working of these *driven* clocks and that of the first-mentioned clocks, in which the *regulation only*, and not the driving, is effected by the electrical current.

In the latter, if the current at any hour fails from some cause to do its duty (and in electrical arrangements of the very best order this will sometimes happen), the only result is that, at the next hour, the correction to be made will be double that which would have been required if the former current had acted rightly; and the error in the clock before that correction will be double that which it would have been for the one hour; but as the error for two or three hours run must be very small, and *as it is wiped out completely by the first current that comes after the failure*, this is of little consequence.

In the former case, however (that of the driven clock), any error that occurs is not wiped out by any of the succeeding currents, but remains there until set right by human agency; and if the errors, though only occasional, be (as is likely) mostly of the same character, *i.e.*, gaining or losing, they will accumulate, and in time amount to a serious quantity.

For the above reasons I would recommend for this purpose, *where convenient*, the adoption of clocks which have a motive power of their own, and which only depend on the central clock for periodic *correction* of any accumulating errors; or if, as is sometimes the case, it is highly desirous to avoid the necessity of periodic winding, clocks of the self-winding principle may be used, corrected periodically from the central or distributing clock.

In the case under consideration, however, where the number of rooms, and therefore of clocks, amounts to so large a number as 200, it is evidently important to simplify and keep down the cost of each individual clock; therefore, it will probably be found more economical to run an additional wire through the various rooms, and use two distinct currents, one of which will supply the small necessary motive power for driving the wheelwork, which, in this case, may only mean the few wheels and pinions necessary for the dial-work; and the other current to work, once a minute, the escapement which allows the hands to move forward at each minute.

This latter arrangement has many advantages; and it can easily be arranged that an overplus of winding power be supplied, so that even if there be one or two, or even five or six, misses in each minute, there will still be ample left to do the necessary work, and there need be no error. As it is very unlikely that a greater number of failures than this will ever occur in one minute, practically the only danger is, that of the other or minute current missing—that which allows the hand to move forward. As there are only 1442 of these in the 24 hours, as against 86,400 of the others, the danger is proportionately less; but to avoid even this danger, I have devised an arrangement by which, if the minute current should by any chance fail, the escapement will be let off *mechanically* a second or so *after it ought to have been let off electrically*, the result being, that that particular minute will be late by one or two seconds, but there will be no cumulative error, and when the next minute current comes it wipes out the error completely.

In this clock, therefore, it is possible to actually disconnect the wires for several seconds during any part of the minute, and still the clock will show correct time.

I would suggest that this last form be used in the more important positions, and the simpler form for the rest.

[Explanation of Plates.

EXPLANATION OF PLATES IV. AND V.

In Plate IV., AA is a shaft which is in direct connexion with the 15-seconds shaft of the uniform motion clock, and revolves approximately at that rate.

A toothed wheel, No. 1, is fixed upon this shaft; all the other wheels, with the exception of Nos. 7 and 8 at the other end, are loose upon the shaft.

Wheel No. 2, which is cast in one piece with No. 3, is cut with a slightly different number of teeth from No. 1, and is driven from it by means of the pair of pinions, *p p*, which act as couplers so long as the rate is normal; if, however, the disc *b′ b′* is arrested momentarily, the motion is conveyed from No. 1 to No. 2 through the pinions *p p*, and consequently a slight differential rate is produced, as Nos. 1 and 2 have not quite the same number of teeth.

The same description applies to Nos. 3 and 4, the result being that a momentary stoppage of the disc *b b* causes a slight acceleration of the rate of the rest of the moving parts, including wheel No. 6; whereas a momentary stoppage of *b′ b′* causes a slight retardation.

No. 6, shown in black, is an ebonite ring, mounted with a pair of nearly half circles of silver shown enlarged in fig. 4, Plate V.

No. 7 is a light metallic disc with a notch or notches, better shown in figs. 2 and 4, Plate V.

(*c*) is an electro-magnet with an armature better shown in fig. 2, Plate V. This armature is worked from the sealed or standard clock through the relay (*f*), shown enlarged in fig. 3, Plate V., and the tooth of the armatures of this electro-magnet engages into the notch on wheel No. 7, and will not allow that wheel to revolve so long as it is engaged.

A current is sent into the electro-magnet (*c*) every 15 seconds from the standard clock. If the uniform clock has gone correctly, that current occurs at the moment that the V notch comes opposite the V on armature. If the uniform motion clock has gone either fast or slow, the notch will not be exactly opposite the tooth; but when the current arrives, the impact of the tooth on the side of the V notch, in wheel No. 7, sets that wheel, which is driven only by friction, backwards or forwards the necessary quantity.

By means of this device, the revolutions of the disc No. 7 are controlled from the standard clock, and kept in an exact uniformity at every 15 beats of the pendulum.

Fig. 4, Plate V., shows that the disc No. 7 has mounted upon it a small arm which plays round the silver half rings on the ebonite disc.

In the normal state, the contact of this arm with the silver-shod disc occurs in the break between the two silver rings, where a small piece of agate is inserted; but if the shaft AA has revolved too quickly or too slowly, and thus has necessitated an alteration of the position of the disc No. 7, the contact finger moves off from the agate block to one or other of the silver half-rings which forms an electrical connexion with the accelerator or retarder, *d* or *d'*. These remain sufficiently long in action to correct the error and bring the contact pin on to the agate block once more.

By this means, which is practically the same as what I have used with such success for many years past on my equatorial telescopes, I can ensure that the corrected portion of the apparatus on the shaft AA keeps time as accurately as the standard clock which controls it.

BB is a second shaft worked from the first by a pair of wheels of 4 to 1, and revolves once in a minute. This second shaft is supplied also with a pair of correctors and a checking arrangement worked, so far as this is concerned, only once in 24 hours, through a relay which receives the Greenwich signal. There is no occasion to describe this second shaft, as it is practically identical with the first, its duty being to remove, every 24 hours, any difference that may exist between the time given by the standard clock and that of the Greenwich signal. Without this second shaft, the rate of the clock would be exactly that of the rate of the standard clock which controls it, and which would, no doubt, be excellent day by day; but the reception of the Greenwich signal and the automatic corrrection of it by the apparatus on this second shaft ensures that this clock will never be different from the true time as emanating from Greenwich by a quantity greater than what the standard clock errs in 24 hours.

Fig. 5, Plate V., shows a modified arrangement of fig. 2, by which the accelerator is dispensed with. The clock is given a slight gaining rate, and, consequently, it is only necessary to provide a retarder.

Fig. 6, Plate V., shows the suggestion for recording the amount of error in the standard clock every day. A tape of paper is arranged to pass round a roller which, in a general way, is not in contact with anything on the revolving shafts, but if either the accelerator or the retarder comes into action for any given number of seconds (say 5 or 6 seconds), this roller carrying the tape is pressed against another roller on the revolving shaft, and a capillary tube filled with ink draws a mark upon the tape, the length of which corresponds to the amount of correction which has been necessary to bring the clock into synchronism with Greenwich. Two of these capillary tubes would be provided, one to show the + error, and the other the – error.

VII.

PROPOSAL FOR THE UTILIZATION OF THE "MARCONI" SYSTEM OF WIRELESS TELEGRAPHY FOR THE CONTROL OF PUBLIC AND OTHER CLOCKS. By SIR HOWARD GRUBB, F.R.S., VICE-PRESIDENT, R.D.S.

[Read January 18; Received for Publication January 21;
Published March 25, 1899.]

In a Paper read before this Society last November on "The Correction of Errors in the Distribution of Time Signals," I described a scheme of time distribution suitable for a large institution containing some two hundred rooms, all of which it was desirable to have furnished with clocks synchronized with one another, and controlled from one central clock. This central or distributing clock was itself to be controlled from the best procurable standard timekeeper placed under exceptionally favourable conditions, and was further checked and corrected once every twenty-four hours by an electric signal from Greenwich Observatory.

The scheme proposed in the Paper referred to dealt only with the control of clocks in the one building, but I incidentally mentioned that the Royal Dublin Society had some years ago established a system of synchronized clocks in Dublin controlled from a central clock in this building, and that for some time this system worked satisfactorily, and proved a great convenience to the citizens, but with the introduction of the telephone system, and the multiplication of the telegraph wires, troubles arose from induction and other causes which finally necessitated the abandonment of the system.

Adventitious currents produced by induction or other causes which, in the case of telephone and telegraph circuits, produce but a slight error or gap in the messages, cause errors in synchronized clocks which remain permanent until corrected by human attention, and practically destroy the value of the installation.

In working out the scheme above referred to, it seemed to me a pity, if such a perfect installation should be erected in a public building in the midst of a large city, that advantage could not be taken of it by those living or having their houses of business in the vicinity, and I therefore naturally looked about to see if I could find any system that would be free from the disadvantages of that which was tried and abandoned in Dublin and other cities.

Having taken an active interest in the work of the Committee appointed by this Society to carry out the scheme of clock control in Dublin, I was fully aware that this scheme was only abandoned after most careful and searching investigation of all the various systems then available; I refer to a period about fifteen years ago. It then occurred to me that possibly the system of Wireless Telegraphy, which has lately been raised from the sphere of a laboratory experiment to that of a practical achievement by the invention of Signor Marconi, might be utilized, and a little investigation has convinced me that his system is particularly well adapted for this purpose, and is free from all the disadvantages which caused the abandonment of the other systems.

Looking back at the various failures we had in the old system, I find they may all be said to be due to one or other of three causes:—

(1) Induced currents in the clock wires, mainly produced by currents in adjacent telegraph or telephone wires.

(2) False currents, or failure of currents produced by short circuiting of the clock system, generally caused by telegraph line-men erecting or repairing adjacent wires, and drawing one wire over others, &c.

(3) Failure of current owing to improper action of some of the users of the system. It not infrequently occurred that on failure of the current, it was found that some user had entirely disconnected his wires for the purpose of repairing his clock, thus disarranging the whole system.

Now let us consider what effect these would have when using the "Marconi" system.

(1) The nature of the high-frequency currents is such that they are not in any way affected by currents in adjacent wires.

(2) As there are no wires, this cannot take place.

(3) Each user is absolutely independent of all others, and he cannot by any action of his own interfere with the efficiency of any one else's apparatus.

It therefore appears that this system is exceedingly well fitted for this particular work, and I hope it may be allowed a fair trial before long.

The whole arrangement would be of exceeding simplicity.

In some central position in a town a standard clock would be fixed whose duty would be that of starting at stated intervals a generating apparatus such as is used by Mr. Marconi, and which, consists mainly of a strong induction coil. The current having been turned on to this for a fraction of a second causes a spark of high tension to pass between the terminals. Instantly an electrical wave is transmitted from this centre and passed over the town, its influence extending a greater or less number of miles according to the strength of the current.

Each establishment that is included in the system is furnished with one of Mr. Marconi's exquisitely delicate little "coherers," and a relay with a small local battery to work the correcting apparatus (of whatever nature it may be) for setting his clock.

As the electrical wave passes, the coherer is excited, the relay is attracted, bringing the local battery into action, that particular clock is set, and any error that may have existed is entirely wiped out.

There is something very beautiful in this action of the "Marconi" wave. In a city supplied with this apparatus we should be conscious as we hear each hour strike that above us and around us, swiftly and silently, this electrical wave is passing, conscientiously doing its work, and setting each clock in each establishment absolutely right, without any physical connexion whatever between the central distributing clock, and those which it keeps correct by means of this mysterious electrical wave.

We might go even still further, and though I do not put it forward as a proposition likely to be carried out in any way, except as an experiment, yet it undoubtedly would be perfectly possible to carry an apparatus in one's pocket, and have our watches automatically set by this electrical wave as we walk about the streets.

As to the best arrangement of correcting apparatus to attach to our clocks. Once we have the relay in our houses worked by the electrical wave, we can use it (the relay) to work any kind of apparatus we choose. I would prefer for all commercial and social purposes that only one wave be sent per hour, and that the correcting apparatus be of the simplest possible form such as described in my Paper read last November.

It will be observed that, in this arrangement,[1] even if a current fails for one hour, the only fault will be an error in the clock for the succeeding hour, but the next wave that comes wipes this out, and there can be no cumulative error.

I think it will be evident to anyone who has followed my remarks that the system of synchronizing clocks by the "Marconi" wave is a perfectly practicable one.

For convenience of exhibition we have necessarily had to place the distributing arrangement and the receivers within the same building, but it will be easily understood that the same influence which has been so successfully working this Morse pen, and sending messages through it every day, for months past, eighteen miles across the sea, from Alum Bay to Bournemouth, is quite capable of working this other equally simple apparatus for synchronizing clocks, and that, in fact, if the clocks in Bournemouth were supplied with the necessary receiving apparatus, they could all be checked, and kept to correct time by a standard clock in the Isle of Wight.

It will be observed that in the course of my remarks I have spoken only of the "Marconi" system of Wireless Telegraphy. It may be asked whether this is the only system available. I have had no experience whatever with any other form of wireless telegraphy. It may be found possible to work with some other, but I have confined my remarks to the "Marconi" system because, as I have said before, while other systems can hardly be said to have emerged from the experimental stage, the "Marconi" system of wireless telegraphy is an accomplished fact.

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[1] A practical illustration was here given of the proposed arrangement.

VIII.

ON A HYDRO-DYNAMICAL HYPOTHESIS AS TO ELECTRO-MAGNETIC ACTIONS.

By PROFESSOR GEORGE FRANCIS FITZ GERALD, F.R.S.

[Read December 21; Received for Publication December 23, 1898; Published March 25, 1899.]

For many years I have been advocating the hypothesis that the ether is of the nature of a fluid full of vortical motion, and that electro-magnetic actions are due to particular arrangements of this motion, which is, in general, irregular or at least undirected.

Some years ago, Lord Kelvin, at a meeting of the British Association, and subsequently in the *Phil. Mag.*, ser. v., 1887, vol. xxiv., p. 342, published an investigation as to a possible transference of laminar wave disturbance through a turbulent liquid. He was not satisfied with the investigation, principally, I believe, because it presupposed that there would be inappreciable diffusion of motion. I am, however, inclined to think that, if a liquid become turbulent by drawing out and twisting together long thin vortices, the rate of translation of the vortex cores would ultimately become very slow, and that the consequent diffusion of motion would become slower and slower as time went on, and the turbulence become more and more fine-grained. This result follows from the continual drawing out of the vortex filaments by their tangling with one another. In being thus drawn out, their energy of circulation is continually being increased; and as the total energy per unit volume of the fluid must remain constant, it follows that the energy of translation of vortex core would continually diminish. Hence there seems to me every reason to believe that wave disturbance can be propagated within such a turbulent liquid.

Subsequently Lord Kelvin showed (Royal Irish Acad. Proc., ser. III., 1889, vol. i., p. 340) how to calculate a stable, steady motion for a hollow vortex surrounded by a tore round which the liquid was circulating, and concluded that it would be possible to fill space with a series of approximately straight hollow vortex filaments which would be in stable steady motion. This seems to finally dispose of the objection that diffusion of vortices must take place, at least in the case of hollow vortices; and by making the vortex filaments sufficiently fine, the space might be filled with full vortices whose rate of diffusion could be made as slow as necessary to explain the ether, even if it could be shown that such an arrangement of full vortices would not be stable.

What I now desire to call attention to, is a hypothesis as to the nature of the wave motion which can be transmitted by a system of vortex filaments.

A vortex filament can have a spiral wave superposed upon it. The irrotational motion in the neighbourhood of this screw will be essentially the same as the distribution of magnetic force near a similar spiral wire carrying an electric current. There will be, on the whole, a flow along the inside of the spiral, but the motion of the fluid is complex. It could, however, be defined by a vector, whose direction was parallel to the axis of the spiral, and whose magnitude was measured by the square root of the mean square of the additional energy per unit length of the moving fluid above that of the undisturbed vortex. If then a space were filled with spiral vortices, all parallel to a given line, and causing flow in the same direction, there would be an increase in the energy per unit volume which could be measured by the square of a vector, say E. There would be, on the whole, a flow of fluid along the axes of these spiral vortices. Now, consider the case of a single spiral vortex surrounded by other parallel straight ones. These latter would not stay straight. They would be bent by the action of their spiral neighbour, and spiral waves would be set up along them. How can we describe this transference of spirality from one vortex to one of its neighbours? It depends upon two vectors—one the vector parallel to the axis of the spiral, and the other a vector perpendicular to the two vortices. The vector then defining the transference, being itself defined by two rectangular vectors, must be a vector perpendicular to both, *i.e.* must, in the case of a spiral vortex surrounded by others which it is setting in motion, be distributed in circles round the spiral vector. What will the magnitude of this new vector depend on, and how can we define it further? Its magnitude will depend on how fast the spirality is being lost by the original spiral. If we call this new circularly distributed vector H, and make its magnitude such that its square is equal to mean energy of this new motion, then, assuming wave propagation, we get, on account of the relation of direction between E and H, and of their velocities being small compared with the irregular motions already existing (so that we can assume them to be superposable linearly), that H must depend linearly on $\dot{E}$, thus

$$\dot{E} = A.V\Delta H$$

where A is a quantity, a velocity depending on the structure of the medium, *i.e.* depending on the nature of the turbulency in the undisturbed ether.

If we now can assume that, in the general case, the energy of the medium is the sum of its energies due to these two vectors, which, so far as they affect one another, are at right angles to one another, then we can write for the energy per unit volume of the ether

$$e = E^2 + H^2.$$

From this, and the principle of conservation of energy, we can conclude that $\dot{H} = -AV\Delta E$, and from these that

$$S\Delta\dot{E} = 0, \text{ and } S\Delta\dot{H} = 0,$$

so that, if at any time $S\Delta E = 0$, and $S\Delta H = 0$, they will continue so.

Now, these are the fundamental equations of wave propagation in the ether, and it only remains to explain wherein electric charges consist upon this hypothesis.

If we consider a point on a spiral vortex, and suppose that the spirality is so arranged that on both sides the flow of fluid within the coils is away from the point, then the spirality on one side of the point must be a right-handed screw, and on the other side a left-handed screw. Now, a point of this kind would be unique in the vortex. It would, so far as the fluid outside the vortex coils was concerned, be a sort of source from which fluid was flowing in all directions. This flow would, at a short distance from the source, be extremely slow, and the action between such points with their vortex spirals would be almost entirely confined to the actions already described between the spirals and the accompanying flows within and near them. On this hypothesis these vortex spirals would be representatives of the Faraday lines of force.

The hypothesis here put forward very tentatively does not include any supposition as to the nature of matter, nor as to how the singular points that represent electric charges, or electrons, can be connected with matter. At the same time it goes some way towards showing that the hypothesis—that the ether is a turbulent liquid—has great possibilities underlying it.

In explanation of the above, it may be well to state clearly the assumptions underlying it. It is *assumed* that the spirality described is propagated unchanged as a wave. This is justified by pointing out that this spirality is essentially the laminar motion investigated by Lord Kelvin, because it involves a flow in the direction of the axis of the spiral, and such a flow cannot take place along the direction of a vortex filament without a spiral deformation of the filament. Lord Kelvin illustrated his theorem by reference to a system of vortex rings which would, however, diffuse among one another in a way that was contrary to one of his fundamental assumptions: while I am citing, as an example of his theorem, the case of infinite approximately straight vortex filaments which he has shown might, certainly if empty, exist in steady motion in presence of one another.

It has further been assumed that, initially, $S\Delta E = 0$. This may be justified as follows:—If we assume that, initially, the singular points are points from which a large number of long spirals proceed in various directions, it is evident the same number must enter as leave any surface which does not surround one or more of these singular points, and that the excess of those entering above those leaving, will be a measure of the number of their singular points within the surface. Calling this latter ρ, per unit volume, we get at once $S\Delta E = 4\pi\rho$, initially. Where $\rho = 0$, we have $S\Delta E = 0$, and as $S\Delta\dot{E} = 0$ at all these points, we see that, even though the original distribution in long spirals rearranges itself among the surrounding vortices, nevertheless $S\Delta E$ will continue to vanish at all these places where there are no singular points.

It may also be worth while calling attention to the method of analysis used in this note. I have taken a vector E, to represent the various very complex and undescribed movements accompanying the spirality described, and the vector H to represent the still less clearly described movements accompanying the propagation of E. This may seem, at first sight, an unsatisfactory method, but it is really quite in accord with our methods of investigation in other cases. Besides, the obvious case of temperature and entropy which measure properties of bodies whose dynamical character is only very vaguely known, I may take the example of pressure in a gas as very similar. The pressure of a gas was for generations dealt with and most usefully employed long before the structure of a gas was understood. This state of affairs is quite analogous to the condition in which Maxwell left the ether theory of electro-magnetism. He postulated and discovered the properties of electric and magnetic force, without explaining them by any dynamical theory as to the structure of the ether. The analogies he put forward were just as vague and unsatisfactory, but certainly not more so than the gaseous theories that depended on explaining the elasticity of a gas by that of atmospheres of the hypothetical caloric. The kinetic theory of gases explained their pressure and other properties upon dynamical principles, but when first propounded, and even still, the actual distribution of motion amongst the molecules, atoms, and within the atoms of gases are unknown, but that does not detract from the value of the dynamical theory, nor make us hesitate to use pressure as a function of the state of the gas, although we do not know exactly what that state is.

I give these examples of pressure, temperature, and entropy to show that there is nothing abstruse or contrary to precedent in my assumption of E and H as representing states which are not, in their entirety, described or analysed. I might have instanced directed quantities as examples, such as the stress in a wire subjected to longitudinal pull. This is a very complicated state of stress which can be represented by a single vector, although in no single instance have we any except the very vaguest conception of what the actual state of affairs is inside the wire subject to this stress.

IX.

NOTE ON THE RESULTS THAT MAY BE EXPECTED FROM THE PROPOSED MONSTER TELESCOPE OF THE PARIS EXHIBITION OF 1900. By SIR HOWARD GRUBB, F.R.S., Vice-President, R.D.S.

(ABSTRACT.)

[Read JANUARY 18; Received for Publication MARCH 15;
Published APRIL 22, 1899.]

THE Author stated that so many exaggerated reports had appeared lately in the newspapers as to the wonderful results expected from the great refracting telescope proposed for the 1900 Paris Exhibition, that he thought it might interest the Royal Dublin Society to know what might reasonably be expected from such an instrument.

According to some papers the Moon is to be brought within four miles of the Earth; while in one account, purporting to be extracted from the *Morning Post*, this telescope was to be capable of taking photographs of celestial objects on a scale 10,000 times larger than would be possible by any existing telescope.

After describing the general features of the proposed Paris telescope, showing how the light-collecting power and magnifying power of telescopes can be estimated, and why it is possible to use high powers with larger apertures &c., the author showed that the light-collecting power of this Paris telescope was only about 50 per cent. greater than that of the 40-inch refractor of the Yerkes Observatory, Chicago, or more strictly speaking, 35 per cent., allowance being made for the light lost by the reflector. In magnifying power, or power of bringing objects apparently closer, it only exceeded the "Yerkes" instrument by 20 per cent., while in both respects it fell far below the reflecting instrument of Lord Rosse erected more than half a century ago.

X.

ON THE CONCENTRATION OF SOAP SOLUTION ON THE SURFACE OF THE LIQUID. By DAVID HENRY HALL, B.A.

[COMMUNICATED BY PROFESSOR G. F. FITZ GERALD, F.T.C.D., F.R.S.]

[Read April 19, 1899; Published May 8, 1899.]

In order to determine whether there is any concentration of soap solution in the superficial film of the liquid, the following experiments were made at the suggestion of Professor Fitz Gerald. Lord Rayleigh had observed that the superficial tension of a soap solution while the surface was being extended differs from that of the surface shortly after it has ceased to be extended. He attributed this to a possible concentration of the soapy matter in the superficial film which took place after the surface was formed. He showed that this large superficial tension of a recently-formed surface explained the stability of soap-bubbles and of the foam on frothing liquids. When any part of the surface is thinned out, the tension then becomes great; and, in consequence, the tendency to thin is counteracted, and the film is stable. He analysed the foam of a mountain stream, and found much more organic matter in it than in the rest of the stream-water. This observation is, however, hardly conclusive, and to study the matter further, a soap solution was frothed up, and allowed to drain for a short time, and then the froth was separated from the drained-off liquid, and each separately analysed. The experiments were conducted as follows:—

A large stock of saturated soap solution was prepared by allowing distilled water, previously shaken up with pieces of soap, to settle, and then filtered off into a large airtight reservoir of two gallons capacity. A weak solution of standard $CaCl_2$ was also made by mixing 10 c.cs. of the standard $CaCl_2$ solution with 200 c.cs. of distilled water. A large Winchester bottle, of a couple of gallons capacity, was cleansed thoroughly, and about two quarts of the soap solution introduced, and shaken up vigorously until the rest of the bottle was full of froth. The bottle was then put aside to allow the small bubbles to rise, and then the solution was filtered from the froth, and the froth allowed to settle in the bottle, which was corked tightly to prevent oxidation. The solution poured off was now titrated with the $CaCl_2$ from a burette by the usual method for determining the strength of soap solution. The condensed froth was likewise titrated, and the following results obtained :—

First Experiment.		Second Experiment.	
25 c.cs., without froth.	25 c.cs. condensed froth.	25 c.cs. solution.	25 c.cs. condensed froth.
c.cs. $CaCl_2$.	c.cs. $CaCl_2$.	c.cs. $CaCl_2$.	c.cs. $CaCl_2$.
6·65	7·2	6	6·2
6·4	7·3	5·4	6·1
6·65	7·3	5·2	6·25
6·7		6	6·3
		5·7	6·2
		5·5	
		5·8	
Mean, 6·6	Mean, 7·26	Mean, 5·65	Mean, 6·21

The third experiment was made, and a large amount of froth, from a couple of gallons of solution left to settle all night in a closed vessel.

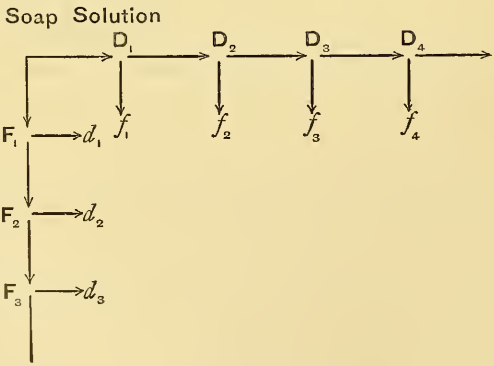
On titrating next day it was found to be of less strength than the solution from which it had been filtered, and which had been titrated at time of filtration. Evidently this was due to oxidation, and so another experiment was made, the filtered solution being titrated, also part of the condensed froth, the rest of the froth allowed to settle all night.

Filtered Solution, 25 c.cs.	Condensed froth at same time.	Froth titrated next day.	Filtered solution titrated next day.
c.cs. $CaCl_2$.	c.cs. $CaCl_2$.	c cs. $CaCl_2$.	c.cs. $CaCl_2$.
5·6	6·2	5·4	5·5
5·5	6·25	5·3	5·3
5·45	6.3	5·3	5·35
5·5			5·4
Mean, 5·5	Mean, 6·25	Mean, 5·3	Mean, 5·38

To avoid, as far as possible, oxidation, and yet still further to increase the difference between the solution and its froth, as regards the amount of soap in each, the following plan was followed out:—

Three Winchester bottles were now used, and the froth fractionated twice, the amount of condensed froth not allowing of further fractionation.

The filtered solution was also fractionated, the froth thrown away, and the filtered solution fractionated ten times. It is represented diagrammatically as follows:—



D_{10} and F_3 were titrated and compared.

F_3, 10 c.cs.	D_{10}, 25 c.cs.	
c.cs. $CaCl_2$.	c.cs. $CaCl_2$.	
2	3·9	
1·8	3·8	
1·9	3·85	
	3·8	
Mean, 1·9	Mean, 3·83	
∴ 19 for 100 c.cs. F_3.	∴ 15·32 for 100 c.cs. D_{10}.	Hence 3·68 mean difference.

Again, take F_1 and D_{12}, as oxidation has most effect on the froth :—

F_1, 50 c.cs.	D_{12}, 100 c.cs.	
c.cs. $CaCl_2$.	c.cs. $CaCl_2$.	
7·7	11·8	
7·9	12·2	
8	12	
7·8	12·1	
Mean, 7·85	Mean, 12·025	∴ 3·7 c.cs. difference in 100 c.cs. of each.
15·7 for 100 F_1.		

Hence it appears that the froth of a soap solution contains more soap than the solution from which it has been obtained.

Several experiments were necessary to get the best working strength of the $CaCl_2$ solution, and that of 10 c.cs. $CaCl_2$ standard solution in 700 c. cs. distilled water was found best.

The original soap solution must not be supersaturated, and this source of error was avoided.

It appears, therefore, from the experiments, that the soapy matter is concentrated into the superficial layers in accordance with the suggestion of Lord Rayleigh.

XI.

THE RIO DEL FUERTE OF WESTERN MEXICO, AND ITS TRIBUTARIES. By KINSLEY DRYDEN DOYLE, M.A., Assoc. M. Inst. C.E. (Plates VI.–XV.)

[COMMUNICATED BY PROFESSOR J. JOLY, F.R.S.]

[Read April 19; Received for Publication May 30; Published August 31, 1899.]

The Fuerte river is a powerful stream, named from its torrential character, draining a basin of 17,000 square miles, including that part of Western Mexico called the Sierra Tarahumare, and falling into the Californian Gulf just south of the 26th parallel of north latitude. (See map, Pl. XV.) The rainfall of this region is a mean between the extreme aridity of the Colorado desert and the tropical copiousness of Tepic and Jalisco; there is a long dry season from November to June, broken only by a few thunder-showers, during which the vegetation is mostly leafless; and the only green objects in the low country are numerous varieties of cactus, agaves, and a few other kinds of plants whose bark serves the purposes of leaves, except in places where the roots can reach water. The prolonged drought dries up all the rivulets in the low land or "tierra caliente" as it is called locally, but the immense rock masses of the plateau—rightly named Sierra Madre, mother of mountains—store up and give out a perennial stream, never falling below 64,000 cubic feet per minute.

The Fuerte is 275 miles long from source to mouth, and the united river for a third of the whole length flows through the low plain; the remaining part and all the chief tributaries pass through rugged foot hills and in deep cañons worn in the Sierra itself.

This country was traversed by the author in 1897 from west to east, but it will be more convenient for the purpose of description to start near the watershed.

Proceeding therefore from the town of Chihuahua on the Mexican Central Railway, one traverses the central plain, gradually rising from east to west towards the wave crest of the great slope; for the first 70 miles the road or track goes over a rugged country composed of weathered dark volcanic rocks, and studded with abrupt hills which rise like islands in a stormy sea of lava. There is little surface soil, and, except in a few shallow valleys like that of Sta Isavel, the region, owing to drought, is a desert. After reaching Cusihuiriachic, a town depending on very ancient and rich silver and lead mines, the llanos are seen stretching upward toward the watershed of the continent; they are very smooth, broken by few arroyos, and covered with grass forming a good cattle country wherever water is obtainable. Thirty miles to the N.W. of the town is a group of rocky hills whence streams flow in three directions—south-east to the Rio Conchos, which joins the Rio Grande del Norte, and discharges into the Gulf of Mexico —north to the Rio de Sta Maria, an inland system of drainage ending in a salt lagoon near the United States frontier—and west through the mountains to the Gulf of California.

The llanos preserve the original slope and surface of the old lava flows, and are protected from denudation by their lofty elevation, the small rainfall on the inland side of the mountains, and by a coating of soil with permanent grass.[1] Travelling over them, is a pleasing contrast to progress over the stony plain, and the antique-looking, leather-slung coaches drawn by teams of eight or ten, well-matched, closely-clipped, white mules go at a fast canter over the smooth surface. Towards the summit of the slope rounded hills studded with dwarf oaks appear, and the ground is broken; but some attempt at grading the tracks enables wheeled vehicles to go as far as Bocoyna on the head waters of the Rio Conchos, where there is a small settlement of Mexicans and Indians. From this place onwards one must travel mounted or on foot. The highest part of the range in this neighbourhood is Rumerachic, a rounded mountain about 9700 feet above the sea.

Here we enter on the pine-clad mesa, which extends, uniform and monotonous, in a belt 50 miles wide, along the crest of the Sierra; except in a narrow central ridge, the general surface is quite level, and covered by a sparse forest of small pines, with very little other vegetable life. Mammals and insects are alike unseen, and the only winged creatures are an occasional flock of "blue birds" or a stray woodpecker. There being no streams during the

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[1] There are also alluvial deposits in this region, containing bone remains of Quaternary age.

dry season to make the murmuring accompaniment one always hears in the Alps, and as no breath of wind disturbs the constant calm of the air, there is an absolute silence in the forest which is very impressive; even the footfalls of one's own mules are deadened by the carpet of pine-needles.

These mesas are composed of almost level sheets of light-coloured trachyte, and beds of white friable volcanic ash, with local layers of white pumice; incrustations of red and white chalcedony, and crystals of celestine are also commonly seen.

The commencement of the arroyos which feed the Fuerte river is usually a basin-like space of bare stone completely denuded of all soil, and without vegetation; the sides are steep, and the hollows soon plunge down to the depths of the great cañons; they remind one of the streams on the peat-covered Irish hills, Kippure for example, where a furrow in the living fibrous covering of heather and other plants, soon widens into a gully in the soft peat. Though the scale of the phenomena is very different, yet the forest on the mesa seems to play the part of the heather on the peat, and prevent denudation of the underlying material. In the basins and valleys there are often rounded bosses, and sometimes high pillars left standing in isolated positions, or in groups; they appear to be produced by the protection afforded by hard, resistant patches in the trachyte; but, unlike ordinary earth pillars, do not develop into symmetrical conical forms; being always twisted into strange and odd shapes, and sometimes overhanging considerably; some are more than 100 feet high. Besides the summer rains, which are not heavy at elevations of seven or eight thousand feet, there is a winter snowfall of about two feet, and the greater part of this, probably finds its way through the surface soil, and, by subterranean passages of the fissured rocks, to the water-level at the bottom of the gorges; for in early summer the small streams are quite dry, though there is plenty of water far down in the gorges. The most striking feature of the mesa on the way from Bocoyna is the great Barranca of the Urique river; one approaches it through level forest to the very edge of the chasm, where it bends suddenly from E.N.E. to S.S.W. The sides are a series of vertical precipices, formed by the edges of the different lava flows, connected by steep slopes of detritus covered with vegetation suited to the elevation; for the descent to the stream being 4500 feet, bananas, oranges, and cacti will grow at the bottom wherever there is room for them, while there is frost nearly every night on the top; and yet a stone dropped from the edge of the mesa would, in many places, fall and roll all the way to the river. Further up, the cañon contracts to a chasm so narrow that it could be bridged at the top, but here it is a couple of miles wide.

Here and there in this region one comes across cave-dwellings of Tarahumari Indians, a primitive race of fine physique; they are of a dark copper red colour, with long coarse black hair reaching to the shoulder, and confined by a fillet round the forehead. They are very shy and retiring, living by their own tribal customs, and making their own pottery, clothing, and arms, without intercourse with white men. As they are not a warlike race, their continued existence and individuality is due to the extreme inaccessibility and poverty of the country; but in power of enduring cold and fatigue, and performing very long marches with no provision but a little parched corn, few hill tribes could compete with them. After passing the Cerro de Coroibo the track visits some large caves on a high part of the mesa where water can always be found; elsewhere the sources are so far apart that it is desirable to have a guide with local knowledge, to avoid the discomfort of a waterless camp; forage is also so scarce that corn must be carried for the mules. There is a numerous group of grotesque rock-pillars near this place.

The ground here commences to slope down with a more broken hilly surface towards the *tierras templadas*, at an elevation of 5000 to 6000 feet; the tongues of table-land reaching out between river valleys are called *cordōns*, and their level tops enjoy a delightful and invigorating climate; temperate crops and fruits do well here, and the little towns were gay with peach blossoms in March.

Leaving Temoris, a place on the right side of the Septentrion river, we descend to a small ranche at the bottom of the valley, where an artificial water-course irrigates some terraces planted with oranges; there is hardly any level ground, for the steep sides of the V-shaped valley nearly everywhere sweep directly into the stream. Here, mineral veins, which are uncommon in the upper trachyte beds, begin to appear, and there is a large mine close by at Realito. Now, ascending to the crest of the left bank at Pandura, the first view of the foot hills is obtained; they lie extended like a map beneath the giants of the mesa; and were it not for their steep and intricate forms, the windings of the river valleys could be easily traced through the transparent atmosphere. The clearness of the air in these regions is remarkable, even for the Pacific coast; the stars at night shine with astonishing brilliancy; and a lofty mountain of striking form, the Cerro de Alamos, is visible all day at distances over 60 miles, where nothing intervenes, except in the rainy season. To the south-east of Pandura is the peak of Metate standing on a spur of the mesa, isolated by the erosion of two streams, and surrounded on three sides by immense vertical precipices. There is a wide difference between the shapes of mountains in this latitude, and the ice-planed forms of Europe; as long as the rivers can deepen their beds they do not widen the valleys at all, which remain either cañons enclosed by cliffs, or V-shaped cuttings, usually terminating at the bottom in a narrow gorge. On the lower ridges the evergreen flora is more varied and abundant; three varieties of oak, three of pine, and one of arbutus are common; the arbutus, with its thick stem, bright orange red bark, dark green leaves, and white flowers, is very picturesque; and the *Ensina roble*, an evergreen oak, with thick leathery leaves, is very distinct. Lower down, below 5000 feet, agaves, mamillaria, and prickly pears (*Opuntia*) are abundant among the grass that covers old geological formations, or under the dwarf forest that flourishes on recent volcanic ejectamenta. Following the ridge towards Guaza, the track overlooks a wide basin, grass-covered and dotted with dwarf oaks, into which two streams converge at an acute angle, leaving between them a thin slice of table-land, standing up perpendicularly 3000 feet above the stream, and revealing its structure of horizontal beds; the upper pale acid lava, and the lower of dark basic materials. Such wedges are common at the margin of the mesa, and are sometimes isolated into towers that eventually crumble into conical forms; when first isolated, they are locally called *caballos* (horses); the ridges produced by erosion often terminate in a diminishing row of peaks that have been formed in this way. This flamboyant style of mountain sculpture shows that no severe earthquakes have affected this part of Mexico for a long time, as many of the grotesque rock-pillars and lofty partition walls have such slender bases that a violent shock would certainly overturn them.

At Guaza the Chinipas and Septentrion rivers join, and there is a little level ground laid down by the rivers during a temporary obstruction of the lower gorge, caused by recent volcanic eruptions, to be further noticed. Between Guaza and La Junta, where the main river forms, the valley has been eroded to the base of the volcanic series, exposing syenite; a calcareous fossil was also observed in the shingle, though time did not allow a search for its parent stratum.

Turning now east, up the main branch of the Fuerte river, we have before us a portion of country about 40 miles long and 20 miles wide occupied by the wasted volcanoes of a secondary eruption; all the rocks here are dark basic lavas, and some of the flows can be seen little altered, still forming the surface of the ground, or filling former river valleys. Mineral veins are abundant in a belt reaching from San José de Gracia near the boundary of Durango, to Rosario mountain, near that of Sonora, especially at the junction of the dyke-intersected syenite, with the volcanic rocks. Gold occurs frequently, associated with silver and copper as sulphides, and sometimes in veins of iron ore.

As the river runs in a chasm, the practicable track crosses the shoulder of the Cerro de Volcan—a prominent peak among the foothills; its top is evidently the hard core of a crater, and its sides the eroded materials of the cone; denudation is proceeding apace among these small mountains from the action of the heavy autumn rainfall on their loose layers; nearly all the ground stands at the angle of friction, everything is just ready to roll; and the tops of the ridges and bottoms of ravines are quite narrow. Near Volcan there are four or five other extinct cones in the same stage of decay. Descending to the bed of the river at San Francisco, one finds it rocky, and with a rapid fall; numerous waterworn boulders as large as 10 feet in diameter are piled along the margin, attesting the force of the stream when swollen 50 or 60 feet above its dry season level. Above Realito it has cut through a thick homogeneous layer of reddish rock, very free from fissures, and has left perpendicular cliffs nearly a thousand feet high; on emerging from this pass, one stands on a lake terrace over the river; observation of the surrounding hills discloses other parallel terraces at different higher levels. The wide valley is covered by regularly bedded lake deposits through which the river winds in sinuous curves, cutting cliffs from 40 to 70 feet high. Against the sky is the vast wall of the distant mesa, indented with square notches, like the machicolated parapet of a castle, by the straight-sided ravines.

The bed of the ancient lake is 1000 feet above sea-level at its lowest point, and consists of white and bright green sandstones and conglomerates in thin but continuous layers. During the dry season the river bed is a convenient road, though it necessitates frequent fording, as the stream meanders from side to side. The sandstones were examined for fossils, but none were found. After nine miles of gently-sloping, walled-in course, a place is reached where the lake beds have been cleared away nearly down to the present river level: probably by wanderings in the course of the current: and on this plain is the small town of Tubares.

The ancient lake and its fluctuations of level must have been caused by volcanic eruptions in the previous river valley damming the channel up with lava and ash; and when largest, the lake covered 100 square miles, to a maximum depth of at least 1000 feet; the thickness of the lacustrine strata below the present river level could not be ascertained without boring.

Should it ever be desired to regulate the flow of the Fuerte river, either for water-power or for extended irrigation in the low country, it could be done efficiently at a moderate cost, by constructing a dam at the gorge of Realito, where there is a narrow passage, solid rock for foundation, and a long gentle slope for the reservoir.

Above Tubares, low cliffs close in again on the river; here they are of a compact white stone, in appearance like limestone, but probably derived from the waste of the acid lavas; then the valley opens again as the junction with the Urique river is reached, the left branch being the product of the main stream from El Zapori and the Batopilas river.

Long ages elapsed between the eruptions that built up the mesa, and those which formed the Realito group of foot-hills; for during that interval, the Urique and other rivers eroded valleys more than 5000 feet deep, and extended the littoral plain at the expense of the plateau. After the new volcanoes had covered the plain, the rivers deposited the lacustrine beds of Tubares, and cut a deep channel through the erupted material.

All the foothills are covered with a low forest of thorny trees and shrubs, leafless in March, but not without blossoms, the "palo blanco" in particular being covered with corymbs of large, white, sweet-scented flowers, the food of parrots and deer, and the haunt of humming-birds. A yellow variety of the same species is common, and two trees produce large clusters of rhododendron-like blossoms, pink and yellow respectively; logwood of small size is abundant, being used for fuel and for stakes. The commonest large cactus is the *pitahaya* a clustering group of dark green cylinders about 10 feet high, furnished with grey woolly hair near the top, and like all the genus, with *chevaux de frise* of slender sharp spines. There are large echinocacti which are eaten greedily by deer, whenever they can penetrate the defensive armour of spines and hooks. The smaller mamillaria with brilliant starry flowers were not generally in bloom in March. Besides the perennial woody, or fleshy and fibrous plants, there is a numerous and beautiful flora of herbaceous varieties that spring up on the advent of the rains, and many of them are peculiar to this part of the country; it has been only partially worked out, and there are probably many kinds yet undescribed. All the shrubby vegetation is much more luxuriant on the recent volcanic area than on the eroded spurs of the mesa.

Proceeding now, from the junction of the Urique river, a new series of volcanoes is traversed, the highest being the Cerro de San Juan; their form is rounded on top, but with steep slopes, and the lava is a dark basic material full of green spherules, which are not much elongated in any direction; this lava appears to have been exuded in a pasty condition, for it shows no signs of bedding or flow. The river has cut a narrow winding gorge through it, with steep but not vertical sides. Above San Juan de Dios, at San Ignatio, is the junction of the Batopilas river, in a more open country; also showing some signs of alluvial deposits.

The Batopilas river flows between steep cliffs of basalt and diorite, apparently lower members of the great plateau series, and not recent eruptions like those of San Juan and Realito. Near Puebla, granite with numerous dykes and patches of schorl is exposed; and generally the great variety and numerous sections of the rocks in this district would make it interesting to a geologist, who had time to study them. On account of its ruggedness it is useless, except for mining, and is accordingly a retreat for the wild Tarahumare; whose dark red forms may be seen bathing in the river, and at night the light of fires in the caves they inhabit, gleams in the lofty recesses of the hills.

Batopilas is a considerable mining town, its mineral veins have been worked since the early years of the Spanish occupation, and they are now exploited by a United States company, which, alone out of many mining concerns in these provinces, uses modern methods and machinery. The principal veins are of crystallized native silver imbedded in calcite, the country rock being a hard diorite. One mine extends 900 feet above, and the same depth below the adit; and the author saw a blast fired in a vein one foot wide containing 75 per cent. of bright metallic silver. Other neighbouring mines contain silver as sulphide. The mountains round Batopilas have been stripped of their wood for fuel at the mines, and when seen from above appear covered with a ramifying network of small ravines, by which the whole surface is made steep, the slopes from two arroyos always terminating in a sharp ridge; this extreme effect of denudation may be due to removal of the natural covering.

Leaving Batopilas we reach the Cerro Colorado, an immense red mass of low grade, auriferous rock; it was recently worked on a considerable scale at a loss, and the machinery is still on the spot; costly transport was the chief obstacle to success. We now cross over the cordon to the Urique valley, and go up to the town; although the rock walls are 5000 feet high, and very precipitous, the valley has a narrow flat floor composed of alluvial materials deposited under water (during the existence of the volcanic dam). Nearly every kind of tropical fruit does well here. It is possible to go far up the valley near the river, a path having been blasted out by miners, for there is a large copper deposit near the turn of the great barranca, in a most inaccessible position. The valley extends a hundred miles above the town, and contains some old, rich, silver mines. We now proceed to Cerrocahui a small place on the temperate mesa, surrounded by arable land; here is an adobe church built in 1700. There are charming spots on the mesa, well wooded and level, with clear streams which end in a sheer descent of many thousand feet; from one, there is a view over the immense crags of the Arroyo Hondo. They are kept green by a slight deposition of mist or fine rain, in ascending currents of air, forced up the cliffs by wind; a short distance from the edge, such moisture is absent.

The track passes Tecumichic (elevation 5950 feet) and Sinagita, and emerges on the edge of the mesa at El Ojito (the little eye), whence one can see several thousand square miles of country, including points sixty miles distant. On the east, is the Cerro del Pilar, a series of singular forms of eroded trachyte, and the old lake basin of Tubares; to the south, are the volcanoes of Realito, Cobre, and Pinitos; and west, are long tongues of table-land divided by precipitous valleys. Such a view must be uncommon in any country. From this point the track descends rapidly to the hot springs of Huachara situated among a number of small hills with streams winding among them; the remarkable similarity and strange form of these hills can hardly be due to ordinary erosion; they are composed of loose stones, gravel, and sand of a reddish colour, and the entire hollow is filled with them. The track passes over Sausillo, and from El Sillon beyond it, a new view is obtained of innumerable small hills and mountains; it soon passes the boundary between the old trachyte and the recent volcanic area, and reaches La Junta by Tacopaco, a village in a valley containing many palm-trees called *tacos*.

Descending the main river to Agua Caliente de Baca the bed is found to be of syenite; it finally emerges into the low country through the Cajon de Huites, between the Cerro de Santiago and the Cerro de Chuchaca. Below this, the country is generally syenite, but part of it is covered by a lava sheet 20 feet thick, which filled an old bed of the river, moulding itself to the waterworn rocks, sealing up beds of gravel, and sometimes rising into bubbles over pools; the river subsequently cut through the layer and 50 feet of syenite, leaving the junction exposed on a cliff. As auriferous veins are abundant in the upper course of the river, gold might be expected in these gravels; a surmise which was verified by washing a handful of gravel. The top of the lava bears a plantation of large cultivated agaves for making the spirit called *mezcal*: they grow luxuriantly on the decomposing rock. The lava extends to Agua Caliente, where there are springs at a temperature of 120° F., containing sulphuretted hydrogen and carbonates; in the hot water the stones are coated by algæ of a very deep green colour—a remarkable example of adaptation to unusual circumstances. Though much of the lava sheet has been removed by erosion, a few truncated conical hills show its former level and extent.

Rosario mountain, a trachyte peak 5193 feet high (by boiling point), is worth a visit, as it gives an extensive view. At its base there are gold mines, where the metal is extracted from hæmatite in primitive native mills called *arrastras*, consisting of shallow, paved, circular pits, round which heavy stones are dragged by mule power. On Rosario mountain was a curious mass of vegetation, moulded to the shape of a spouting waterfall; it extended from one rock-ledge to another forty feet higher, in a paraboloid form, so that the water would run over its surface in an even sheet. The mass was as dry as hay, but seemed to be a selaginella. There are several sorts of ferns here, which roll up tight in the dry season, and respond to a small shower of rain by immediately expanding the evergreen upper sides of their fronds. Deer and jaguars are common about Rosario.

Below Baca the river takes a sweep to the west, having been diverted by lava-flows from volcanoes near Chois, and it returns to its general direction near Toro; most of the intervening country has been swept clear of lava, exposing syenite. At Toro several hills, like bench-marks in an excavation, show the former level of the lava. The ranches here, are fenced by rows of single-stemmed cacti, growing in contact to a great height; they are only six inches thick, but absolutely unclimbable. A singular tree called *Bebalama* grows in the plain, it has slender stem, branches, and twigs of a bright-green colour, and showers of beautiful yellow flowers, but no leaves in March; the sheltered ravines contain some rubber-bearing plants, though they are not plentiful, owing to the long drought. The immense sahaura (*Cereus giganteus*) or pillar cactus of the Gila valley does not grow so far south. Between Sinaloita and Ocolome, on the river, there are outcrops of mica schist and slate, the general strike of the cleavage being a little west of north; below this the country becomes more level. At the town of Fuerte the river is 300 yards wide, with a rapid current over coarse sand, but only three or four feet deep. There is a colouring about the gorgeous sunsets of the plain which is peculiar to the shores of the Californian Gulf—hues of violet, purple, and rose predominate—and no such displays were seen by the author, since the wonderful sunsets caused by the eruption of Krakatoa.

At San Blas there is a bar of rock across the stream; it is apparently metamorphic, and contains dark-red and green jaspery bands (specimen lost). Just above this place a very cold night was experienced, with dense fog—a surprising thing in the hot country, and the only fog seen by the author in Mexico. The explanation appears to be as follows:—On the mountain sides at night the clear air is chilled by the radiation of the ground; but, being too dry to deposit dew, falls a great deal in temperature, and slides into the bottom of the ravines. Here it is further chilled by radiation, and deposits copious dew; but, still cold, it runs rapidly down to the river and rolls on towards the sea. At San Blas it is checked by a line of low hills, and spreads out as a lake of cold, foggy air. It was observed that everything within about ten feet of the bottom of small arroyos was drenched with dew, while objects higher up were quite dry in the morning. As one proceeds towards the coast the plain becomes quite flat; but hills of volcanic rock rise abruptly from it at wide intervals. The brown leafless forest of small trees gives way gradually to increasing numbers of cacti, especially a large variety of *pitahaya*, and twisted *siviris*, with poisonous thorns, which almost mimic a writhing knot of grey-green snakes. Where water is applied, the sandy plain is fertile; and the banks of the river, like a little Nile, are fringed by irrigation farms, where excellent cane for sugar, with oranges, bananas, and maize are raised.

The margin of the water is alive with the bright plumage and songs of birds; but away from it, the plain is covered by groves of cacti, to the exclusion of everything else, and their clustering, green, leafless columns in endless succession, present a singular appearance. An attempt has been made to irrigate on a large scale, but only a small part of the immense cactus groves has been touched. The woody core of these plants contains tar, and yields on distillation a gas of high illuminating power. There is a road through the cacti to Topolobampo, a large landlocked bay which, on account of its possibilities as a harbour, has been carefully surveyed by the Hydrographic Department of the United States Government; their chart shows clearly that this was the old estuary of the Fuerte river before volcanic disturbances diverted its course. The high-tide outline of the top of the bay has the appearance of a delta with numerous channels, though there is now no fresh water there; and the bay, which is very beautiful and surrounded by steep volcanic hills, made a fitting exit for a river having an inland course of great interest and variety. The existing mouth ends ignobly in mud-flats infested by alligators; for the river has not had time to make anything better, but it will probably improve it in the course of a few thousand years. It would be interesting, and probably easy, to trace the old bed of the Fuerte, and the work might result in the discovery of more placers to reward the pioneer.

There are indications that the confluence of the Urique and Batopilas rivers, with those from Chinipas and Septentrion, was formerly a long way from the present fork at La Junta; and that the wild gorge from Realito to La Junta was cut by an overflow of the volcanic dam at a spot different from the old exit of the Urique river. Upon this supposition, the placers near Baca were produced by the Chinipas river only.

The cause of the small volcanic groups outside the edge of the table-land appears to lie in the existence of a great shearing stress acting on the Earth's crust at this place. The mesa sloping down from 9000 to 6000 feet, and then plunging abruptly to river-channels 1000 feet above the sea, causes a sudden change of load, due to the weight of 5000 feet thickness of rock; and, as erosion changes the position of maximum stress, weak places are disclosed, through which any hot fluid matter below is squeezed out, while the plateau settles down. This action may have been repeated several times while the plateau was being cut back, thus accounting for the volcanic hills at Topolobampo, and generally along the coast.

In the clear waters of Topolobampo Bay, pelicans fish day and night unceasingly, turtles bask, and porpoises race by at railway speed, punctuating the silence of night with their rhythmical snorts, while hundreds of thousands of sea-birds feed on the sandy beaches of San Ignacio and nest on islands in the bay, watched over by the paternal care of the Mexican Government.

If we depart by sea the last view of the coast is a weird outline of fantastic shapes, distorted by a veil of mirage.

APPENDIX.

Generally the highest temperatures were observed in narrow, deep river valleys; the low open plains were cool at night, but had a high temperature in the day; the coolest night was April 6, at Orochibo, elevation 7575 feet, on the mesa, when there were 19° of frost and thick ice on still water. There was slight cloud at sunset in the plains on February 6, 8, 10, 13, and 20, with very brilliant colouring; thunderstorms occurred in the foot-hills on March 19 and 27, with heavy rain and small freshets in the river. At San Blas, on February 7, there was a dense fog in the morning, with minimum temperature 40° F. No other fog, cloud, or rain was observed during February, March, and April.

There was a gale from the N.W. in the gulf on January 29 and 30, with clear sky, no rain, and a heavy sea; on the coast the wind was fresh to strong from the west on February 1, 2, and 3. Inland it was generally calm, in the foothills at San Juan de Dios, there was a strong, hot, dry wind down the valley on February 26. During March and April a dead calm lay over the mountains.

Disturbances of the barometric pressure beyond the diurnal oscillations are rare, readings remaining constant for many weeks at a time.

The air is extremely dry; steel articles left on the ground every night do not rust, and no dew is deposited, notwithstanding the clear sky, except at the bottom of ravines.

[SUMMARY OF TEMPERATURES, &c.

SUMMARY OF TEMPERATURES IN DIFFERENT PLACES DURING FEBRUARY, MARCH, AND APRIL.

	Locality.	Date.	Elevation.	Hour.	Temperature Fahrenheit.
"Tierra Caliente" or low plain.	Coast, at Topolobampo,	Jan. 31,	30 feet,	maximum day,	62·5°.
				minimum night,	47°.
	,,	Feb. 1,	30 ,,	maximum day,	79·5°.
				minimum night,	47·5°.
	,,	Feb. 2,	30 ,,	maximum day,	64°.
				minimum night,	37°.
	Near river,	Feb. 5,	55 ,,	8 p. m.,	58·3 air.
	San Blas,	Feb. 7,	120 ,,	minimum night,	40° in fog.
	Fuerte,	Feb. 10,	186 ,,	8 p. m.,	55° air.
	,,	Feb. 12,		8 a. m.,	47·5° air.
	Near river,	Feb. 12,	250 ,,	9 p. m.,	56·7° air.
	,,	Feb. 13,	250 ,,	8 p. m.,	53° air.
				minimum night,	37°.
	San Javier,	Feb. 15,	320 ,,	8 p. m.,	50·5° air.
				minimum night,	39°.
	Baca,	Feb. 17,	384 ,,	minimum night,	41°.
	,,	March 25,	384 ,,	8 p. m.,	52° air.
Valley in foot-hills.	River valley,	Feb. 23,	904 ,,	8 a. m.,	61·2° air.
	San Juan de Dios,	Feb. 26,	1135 ,,	9 p. m.,	84·5° air, hot strong wind all night.
	Old lake basin,	Feb. 24,	1010 ,,	8 p. m.,	69° air.
In deep cañons.	Cañon at Batopilas,	March 1,	2523 ,,	10 p. m.,	76° air.
	,, ,, ,,	March 5,	,, ,,	8 a. m.,	64° air.
	,, ,, ,,	March 6,	2523 ,,	8 a. m.,	62° air.
				maximum day,	99·5°.
				minimum night,	58°.
	Cañon at Urique,	March 9.	1790 ,,	6 p. m.,	72° air.
				minimum night,	62·5°.
	On cordon of mesa,	March 10,	6038 ,,	minimum night,	39·5°.
	,, ,, ,,	March 12,	5950 ,,	7 p. m.,	42° air.
	On foot hills,	March 15,	2540 ,,	minimum night,	54°.
	Uvalama,	March 29,	3150 ,,	7 a. m.,	42° air.
	On mesa,	April 2,	4950 ,,	8 p. m.,	49° air.
High mesa.	High mesa,	April 3,	5674 ,,	8 p. m.,	45·5° air.
	,,	April 4,	7625 ,,	8 p. m.,	54° air.
				minimum night,	38°.
	,,	April 5,	7199 ,,	8 p. m.,	51° air.
	(Ojito de Barranca)			minimum night,	19°.
	High mesa,	April 6,	7575 ,,	8 p. m.,	38° air.
				miuimum night,	13°.
	Bocoyna,	April 7,	7140 ,,	8 p. m.,	38·5° air.
	,,	April 8,	,, ,,	minimum night,	29°.
	,,	April 9,	,, ,,	minimum night,	29°.

Air temperatures by swing thermometers (verified at Kew), maxima in shade, minima exposed to open sky.

The map differs considerably, both in general, and in detail, from existing maps of the district; it is, however, necessarily a hasty sketch. The main triangles were taken by prismatic compass, and Major Verner's cavalry sketch-board proved useful for the smaller features; a great deal of work can be done by it without dismounting, especially as Mexican horses, being trained with severe bits to the use of the lasso, are very intelligent and steady.

Observations for latitude were made with a 6 inch sextant and covered mercury trough.

Heights were measured by boiling-point instrument with thermometers verified at Kew, and two aneroids.

Sketches were drawn in outline at the point of view, and named from local information given by Indian or Mexican guides.

OBSERVATIONS OF LATITUDE MADE BY THE AUTHOR.

The town of Fuerte, .	25°	30′	30″	North.
Agua Caliente de Baca, .	26°	13′	40″	,,
Ranch of Septentrion, .	26°	45′	0″	,,
Santiago near Bahuina, .	27°	0′	30″	,,
Town of Cuiteco, . .	27°	5′	20″	,,
Ojito de Barranca at the bend of the Urique river,	27°	13′	40″	,,
Bocoyna on the Rio Conchos,	27°	40′	20″	,,

LIST OF SKETCHES AND MAP.

(Plates VI.–XV.)

VI. La Puerta Blanca.
VII. Grand Barranca of the Urique River.
VIII. Cerro de Volcan.
IX. Red barrier rock of Realito.
X. River channel through lacustrine deposits.
XI. Eroded edges of lacustrine sandstones.
XII. Batopilas River from San José.
XIII. Urique cañon, near Guapalaina.
XIV. Panorama from El Ojito.
XV. Map of Foothills of the Sierra, Western Mexico.

NOTE ADDED IN THE PRESS.

The Author's attention has been directed to the Bosquejo geológico de México, 1897, numbers 4, 5, and 6, which contain a general account of the geology of Mexico, and some preliminary notes on the provinces of Chihuahua, Sonora, and Sinaloa.

XII.

NOTE ON IMPROVEMENTS IN THE MEANS OF CAUSING OCCULTATIONS OR FLASHES IN BUOY LAMPS AND BEACONS IN WHICH THE LIGHTS BURN CONTINUOUSLY FOR A MONTH OR A LONGER TIME. BY JOHN R. WIGHAM, M.R.I.A.

[Read JUNE 21 ; Received for Publication JULY 3 ; Published JULY 31, 1899].

IN a previous paper read before this Society,[1] I described an arrangement of lenticular apparatus, by which the most powerful light-house light, of oil, gas, or electricity, could be kept continuously in the view of the mariner; thus giving him the advantage of the most powerful beam which it is possible to throw upon him by the most powerful revolving lens, and yet so arranging the apparatus that the light never leaves his eye, fulfilling in this the great desideratum of the sailor; namely, the strongest light-house light which an annular lens can transmit, while at the same time, unlike ordinary revolving lights, it is visible continuously. That such a light will yet be placed within his reach by the light-house authorities I sincerely hope; but, notwithstanding that its feasibility has been practically demonstrated, no one can predict when this great benefit will be conferred upon him.

Such great light-house lights are of course only placed on leading landfalls and prominent positions on the seaboard for the *distant* guidance of the sailor; but it is exceedingly desirable to give him also every possible assistance in the *closer* but often more difficult and dangerous navigation of estuaries, rivers, and harbours. It is, therefore, satisfactory to know that of late years increased attention has been given to making the system of buoyage in such places useful after dark, as well as by day, by placing upon buoys and beacons, lights, by which their positions may be clearly indicated at night. Both compressed gas and electricity have been used as buoy-lights; but both gas and electricity for this special purpose are expensive and troublesome to maintain in a state of efficiency. For example, if compressed gas be the illuminant, oil-gas or rich cannel-gas must be used; because

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[1] Proceed. R.D.S., vol. viii., p. 347.

ordinary coal gas, when compressed, loses its illuminating power to a great extent; special plant also for the production of this special gas must be employed, and special apparatus for its compression and transportation to the buoy must be provided. All this renders the use of compressed gas for buoys complicated and costly, and there are similar objections to the employment of electricity for that purpose.

In the year 1896[1] I read before this Society a paper showing that I had invented a system of buoy illumination by petroleum, much simpler than the employment of either gas or electricity, and so economical, that it costs, in one of its forms, only *one penny for every twenty-four hours*, or *half-a-crown a month;* and I showed the Society how this was done by the use of the ordinary petroleum of commerce burned in special lamps; so that, upon buoys or beacons in places difficult of access, the light is continuous, and does not require the attendance of any light-keeper for a month, two months, or three months, as may be desired. These petroleum buoy-lamps are now used in many of our harbours, and, as a distinguishing mark in certain positions, the character of the light of some of them has been varied by the interposition of opaque or coloured revolving screens. These screens are caused to revolve by the upward current of heated air from the lamp acting on a set of mica blades placed vertically over the chimney of the lamp, these blades being connected with the screens and attached to a vertical steel spindle working in a cup of agate or hard steel. The details of this plan I brought before the Society in the year 1897.[2]

But it was found in practice, that while the *light never failed* even in very stormy weather, yet with respect to the variation by occultation or otherwise, to which I have above referred, two difficulties were experienced, one with respect to the occultations of beacon lights and the other with respect to similar occultations of buoy lights.

The difficulty as to beacons was this: the hard steel or agate cup in which the spindle worked was exposed to the heat of the lamp, and it was found, chiefly in warm weather, that a sticky deposit from the products of the combustion of the petroleum clogged the spindle in its bearing in the cup, and caused the

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[1] Proceed. R.D.S., vol. viii., p.377. [2] Proceed. R.D.S., vol. viii., p. 519.

recurrence of the occultations to become irregular, and sometimes to cease.

The difficulty in the case of buoys was, that when they were placed in situations where they were much exposed to the action of rough seas, the motion of the buoy caused the revolving screen to rub against the lamp or lens; and hence there was friction and consequent irregularity in the occultations of the light.

To remedy both these difficulties I devised the following plan:—I removed the cup from the direct action of the heat, and placed it in a position where it would always be comparatively cool. To do this it was necessary to alter the position of the flue by diverting it from the centre, and the new situation of the cup enabled me so to arrange the bearings of the spindle as to permit of the continued revolution of the occulting screens even in rough weather. Practically this device consists of an apparatus worked as heretofore by the upward heated current generated by the combustion of the illuminant; but this heated current, instead of ascending directly over the flame of the lamp, is carried aside, and again turned upwards in a vertical direction, so that the centre of the flue from which the current issues is not directly over the flame. The revolving blades are attached to a spindle working downwards, and revolving in a cup which is fixed outside of the great heat of the lamp, and thus is avoided the clogging influence to which I have referred. The shades of opaque or coloured material attached to the blades revolve around the burner of the lamp eccentrically, and, as heretofore, produce the occultations or flashes required; but, with this important improvement, that the spindle being held between two points, the continuous rotation of the shades is ensured, even when the lamp may, by the motion of the sea, the force of the wind, or other agency, be moved considerably from the perpendicular.

In connexion with the eccentric arrangement above described, a cog-wheel could be placed on the spindle, and, geared into it, a toothed wheel revolving in a direction at right angles to the revolution of the spindle. It would then be easy to actuate an extinguisher in the lamp itself, and thus dispense with the necessity for the interposition of revolving shades, the light being extinguished and re-ignited very much in the same manner in which ordinary gas can be turned off and on.

XIII.

SURVEY OF THAT PART OF THE RANGE OF NATURE'S OPERATIONS WHICH MAN IS COMPETENT TO STUDY.

By G. JOHNSTONE STONEY, M.A., D. Sc., F.R.S.

[Read March 22; Received for Publication May 1; Published August 18, 1899.]

Preface.

In the year 1860, Professor Clerk Maxwell published, in the pages of the Philosophical Magazine, a remarkable investigation, aided by which the present writer, in that year, drew up for his own information the scheme of magnitudes described in the following pages, from the use of which he has ever since derived advantage when studying the operations of Nature, whether those carried on upon a large or on a small scale. (See fig. 6, opposite p. 96).

At the suggestion of some scientific friends, he now publishes the diagram, in the hope that it may prove of equal assistance to others, by contributing towards the formation of a correct estimate of what that little is which man can truly know; and of the contrast which necessarily prevails whenever the boundless range both in time and space of each actual operation in nature, is considered in its relation to the limits in both directions at which any clear human knowledge concerning it must stop.

Definitions.

When interpreting Nature's work, we are obliged frequently to speak of high numbers and small fractions. To do this conveniently we shall employ the affix -o to signify a decimal multiple. Thus, a uno will mean some decimal multiple of the arithmetical unit, that is, some member of the series 10, 100, 1,000, &c. The uno-eighteen is to be understood as the name of the eighteenth of this series: it is accordingly the number represented by 1 followed by eighteen ciphers. Similarly a metro will mean some decimal multiple of the metre, and the metro-sixteen will mean the sixteenth of this series of metros. In other words, it is a uno-sixteen of metres. So, again, we shall use the syllable -et for decimal sub-multiple. Thus the sixthet will mean the sixth of these -ets, that is, a unit in the sixth place of decimals. In this nomenclature, the tenthet of a metre is the same as the tenth-metret, *i. e.* the tenth of the series of metrets or decimal submultiples of a metre. Or, it may be spoken of as the tenthet-metre, using this word as an abbreviation for "tenthet of a metre"; just as we may say half-ounce or quarter-inch.[1]

MAXWELL'S DETERMINATION.

In the year 1860, the late Professor Clerk Maxwell published the first determination made by man of any actual molecular interval.[2] The principles upon which he proceeded may be described as follows:—In accordance with the Kinetic Theory of

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[1] It is as necessary to be able to write the quantities we have to deal with in some convenient form, as it is to be able to describe them briefly. The usual plan is to employ positive and negative powers of 10 to express decimal multiples and submultiples. Another contrivance is to represent them by Roman numerals in the way indicated by the following examples:—

As specimens of decimal multiples, let XVI (a uno-sixteen) mean 1 followed by sixteen ciphers, and let 4 VII (four uno-sevens) mean 4 followed by seven ciphers. In multiples the Roman numeral indicates the number of ciphers.

Similarly, to represent sub-multiples, let VIII^{t} (an eighthet) be used as the symbol for a unit in the eighth place of decimals, and let 6. XIII^{t} (six thirteenthets) mean 6 in the thirteenth place of decimals. In sub-multiples the Roman numeral indicates the decimal place.

In manuscript it is more convenient to employ a little curved line, the left-hand half of the letter o, instead of the letter *t*, which has been used in the last paragraph for the convenience of the printer. The small curved line is easily written, and it is appropriate, as it is the symbol in Pitman's Phonography for the group of letters tht, or thet.

We may extend the same convention so as to write in a condensed form multiples and submultiples of the metre, &c. Thus m XVI, 15 m X, IX^{t} m, and 7 VIII^{t} m, will mean a metro-sixteen, fifteen metro-tens, a ninthet-metre (or ninth-metret), and seven eighthet-metres (or seven eighth-metrets).

When once we have got accustomed to this use of the Roman numerals, they will be found to work more conveniently than the positive and negative powers of 10, which are usually employed.

[2] Philosophical Magazine for 1860, vol. xix. p. 19, and vol. xx. p. 21.

Gas, a gas consists of an enormous swarm of little missiles, all alike in each kind of gas, though differing from one gas to another. These molecules dart about among one another with almost incredible activity, and are, to use Maxwell's simile, like the individuals of a swarm of bees which furiously make short flights in every direction, while the swarm as a whole is either stationary or quietly sailing along. In a gas each molecule dashes forward in an almost[1] straight line till it gets close to another molecule. Then an encounter takes place: the molecules struggle together for an excessively brief period, after which they fling asunder in two new directions. The average velocity with which the molecules dart about had been known before Maxwell's investigation. It is about 500 metres per second in the air which we breathe. It was also known that, except in very high vacua, the molecules are so crowded that their journeys between their encounters can be but short; but the length of these journeys was not known. What Professor Maxwell effected was an actual determination in certain gases of the *average* length of these "free paths." He did this by showing that upon this average depends what is called viscosity in a gas—that property which gradually brings a gas to rest after it has been disturbed and currents established in it. He further showed that the average length of the free paths is what determines the rate at which gases diffuse into one another. Accordingly, from experiments on viscosity made by Sir George Stokes, and from Graham's experiments on diffusion, he was able to ascertain what the average length of the free paths must be to produce the observed amount of effect. He thus found it to be about six eighthets[2] of a metre—that which would be represented arithmetically by 0·000,000,06 of a metre—in atmospheric air, at the temperature and pressure of the experiments, which we may take to have been a barometric pressure of 760 millimetres of mercury and a temperature of about 17° centigrade. This length is smaller than any interval which the microscope can show, and yet it is a length which must be regarded as very large among molecular magnitudes.

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[1] The gravitation of the molecules towards the Earth must bend the free paths, but the curvature is insensible until, near the boundary of the atmosphere, the attenuation of the air far exceeds any that can be reached in artificial vacua.

[2] Subsequent experiments by Maxwell himself on the viscosity of air (Phil. Trans., 1866, p. 258) assign a length of 10·6 eighth-metrets to the average free path. The mean of all the determinations is 7·6 eighth-metrets.

NATURE'S WORK AT CLOSER QUARTERS.

We can, however, extract from Maxwell's determination information about still smaller quantities. In fact, Clausius had previously been able to show[1] that in the more perfect gases at ordinary temperatures and pressures, the mean length of the free path is about sixty times what the average spacing of the molecules is at any one instant of time. By combining Clausius's estimate with Maxwell's determination, the present writer was able, in 1860, to infer that the average spacing of the molecules of a gas at the temperatures and pressures which prevail in our houses is about a ninth-metret, and that accordingly there are about a uno-eighteen of molecules (one followed by eighteen ciphers) in each cubic millimetre of the gas. This estimate was communicated to the Royal Society in May, 1867, and will be found in the Phil. Mag. for August, 1868, p. 141. Further, it is known to chemists that there are two chemical atoms in each molecule of many gases. From this and from the known degree in which vapours contract when they are condensed into the liquid or solid state, we may infer that the average spacing of chemical atoms in solids and liquids lies somewhere in the neighbourhood of the tenth-metret (0·000,000,000,1 of a metre), and that accordingly there are something like a uno-twentyone of chemical atoms in each cubic millimetre of solids and liquids—not exactly that number, but somewere near it. He thus arrived at an estimate—an estimate, not a determination—as to the number of molecules in a gas, and as to the number of chemical atoms in solids and liquids. Such knowledge is imperfect, but is much better than knowing nothing about the scale on which Nature is working in this branch of her operations.

The general results of the information acquired in 1860 was :—

1. That the mean length of the free paths of the molecules of air at a barometric pressure of 760 millimetres and at a temperature of 17° C. is about six eighth-metrets. This was a determination.

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[1] Pogg. Ann. 1858, vol. iii. p. 251; or Phil. Mag. 1859, vol. xvii. p. 89.

2. That the mean spacing of the molecules in a gas at the same temperature and pressure is of the same order as[1] a ninth-metret. This was an estimate.

3. That the mean spacing of the chemical atoms of which solids and liquids consist lies somewhere in the neighbourhood of a tenth-metret. This, like the last, was an estimate.

The tenth-metret, the smallest of the above measures, is the ten-thousand-millionth part of a metre. It is about the two-thousandth part of the smallest interval which the best microscope can detect when most carefully handled.

Another branch of physical inquiry has introduced us into the same region of magnitudes, and has even carried us farther. The wave-lengths of visible light range from 38 to 76 eighth-metrets, and can, by methods which will be described farther on, be measured with such marvellous precision that it is possible to detect differences of wave-length which amount to a very small fraction of a tenth-metret.

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[1] In Molecular Physics, where our estimates, and even our determinations, inevitably fall far short of attaining exactness, it is very convenient to be able to describe the result as being "of the same order as" some specified magnitude.

To give definiteness to this expression, imagine units where there are ciphers in fig. 6. They are a geometrical series, each unit having a value ten times that of the unit to its right. Next form the corresponding series with $\sqrt{10}$ as its factor. This will interpolate a new term between every two consecutive terms of the former series. Thus, on either side of the unit so situated in our table as to represent a ninth-metret, will be terms one of which will have the value $\sqrt{10}$ ninth-metrets, and the other $1/\sqrt{10}$ of a ninth-metret. Now, any quantity between these two limits may be spoken of as "of the same order as a ninth-metret." In accordance with this convention, 3 ninth-metrets, 2 ninth-metrets, 1 ninth-metret, $\frac{1}{2}$ ninth-metret, and $\frac{1}{3}$ ninth-metret are all quantities "of the same order as" a ninth-metret.

When we deduce the number of molecules in a gas from the spacing of the molecules we have to deal with the cube of an already estimated number, and accordingly the range implied by the phrase "of the same order as" becomes widened. It now ranges from $\sqrt{1000}$ times the assigned value (in this case a uno-eighteen per cubic millim) to $1/\sqrt{1000}$ times this value; so that it includes 30, 20, 10 times, and 1/10, 1/20, and 1/30 of a uno-eighteen. The knowledge thus reached as to the number of molecules that are present may seem very indefinite; but it is far from being valueless.

NATURE'S OPERATIONS ON A LARGE SCALE.

When we turn our attention to Nature's operations on the large scale we find that the greatest lengths we can as yet succeed in measuring are the distances of those few stars which have perceptible parallax.[1] The distances of these stars from the Solar System range from four to fifteen metro-sixteens; and it is not likely that any star could send us light enough to be visible in any of our telescopes if a thousand times more remote. At a distance, then, of about ten thousand metro-sixteens, that is, at a distance of about a metro-twenty, our knowledge of the starry universe comes to an end. It is perhaps possible, that the great Nebula in Andromeda, and a few other non-gaseous nebulæ, are stellar systems distinct from that of which the Milky Way is the outlying portion, and which is commonly spoken of as the stellar universe. If so, such of these other "universes" as can be visible to us probably lie within a sphere which extends into the space beyond our stellar system, perhaps some 100 times further than the boundary of the Milky Way, and may accordingly need, to represent the distances of some of them, numbers inserted in the next column of our table (fig. 6). Accordingly, the column of metro-twentyones is in the table indicated as one of those included within the range of what man possibly already knows something about.

From this preliminary survey, it appears that man is only acquainted with a strictly limited portion of the scale upon which the real operations of Nature are being carried on. All her operations upon an ultra-stellar scale, all her activities at infra-molecular degrees of proximity, are kept from our view by that heavy veil of Isis which man's limited senses and his restricted intellectual powers cannot lift. It raises us in the scale of thinking beings to

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[1] Attempts have been made to infer the parallax of binary systems from a spectroscopic determination of the difference of velocity in the line of sight of the constituent stars, combined with the known periodic time and the apparent angular size and form of the system. This method has been applied to γ Virginis and to the companion of γ Andromedæ with results which are not yet free from doubt on account of the extreme delicacy of the observations, but which seem to place these stars about one step of our scale farther, *i.e.* about ten times farther, from us than those of which the parallax can be directly measured.

see *clearly* where our knowledge must end, and to have ascertained definitely which part of the boundless range of Nature's actual operations is that which human powers are able to gauge and which human minds can adequately grasp. The survey may be rendered definite with the help of the table comprised in fig. 6, in which numerical digits are to take the place of some of the ciphers. According to the place where we insert these numbers we can make them express by how many metres, or by what fraction of a metre, we are to measure any of the magnitudes with which man has become acquainted throughout the whole range of his study of Nature.

In this table metros mean decimal multiples of the metre; metrets mean its decimal sub-multiples; and kīlem (to be pronounced with the *i* long[1], as in *mile*) is used as convenient English for the French "kilomètre." The first few places in the table and the last four or five lie beyond the range of our present knowledge. Nevertheless they are included; in order that the table may not be unduly shortened by temporary ignorance on our part, but may provide a large margin for possible future discoveries.

The significance of the survey is best appreciated by examining separately the four groups into which the table is divided, and it is convenient to begin with Group C, as it includes the measures most familiar to us.

GROUP C (LABORATORY MEASURES).

Group C extends from kīlems (kilomètres) on the left down to tenths of a micron on the right. The central sub-section *v* includes the measures most in use in our laboratories, from metres down to tenths of a millim or millimètre. Sub-section *u* includes those larger measures which men have also in every-day use—from tenths of a metre up to kīlems or kilomètres. The third sub-section *w*, from millims (millimètres) down to tenths of a micron, *covers the entire range of the microscope*, and indeed travels somewhat beyond the grasp of that instrument, since the smallest interval at which two objects can be seen as two by the best immersion objectives supplemented by the best immersion condensers, and most carefully handled, is but little less than two tenths of a micron

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[1] In χιλιάς, 'a thousand,' and in all Greek words derived from χιλιάς, the ι is long.

which is the 127,000th of an inch; whereas sub-section *Cw* extends twice as far, *i.e.* down to one tenth of a micron. This brings us within the border of the next group, the group of molecular intervals, almost all of which lie farther beyond the reach of the microscope than microscopic objects lie beyond the grasp of the naked eye.

GROUP D (MOLECULAR QUANTITIES).

On the borderland between Groups C and D, we find the lengths of waves of light, all of which can be represented by numbers inserted in the column which is the extreme right-hand column of Group C, and the extreme left-hand column of Group D. The wave-lengths of visible light extend from a little less than 4 seventh-metrets to a little less than 8 seventh-metrets. The ultra-violet light which reaches the Earth from the Sun carries us down to about 3 seventh-metrets; the light which has been explored by Professor Hartley extends the range nearly down to 1½ seventh-metrets; and Professor Schumann has got down to light whose wave-length is about one seventh-metret. Thus the wave-lengths of light come all of them upon the column which, in our table, is on the border between microscopical magnitudes and molecular. Almost the only true molecular length long enough to be measured in this column is the average free path in attenuated air, or in some other gases. On the other hand, when air is as dense as it is at the surface of the Earth, the average length of these free paths has to be recorded in the next column (the column of eighth-metrets), and may be considered as about the longest of legitimate molecular intervals. According to Maxwell's determinations it seems to be about 7½ eighth-metrets. The wave-lengths of Röntgen rays perhaps extend into this column.

One or two units in the next column, the column of ninth-metrets, may be taken as about the average interval at which the molecules of ordinary air are spaced; and a unit or two in the following column, that of tenth-metrets, is about the average spacing of the chemical atoms of which solids and liquids consist. It will be seen that none of these intervals extend beyond *Du*, the sub-section of *large* molecular magnitudes.

When we attempt to penetrate farther, we find that we can only obtain a glimpse of those more fundamental events in Nature, the size of which or the range of which has to be measured in the next three columns, *i. e.* in tenthets of the decimetre, of the centimetre, of the millimetre. These all come into subsection *v*, the sub-section of medium molecular magnitudes. That there are events of this kind going on unremittingly within every chemical atom is indicated to us by the lines in the spectra of the chemical elements; for these are caused by such events. Here, at present, human knowledge stops: the whole of the work which Nature is carrying on at still closer quarters, although we are well aware that it must lie at the basis of all the rest, is totally hidden from our view, except so far as the speculations of mathematicians may doubtfully attempt to probe it; and in all such conjectures the speculator has to substitute something very much simpler for what is really going on. However, Group D is represented in our diagram as including another subsection, *w*, going 10,000 times farther still; in order by this extension to provide for the possibility of future discoveries which we hope may some day be realised.

Very little is known about the events going on within chemical atoms, of which we have found that the range is to be measured in tenthet-decimetres, tenthet-centimetres, or tenthet-millimetres, and even the fact that there are such events lies near the limit of our knowledge; and yet these excessively minute quantities can be dealt with accurately when they present themselves as differences of wave-length. This is truly astonishing, when we remember that we are here measuring lengths that are from 100,000 to 1,000,000 times smaller than the most minute interval that can be detected by the microscope—as much smaller than a micron, as a tenth or hundredth of an inch is less than three quarters of a mile. Nevertheless these lengths can be determined with precision because the position of a line in the spectrum depends on its wave-length, and the difference of the wave-lengths of the closest lines which can be photographed as double is excessively small; and again, because two rays with a still smaller difference of wave-length may give rise to interference effects which can be detected by the interferometer. By the spectrometer measures can be carried at all events as far as the 50th of a tenthet-metre, *i. e.* as far as to one or two tenthet-centimetres, while with the interferometer determinations can probably be carried one step of our scale farther, *i.e.* to one or two tenthet-millimetres. Here, for the present, our powers end: and we cannot fail to be impressed by the extraordinary accuracy which has been attained in measuring wave-lengths by the methods spoken of above. It is a degree of accuracy which ascertains the length of a wave of light within a millionth of its entire length, thus equalling and even surpassing the best results obtained when comparing with excessive care international standard yards or metres; in which a determination within one fifthet (the 100,000th) of the whole length is probably the most that can be *fully* relied on.

DISTANCES OF THE PLANETS FROM THE SUN, IN METRO-TENS.

(*The Sub-section* Bu *provides for all of these.*)

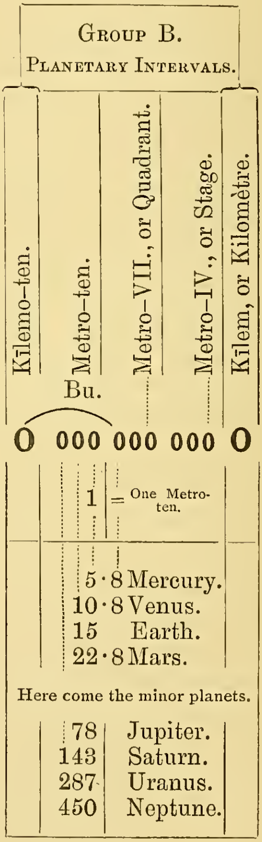

FIG. 1.

GROUP B (PLANETARY INTERVALS).

We have next to direct our attention to Nature's operations on a great scale, and first to Group B which deals with events within the solar system. This group, like the others of our survey, may conveniently be divided into sub-sections—*u*, *v*, and *w*.

Bu, the sub-section of large planetary measures, indicates the place in our table in which to record the distances of the planets from the Sun, or from one another, as is seen from fig. 1. These distances are most conveniently read out as so many metro-tens.

The next sub-section, *v*, makes similar provision for representing the distances of the satellites from their primaries, and for recording the size of the Sun, which belongs to the same order of magnitude. This appears from fig. 2, in which the distances may conveniently be expressed as so many Earth-quadrants, meaning by the "quadrant" 1000 stages, or 10,000 kīlems, which is approximately the distance on the Earth's surface from the Equator to the Pole.

There remains the *w* sub-section, the sub-section of smallest Planetary measures. These stand related to the other Planetary distances in somewhat the same way as Microscopical intervals are related to other Laboratory measures. They may be called *geographical* intervals, since in this sub-section we measure the radii of the planets and distances on their surfaces: quantities which can conveniently be expressed as so many stages, each stage being ten kīlems (or 6¼ miles),[1] as shown in fig. 3.

DISTANCES OF SATELLITES FROM THEIR PRIMARIES, EXPRESSED IN EARTH-QUADRANTS.

(*The Sub-section* Bv *provides for all of these.*)

Group B.
Planetary Intervals.

	Kilemo-ten.	Metro-ten.	Metro-VII., or Quadrant.	Metro-IV., or Stage.	Kilem, or Kilomètre.
			Bv.		
	0	000	000	000	0
Quadrant, or Metro-VII.			1		
Radius of Sun,			69·75		
Distances of					
Moon,			38·4		
Satellites of Mars,			0·9		
			2·3		
(Nova),			18		
			43		
Satellites of Jupiter,			68		
			109		
			192		
			19·5		
			25		
			31		
			39·5		
Satellites of Saturn.			55		
			128		
			162		
			380		
(Nova),		1	200		
			19·8		
Satellites of Uranus,			27·5		
			45		
			60		
Satellite of Neptune,			35·4		

Fig. 2.

RADII OF PLANETS, EXPRESSED IN STAGES.

(*The Sub-section* Bw *provides for all of these.*)

Group B.
Planetary Intervals.

	Kilemo-ten.	Metro-ten.	Metro-VII., or Quadrant.	Metro-IV., or Stage.	Kilem, or Kilomètre.
				Bw.	
	0	000	000	000	0
Earth quadrant,			1	000	
Radius of Sun,			69	750	
Radii of					
Mercury,				240	
Venus,				610	
Earth,				637	
Mars,				340	
Jupiter,			7	000	
Saturn,			6	100	
Uranus,			2	500	
Neptune,			2	600	

Fig. 3.

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[1] That is, 6¼ *metric* miles. In Science the mile of 1600 metres, the furlong of 200 metres, the chain of 20 metres, and the perch or pole of 5 metres, should always be used instead of the so-called "imperial" measures of the same names. Here the old or imperial measures are to the new or metric measures in the ratio of 100·582 to 100, which is the same as the ratio of 172·8 to 171·8, between which last numbers the difference is 1.

GROUP A (STELLAR DISTANCES).

The last group is that of stellar distances. These are most conveniently measured in metro-sixteens.

The four units we have found it most convenient to use in dealing with large magnitudes are very simply related to one another, as appears from the following list of them.

The unit we have found it convenient to use for geographical distances is the *stage*, the stage being ten kīlems or $6\frac{1}{4}$ miles.

The unit for the distances of satellites from their primaries is the Earth *quadrant*, the quadrant being 1000 stages.

The unit for the distances of planets from the sun is the *metro-ten*, the metro-ten being 1000 quadrants, which is the same as a million stages.

The unit for stellar distances is the *metro-sixteen*, the metro-sixteen being a million metro-tens, or one billion stages.

The position which the metro-sixteen, or billion stages, occupies is indicated on the table. Light in the open æther takes 1·056 year (nearly a year and three weeks) to travel a metro-sixteen, so that the metro-sixteen is a little more than what, in astronomy, has sometimes been called the "light-year."

The distances of the nearest stars, those few of which the parallax can be directly measured,[1] fall within *Aw*, the sub-section of smallest stellar distances, as appears from the examples shown in fig. 4.

EXAMPLES OF MEASURED STELLAR DISTANCES, EXPRESSED IN METRO-SIXTEENS.

(*The Sub-section* Aw *provides for all of these.*)

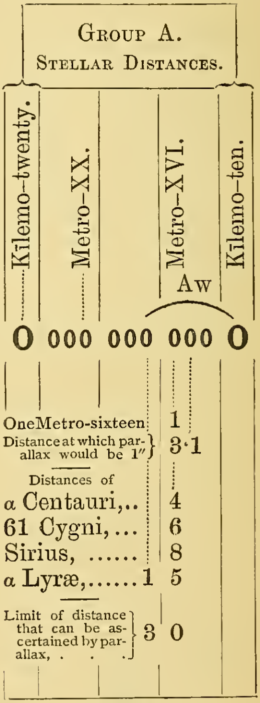

FIG. 4.

Thus *Aw* includes the distances of the nearest stars along with sub-stellar distances, that is, distances from the Sun to stations between the solar system and the nearest star. Such sub-stellar intervals probably exist between the stars of a cluster.

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[1] See foot-note on p. 84.

The farthest stars visible to us are probably less than 10,000 times farther than the few whose parallax can be directly measured, since a star sending us one hundred-millionth part of the light of Sirius would probably not be visible.

If this view is correct, *Av*, which is the middle sub-section of Group A, provides places to represent the distances of the stars visible to the naked eye, along with *all* those which our telescopes can reach. Accordingly, a sphere of which the radius is a metro-twenty, or some two or three metro-twenties, would include our whole stellar universe. Now, our table extends 1000 times beyond the column of metro-twenties; so that the greater part of sub-section *Au* makes provision for measuring distances as much farther out than the most distant star known to us, as a sphere with a mile for its radius ranges beyond a concentric sphere with less than a yard for its radius.

It is just possible that the inner portion of this extension is necessary to represent man's present knowledge, that, in fact, some of the non-gaseous nebulæ, *e.g.* the great Nebula in Andromeda, may be stellar "universes" distinct from ours, and located somewhere within the larger sphere. If so, when we looked upon the speck of light which brightened up in the Nebula of Andromeda a few years ago, we may have been then actual spectators of an event which really happened some hundreds of thousands of years ago, the waves of wireless telegraphy which communicated the information to us having occupied the whole of that immense time upon their swift journey.

OF THE RELATION BETWEEN LIGHT AND OUR SCALE.

This leads us to consider the relation in which light stands to our survey. It is useful to do so, since it gives unity to our survey to consider how our table is related to light, which in one direction reaches, by the minuteness of its waves, the borderland of molecular magnitudes, and in the other direction, by reason of its great speed, can traverse immense distances in periods of time which we can grasp. The relationship is exhibited in the lower section of fig. 6, which gives the

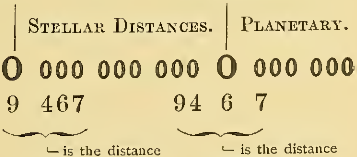

FIG. 5.

times which light must have to enable it to reach us from the distances represented by a unit in each of the indicated parts of the table. The information there recorded may be supplemented by that added in fig. 5 on the preceding page.

ON THE MEASUREMENT OF TIME.

The same table may be employed for measuring time. Intervals of time for the purposes of physical inquiry are best measured by the distances over which light in the open æther would travel in those periods. In this way measures of distance become measures of duration upon that scale upon which a metro-eight (which is the same as the centimo-ten) represents one-third of a second—a scale which in practice is found to be very convenient, especially for the study of molecular physics. To represent a second of time on the diagram, insert the digit 3 instead of the cipher which occupies the middle place in the planetary group of positions. In this way of measuring time 300 metres of time (1000 feet)[1] is the same as the millionth of one second.

OF MOLECULAR EVENTS.

In molecular physics, the periods of time which have to be dealt with are almost inconceivably shorter than any to which we are accustomed. The unit of time which the present writer has found the most generally convenient is the micron of time—the time which light takes to advance one micron forward in the open æther. It is the hundredth part of the jot (or fourth-metret of time), which unit he found it convenient to use in his memoir on the production of double and multiple lines in spectra by perturbating forces acting on the electrons. (See Sc. Trans. R. D. S., vol. iv., p. 565.)

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[1] That is, 1000 *metric* feet. In Science, the yard of 9 decims, the foot of 3 decims, and the inch of 25 millims should always be used instead of the so-called "imperial" measures of the same names. Here the old or imperial measures are to the new or metric measures in the ratio of 101·6 to 100, or in the ratio of $63\frac{1}{2}$ to $62\frac{1}{2}$, or in the ratio of 127 to 125. It may be useful to point out that Lathes and Dividing Engines provided with Whitworth screws, the pitch of which is known in imperial inches, may be made to produce screws or graduate scales in the metric measures, by simply introducing two change-wheels, one with 127 and the other with 125 teeth.

One of the conveniences of the proposed way of representing time is its perfect flexibility. In each investigation we may select as our unit of time that of the whole decimal series which happens to be the most convenient to use in the investigation. In the above-mentioned inquiry it happened that a relatively large unit was the most convenient. In other inquiries the micron, which is 100 times briefer, is a more convenient unit, and in some few, in which very much smaller periods of time were under consideration, he has employed the tenth-metret of time.

The micron of time is the XIV^t (fourteenthet) of the third of a second, that is the 300th part of the billionth of a second. To magnify it till it becomes one second of time is the same process as to magnify the fifth part of the thousandth of a second until it becomes 1900 years, *i. e.* the whole duration of the Christian era. It is instructive to bear this in mind when dealing with molecular events.

In dealing with molecular events, it is well to conceive a magnified model of what is really going on, in which all lengths are so enlarged, and all times so much prolonged, as to bring both within the range of what we can conveniently perceive. In order to do this, the magnification with respect to time will need to be greater than that with respect to space. A good magnification for many purposes is a magnification of all lengths by a uno-ten, and a magnification of the durations by either three or six uno-fourteens.[1] (See Scientific Proceedings R. D. S., vol. viii., p. 372; or Philosophical Magazine for October, 1895, p. 381.)

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[1] The magnification of molecular intervals by a uno-ten may be called *standard* magnification of molecular events; because it means the representing of molecular events which require to be recorded in Group D by a model of them so large that it records them *in the corresponding parts* of Group C, the group of magnitudes with which we are most familiar.

The magnification of the durations by 3. XIV (three uno-fourteens) means that each micron of time becomes a second, so that an event in the molecular world which occupies a fraction of a micron of time is represented by an event of the same kind in our model which occupies the same fraction of a second. This, in the case of a great number of molecular events, brings the events occurring in the model within the range of human perceptions. If the time magnification is by 6. XIV (six uno-fourteens), a molecular event that occupies some fraction of a micron of time is represented by an event in the model which occupies the same fraction of two seconds; and this is sometimes convenient where we wish to compare molecular motions with the motions of pendulums or of the limbs of animals, since a pendulum which beats seconds is one whose periodic time is two seconds.

When by this or other means we have attained the power of viewing events from the molecular standpoint, we begin to perceive that chemical reactions, even those that occur with explosive violence, are far from being the sudden events they seem to ordinary human apprehension. What is really occurring in nature is a *protracted* and eventful struggle between the members of two opposing armies, *each individual of which* has his own personal history during the struggle, and is fully occupied with his own acts, which are, perhaps, as many, as various, and as different from those of his neighbours as are the thoughts and acts of the individual soldiers during the progress of a battle.

What comes under the observation of a chemist is the state of things which preceded this eventful period, and that other state of things which followed it. As to what nature has been really doing, his record is a blank. It is not unlike the inscription one often sees upon tombstones, "Born in such a year; died in such another," while the real *event*, the intervening *life*, is passed over in silence.

How, then, ought the student of Molecular Physics to regard the incidents of the eventful period of a chemical reaction? The incidents of the operations that are then going on are vastly more numerous, are probably as various, and are done with as little hurry when we view them from the molecular standpoint, as are the acts of human artizans or of other animals while accomplishing some piece of work; and they are, relatively speaking, persisted in for an almost immeasurably longer time, inasmuch as the fifth of the thousandth of a second in the molecular world corresponds to something like 1900 years in ours.

An estimate of this kind is of service, because it leads us to see that biological and chemical processes, even where they seem to us to take place with suddenness, are from the molecular standpoint protracted events consisting of individual transactions, each of which can only occur when the opportunity presents itself: they are not the outcome of the ordinary current of molecular events, but, on the contrary, each step of progress in them may have to wait long for some very exceptional combination of circumstances to arise. The present writer once saw doublets thrown thirteen times in succession with unloaded dice, at the close of one game of backgammon and at the beginning of the next game. It must be an unusual experience for a human being to be witness to so rare an event. The probability of it is only one in 13,060,700,000. Yet so great is the number of molecules in a gas, and so frequent their encounters, that some *millions* of cases occur *every second in every cubic micron* of the air about us, in which an encounter between molecules has taken place under conditions as exceptional as the above; and equally unusual events probably occur some thousands of times more frequently in the encounters between the molecules of two liquids, or of a liquid and a solid. It is thus that chemical reactions and events in biology can extend over a duration which is appreciable by us, even in the case of explosions; the fact being that in all such it is their *excessive* slowness from the molecular standpoint that has to be accounted for.

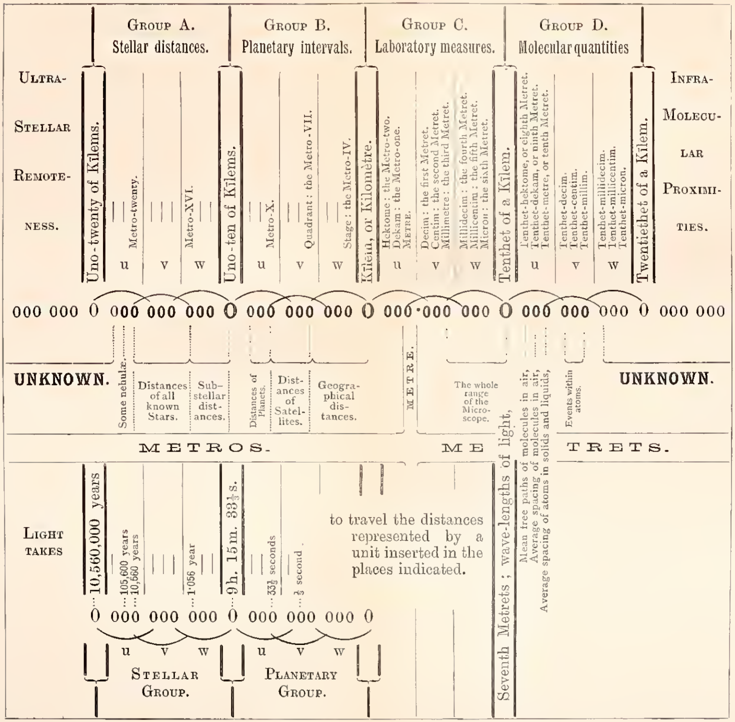
Conclusion.

No physicist can consult the diagram presented in fig. 6 without being struck by its resemblance to an absorption band in a spectrum. Nature is occupied in working everywhere over the entire spectrum; man's knowledge of her works is confined to what occurs within this one absorption band. How much changed would be the aspect under which the human mind would have had to view nature, if the position of the absorption band had occupied a different place—if, for example, the range of our knowledge had been Groups B, C, D, and E, instead of A, B, C, and D; with such a full knowledge of molecular objects and events as we now enjoy of objects that range from kīlems down to microns; and with such a lessened knowledge of Group C as we now have of planetary events! An equally startling change would be made if the range had been shifted the other way: if we had no knowledge of microscopic or molecular events, just as we now possess none of those which go on within and beyond subsection *w* of Group D; if at the same time we had only a smattering of knowledge about Group C, such as the fragments we are now able with difficulty to obtain about Group D, accompanied by some real acquaintance with the immense universe that lies beyond Group A.

Along with these considerations we should ever bear in mind that behind and above the great universe of natural objects, and the true cause of all the rest, there stands the Autic Universe, the mighty Autos, to which the present writer endeavoured to draw attention in an earlier paper, and of which the THOUGHTS that are our real selves are part. (See Scientific Proceedings of the Royal Dublin Society, vol. vi. (1890), p. 475.)

FIGURE 6.

SURVEY OF THAT PART OF THE RANGE OF NATURE'S OPERATIONS WHICH MAN IS COMPETENT TO STUDY.



XIV.

AWARD OF THE BOYLE MEDAL TO GEORGE JOHNSTONE STONEY, M. A., D. Sc., F. R. S., at the Evening Scientific Meeting of the Royal Dublin Society, held March 22nd, 1899.

Dr. J. Joly, F.R.S., read the following statement which he had prepared upon the institution of the Boyle Medal:—

In former years, it is on record, that the Royal Dublin Society occasionally presented medals to men distinguished in science. But the Society never at any time possessed a medal specially instituted for the purpose—a medal dedicated to the memory of a great Irishman, and destined to mark the Society's appreciation of the scientific work of those happily still living amongst us. The awarding of such a medal is a recent addition to the functions of this Society. The value of such an institution is unquestionable. It is to the Society a power of speech, a means of expressing her measured opinion that the work of the recipient is worthy of the highest honour. But not only is this old Society thus enabled to speak her thoughts and to place them upon record, but as the roll of the Boyle Medallists lengthens with the passage of time, will not this roll be an honourable record for her? The greatest Irishmen will, as we hope, have their names inscribed upon it, and be numbered among those who have honoured her by accepting her honours.

It was not without due consideration that the life-work of the Hon. Robert Boyle was chosen as that which might be most fitly commemorated by this medal. That Boyle did more for science than any other of the great Irishmen who have passed away is not too much to maintain. His name is not, indeed, associated with any profound discovery; the celebrated law by which it is known to every educated man might have been achieved by a lesser mind. Boyle stands before the world as the great pioneer in the application of the Experimental Method. By its aid he shed light on many dark places in science. Many valuable methods and facts have their origin in Boyle's labours. His wide intellect made its influence felt over the entire range of the science of the 17th century.

Born in 1627 at Lismore, county Waterford, he was an accomplished boy of fifteen in that eventful year when Galileo died and Newton was born. He was, therefore, Newton's predecessor by fifteen years, and beginning systematic experimental work when but eighteen years of age, he stood before England for nearly twenty years as high priest of the Baconian method before the lustre of Newton's work began to dazzle men's eyes. The influence of Boyle on Newton and on Robert Hooke must have been immense. His discoveries agitated the whole country. Notwithstanding the many brilliant contemporaries who sprang up around him, he retained his great influence, although not, indeed, his supremacy, to the last days of a life of sixty-four years duration. Boyle's most important work was done for chemical science. Everyone remembers the celebrated words which named him "the father of Chemistry and brother of the Earl of Cork." He first distinguished between a mixture and a chemical compound. He defined the elements in a manner strangely prophetic of the most modern speculations of our own times—as all compounds of one universal matter, to the various modes of movement and grouping of which the constitution of the entire visible part of the universe was to be ascribed. He showed more clearly than his predecessors that air was necessary to combustion and respiration. He prepared phosphorous and hydrogen, although he failed to recognise the independent nature of the last. He first used vegetable colour tests for alkalinity and acidity, and introduced the use of chemical reagents into investigation. He believed heat to be a brisk molecular motion and not a material substance, thus forestalling in part ideas which only assumed full sway in this present century. He first suggested the freezing and boiling points of water, as fixed points on the thermometer. He studied light (which he endeavoured to weigh), as well as sound (the propagation of which, by the atmosphere, he is said to have first demonstrated)—also electricity, magnetism, and hydrostatics. He invented what is practically the modern air pump, and, by its aid, many new experiments. His discovery of the elastic law of gases in 1662, fourteen years before Mariotte confirmed it, is known to all, and, doubtless, inspired Hooke to his celebrated investigation of the elastic law of metals.

But physical and chemical science did not limit him. He contributed much valuable material to medicine, and devoted himself with ardour to the study of anatomy. The occasion for entering on this latter study was a visit to his native land, then (1652) in a very unsettled state. His description of it reads like a contribution to the science of heredity :—" A barbarous country where chemical spirits were so misunderstood and chemical instruments so unprocurable that it was hard to have any hermetic thoughts in it." Accordingly, for lack of hermetic thoughts, he fell to practice anatomy, satisfying himself as to the truth of Harvey's revolutionary discovery, then recently made of the circulation of the blood. There is, unfortunately, on this side the grave no means of estimating to the full the value of a man's life-work. We cannot place that work on the one side of a balance and on the other place units of usefulness to mankind. Could we do so, many of the estimates which historians have made of the worth of past lives would be found wanting. One arises from the consideration of Boyle's life with the feeling that much of that life's work was of the kind which finds no record; which effects, indeed, the deepest currents of human life, but not the less, is writ in water so far as the future historian is concerned. Contrast the fame of Newton with that of Boyle. The estimate which we possess of Newton is probably far more complete than that which we have of Boyle. In Newton's writings we have his work, but while Newton shrank from the bustle and contention of scientific advance, Boyle stood with ready counsel and ready liberality to help every effort after truth. Both alike appealed to nature at every step of advance. Newton's great mathematical genius gave him the advantage of the Seer. Here Boyle failed; but, on the other hand, while Newton's soul dwelt apart, Boyle's heart beat with that of his fellow-man. He it was, in chief, who first brought the great powers of the social instinct to bear upon scientific advance in England—that power which we to-day recognise as an essential ally of every movement destined to endure. He principally founded the Royal Society of London and befriended its early years. The beneficent effects of such deeds admit of no evaluation by human judgment.

The reader of Boyle's life bears from it yet another impression, that his character was as nearly faultless as human nature can attain to. His work widened out beyond science. Whatever was for the good of humanity and for truth was Boyle's work. Boyle's greatest failing was, perhaps, the extremes to which he carried his utilitarianism. But in this the times themselves were at fault. Some will maintain that in the abstract Boyle was right. Science was still in her youth, and possessed no such rich store of memories as serve to guide the adult science of to-day. The important bearing of remote theoretical facts on ultimate advance had not been emphasised again and again, as it has been since Boyle's time. He held to a philosophy "that valued knowledge, but as it had a tendency to use." Referring to the error of believing in the direct influence of the planets on human life, he asks, "Why then study them? Why know them only to know them?" The magnificent use made by the navigator of those heavenly timekeepers was not prophetically revealed to Boyle, nor the vast facts in science which the motions and physical states of the planets and stars to-day reveal, illustrate, and confirm. The fitness of attaching Boyle's name to our medal resides not alone in his universality, but in the fact that he it was who chiefly introduced the Scientific Society into our civilization. Lastly, he was an Irishman. The Oxford Junior Scientific Club has celebrated him by founding Boyle Lectures. To these the greatest living thinkers have already contributed. If the Royal Society has omitted to commemorate him with a medal, it is fitting that we should make good the omission and claim what is our own.

Dr. Joly then read the following Report of the Science Committee:—

The name of Dr. G. Johnstone Stoney is recommended by the Science Committee as that of a worthy and fit recipient of the first Boyle Medal awarded for research in Pure Science.

In consideration of the many years during which Dr. Stoney's scientific work has been before the world, and the manner in which it has stood the test of time, and served as the basis of fresh advance—ever the test of true scientific work—your Committee feel that this award is but a tardy recognition of his labours, and rejoice that it is at length in the power of the Society to express its appreciation of such work.

Dr. Stoney's work extends into many branches of Science.

In 1858 he was associated with the late Provost Lloyd in making a magnetic survey of the southern half of Ireland. In 1860 two of his earliest papers appeared in the Transactions of the Royal Irish Academy, one explaining the phenomena of rings seen in fibrous specimens of calc spar, the other reconciling the forward propagation of waves in a uniform medium with the fact that from each point of the medium the disturbance is propagated equally forwards and backwards.

His contributions to the Kinetic Theory of Gases are many and valuable. The brilliant achievement of first finding a numerical estimate of the number of molecules in a unit volume of a gas at atmospheric temperatures and pressures is his. Maxwell had found the mean free path, Clausius and Joule had estimated the velocity of mean square, Loschmidt of Vienna had first estimated the diameter, but it remained for Dr. Stoney, in a paper "On the Internal Motions of Gases compared with the Motions of Waves of Light," which appeared in the Philosophical Magazine of August, 1868, to deduce from the work of Clausius and Maxwell the number of molecules in a cubic millimetre of a gas.

Later, in the year 1876, Dr. Stoney applied his vivid appreciation of the molecular theory to solve the problem of Crookes's Radiometer and the allied phenomena in a succession of papers appearing in the Philosophical Magazine and in the Transactions and Proceedings of the Royal Dublin Society, dealing with polarisation stresses in gases. Part of this work was done in conjunction with Mr. R. J. Moss, F.C.S.

Turning to another branch of Dr. Stoney's investigations in this domain of Physics, we must go back to 1867, when a Memoir was read by him before the Royal Society, pointing out the conditions which limit the heights to which the constituent gases of an atmosphere extend ("On the Physical Constitution of the Sun and Stars," Proc. Royal Society, 1868). The considerations contained in that paper were, in 1870, extended and brought before the Royal Dublin Society in a discourse which embraced an explanation of the absence of a lunar atmosphere. Subsequently further notes were brought before the Society; and finally, in 1897, in the Transactions of the Royal Dublin Society, Dr. Stoney gave a full account of a theory which accounts for many observed facts regarding the atmospheres of heavenly bodies, *e.g.* the prevalence of large quantities of light gases—hydrogen and helium—in the Sun, the absence of atmosphere in the Moon, the apparently arid state of Mars, and his poverty of atmosphere, as well as the seemingly abundant atmosphere of Jupiter. The almost complete absence of helium and hydrogen from the terrestrial atmosphere also received explanation from the interesting theory first put forth by Dr. Stoney.

Other papers dealing with collateral applications of the Kinetic Theory, although of much interest, can only be referred to here by title. Such are—"On the Possible Source of Energy required for the Life of Bacilli," Proc. Royal Dublin Society, 1893; "On the Kinetic Theory of Gases regarded as Illustrating Nature," Proc. Royal Dublin Society, 1895, &c.

The work which Dr. Stoney has done in the Kinetic Theory of Gases, considerable as it is, at the present moment, in a comparison of his many achievements, has to yield place to his still profounder work on the nature of the internal motions of the atom.

Attacking the problem so long ago as the year 1868, in the paper already referred to in this Report—"On the Internal Motions of Gases compared with the Motions of Waves of Light" —he begins with a speculation, which little by little he brings nearer to verification in subsequent years. In this early paper he urges that definite wave-lengths in the spectrum of a gas involve periodic motions within the individual molecules, and that something like from 50,000 to 100,000 of such periodic and, probably, orbital motions must be executed between successive collisions in a gas, thus explaining why matter in the gaseous state can furnish a spectrum which consists of distinct lines. Independently of the suggestion of Maxwell, in 1873, Dr. Stoney, in 1874 (Belfast Meeting of the British Association, 1874, and Proceedings of the Royal Dublin Society, 1881), suggested the adoption of the Faraday molecular charge as a natural unit of electricity, more recently suggesting for it its present name of "Electron." Somewhat before this period, in 1871, two papers appeared by him on "An Inquiry into the Causes of the Interrupted Spectra of Gases," in the Philosophical Magazine, the last of the two being in conjunction with Professor Emerson Reynolds, F.R.S. These deal with the sequences in the line spectrum of hydrogen and the absorption spectrum of chlorochromic anhydride. In the spectrum of this vapour a significant relation was detected between the intensities of the lines of the spectrum and the succession of the intensities of the harmonics of a definite point on a violin string when set in motion by the bow. In 1891 he added to these "An Analysis of the Spectrum of Sodium" (Proc. Royal Dublin Society). Finally, in the earlier part of 1891, appeared his paper, "On the Cause of Double Lines and of Equi-distant Satellites in the Spectra of Gases" (Trans. Royal Dublin Society). This is a summation and completion of his theory in its bearings on his previous work.

According to Dr. Stoney the successive series of lines which he, and—following in his footsteps—others, had determined in the spectra of gases, are referable to the motion of an electron within the molecule, or to an event following the same mathematical law. This motion gives rise to a definite series of elliptic partials, to each of which the motion of the electron may be referred and consequently the electro-magnetic disturbance represented by a definite line of the spectrum. The existence of double lines is attributed to perturbations of these orbits of the nature of apsidal motions.

The bold realisation of events which we are accustomed to associate with the vast cycles of astronomy as occurring within orbits too minute and during periods too transient for the mind to grasp is characteristic of the writer.

The recent and powerful method of research with which the work of Lorentz and of Zeeman has armed physicists is every day rendering acknowledgment to this beautiful theory of Dr. Stoney's.

Dr. Stoney appears to have been one of the first to recognize the great importance to science of properly selected units and systematic nomenclature. Many of his physical papers contain tentative and often valuable suggestions in this connexion. His services on the committee appointed by the British Association in 1873 are well known.

In this Report we can only further refer to the very complete and profound treatment of the subject of the limits of microscopic vision (Phil. Mag. 1896); to an important work "On the Relation between Natural Science and Ontology" (Proc. Royal Dublin Society, 1890); and, by their titles only, to a long list of thoughtful Scientific Memoirs:—

"On an Improved Arrangement of Grove's Battery."—British Association Report, 1857.

"On the Adjustments of the Needle of a Tangent Galvanometer" (Phil. Mag., 1858).

"On the Amount of Direct Magnetic Effect of the Sun or Moon on Instruments on the Earth's Surface."—Phil. Mag. 1861.

"Explanation of the Electrical Experiment of Mahomet's Coffin."—Phil. Mag., 1868.

"Approximate Formulæ for the Volumes and Weights in Gases."—Proc. Royal Dublin Society, 1880.

"On the Physical Units of Nature."—Proc. Royal Dublin Society, 1881.

"On the Energy Expended in Propelling a Bicycle" (jointly with Mr. Gerald Stoney).—Trans. Royal Dublin Society, 1883.

"On the Cause of the Iridescence in Clouds."—Trans. Royal Dublin Society, 1887.

"On the Appreciation of Ultra-Visible Quantities."—Proc. Royal Dublin Society, 1887.

"Curious Consequences of a well-known Dynamical Theorem."—Proc. Royal Dublin Society, 1887.

"On Texture in Media."—Proc. Royal Dublin Society, 1890.

"On the Limits of Vision and on the Vision of Insects."—Proc. Royal Dublin Society, 1894.

"Explanation of Spurious Double Lines in Spectra."—British Association Report, 1894.

"On the Kinetic Theory of Gases regarded as Illustrating Nature."—Proc. Royal Dublin Society, 1895.

"On Motions competent to produce Groups of Lines which have been observed in Spectra."—British Association Report, 1895.

"Evidence that Röntgen Rays are Ordinary Light."—Phil. Mag., 1898.

Many contributions to Astronomy, as:—

"Collimator for Adjusting Newtonian Telescopes."—British Association Report, 1856.

"On the Connection between Comets and Meteors."—Phil. Mag., 1867.

"On the Solar Eclipse of 1868."—Phil. Mag., 1867.

"On the Mounting of Specula."—Monthly Notices of Royal Astronomical Society.

"On a Movement designed to give Astronomical Accuracy to the Motions of Siderostats."—Monthly Notices of the Royal Astronomical Society.

"Lectures on Meteoric Astronomy before the Royal Dublin Society" (1870[1]) and the Royal Institution (1879 and 1897).

"On the Perturbations of the Leonids" (in conjunction with Dr. Downing).—Proc. Royal Society, 1899.

Other Papers on Meteoric Astronomy in the Monthly Notices of the Royal Astronomical Society.

And, what is, perhaps, Dr. Stoney's most valuable contribution to Physical Astronomy:—

"On the Physical Constitution of the Sun and Stars."—Proc. Royal Society, 1867.

This Report would be incomplete without mention of Dr.

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[1] See "Journal" of the Royal Dublin Society, vol. v., 1870.

Stoney's great personal influence on scientific advance in Ireland. The secret of this widespread influence is to be found in his perfectly disinterested enthusiasm for science. To the readers of his papers this enthusiasm is manifest in that "capacity for taking infinite pains" so often characteristic of genius. To those who have the privilege of knowing him, it appears in a never-failing and most infectious longing to take one step further into the unknown; and this circle of friends, be it said, is a large one, for his kindly and simple nature ever gladly extended its sympathy to every earnest endeavour.

The Report of the Science Committee was adopted by the Council on February 2nd, 1899.

The following Papers are published, or destined to be published, in the SCIENTIFIC TRANSACTIONS OF THE ROYAL DUBLIN SOCIETY, *Vol. VII., viz.:—*

I. A Determination of the Wave-lengths of the Principal Lines in the Spectrum of Gallium, showing their identity with two Lines in the Solar Spectrum. By W. N. HARTLEY, F.R.S., and HUGH RAMAGE, A.R.C.SC.I. (Plate I.)

II. Radiating Phenomena in a strong Magnetic Field. Part II.—Magnetic Perturbations of the Spectral Lines. By THOMAS PRESTON, M.A., D.SC., F.R.S.

III. An Estimate of the Geological Age of the Earth. By J. JOLY, M.A., B.A.I., D.SC., F.R.S., F.G.S., Honorary Secretary of the Royal Dublin Society; Professor of Geology and Mineralogy in the University of Dublin.

IV. On the Electric Conductivity and Magnetic Permeability of an extensive series of Steel Alloys. By W. F. BARRETT, F.R.S., W. BROWNE, B.SC., and R. A. HADFIELD. (Plates II. to IX.)

V. On some Novel Thermo-Electric Phenomena. By W. F. BARRETT, F.R.S., Professor of Experimental Physics in the Royal College of Science for Ireland. (Plate IXA.)

VI. Jamaican Actiniaria. Part II.—Stichodactylinæ and Zoantheæ. By J. E. DUERDEN, ASSOC. R.C.SC. (LOND.), Curator of the Museum of the Institute of Jamaica. (Plates X. to XV.)

VII. Survey of Fishing-grounds, West Coast of Ireland, 1890–1891. X.—Report on the Crustacea Schizopoda of Ireland. By ERNEST W. L. HOLT and W. I. BEAUMONT, B.A. (Cantab.). (Plate XVI.)

ERRATUM.

At p. 35, line 3 from bottom, and p. 36, lines 10, 12, and 14 from top, *for* "Loch" *read* "Lough."

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The copyright of Papers read becomes the property of the Society, and such as are considered suitable for the purpose will be printed with the least possible delay. Authors are requested to hand in their MS. and necessary Illustrations in a complete form, and ready for transmission to the Editor.

XV.

THE CARBONIC ANHYDRIDE OF THE ATMOSPHERE.

By PROFESSOR E. A. LETTS, D.Sc., Ph.D., and R. F. BLAKE, F.I.C., F.C.S.

(Plates XVI.-XVIII.)

[Read, Part I., June 22, 1898; Part II., April, 1899; Received for Publication July 7, 1899. Published March 9, 1900.]

[COMMUNICATED BY DR. W. E. ADENEY, F.I.C., F.C.S.]

PART I.

Section I.—Introduction and Methods of Determination.

The existence of carbonic anhydride in the air was first demonstrated by Dr. Black of Edinburgh, and probably between the dates 1752 and 1754.[1] In his Lectures we find the following statement concerning lime water[2]:—

"When this fluid is exposed to the open air, the particles of lime which are at the surface gradually attract fixed air which is mixed with the atmosphere. . . . In framing this theory I was necessarily led to perceive a distinction between the atmospheric air or the greater part of it, and that sort of air with which the alkaline substances are disposed to unite. It was plain that the lime of lime water, for example, is not disposed to unite with the whole mass of atmospherical air that happens to be confined with it or with every part of it equally. . . . The only circumstances in which lime water loses its qualities and throws up the lime to its upper surface are when we expose it to the open air or keep it in bottles that are left open. From this it was evident that the sort of air with which the lime is disposed to unite is a particular species which is mixed in a small

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[1] Preface to "Lectures on the Elements of Chemistry," by Joseph Black, M.D. Edinburgh, 1803. By John Robison, p. xxiii.

[2] Lectures, vol. ii., p. 74.

quantity only with the air of the atmosphere. To this particular species I gave the name of fixed air."[1]

The elder De Saussure[2] employed diluted lime water as a test for carbonic anhydride on the summit of Mont Blanc and the Col du Géant, and also detected the gas by a second method, viz. by means of strips of paper moistened with caustic potash solution, which after exposure to the air for about an hour and a half became dry and then gave a brisk effervescence with acids. He further states that he repeated the experiment with lime water on the seashore (the lake of Geneva?), and found that in the same time a thicker deposit of chalk was produced.

"The first chemists who have left us instructions concerning the investigation of atmospheric carbonic acid admit that free air, when washed with alkaline solutions in a eudiometric tube suffers a diminution in volume, which indicates, according to circumstances, one or two hundredths of carbonic acid; for, as they inform us, its proportion, as well as that of the oxygen, vary in different places."

The younger De Saussure[3] (Théodore), to whom the above statement is due, mentions the names of Fourcroy[4] and Humboldt[5] as the first chemists who sought to determine atmospheric carbonic anhydride. According to Blochmann,[6] Humboldt[7] initiated this

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[1] Thorpe (Chem. Soc. Journ., 5 [1867], p. 189) attributes Black's discovery to M'Bride of Dublin, in 1764, and the same statement has been made by others (Symons and Stephens, *ibid.* 69 [1896], p. 869); but this is incorrect, for Black tells us (Lectures, vol. ii., p. 88), "Some time after I had made and published, in my inaugural dissertation, the experiment you have seen, the attention of some other persons was excited, and keenly engaged with this new and interesting subject. The late Dr. M'Bride of Dublin began to attend to it, in consequence of some letters which I wrote to my friend Dr. Hutcheson, then lecturer on chemistry in Trinity College." Moreover, M'Bride himself ("Experimental Essays," p. 178) distinctly gives the credit of the discovery to Black, and does not appear to have made any experiments of his own to prove the presence of carbonic anhydride in air. He merely made use of lime-water as a test for that substance in the gases evolved from putrefying vegetable and animal matters.

[2] Horace Bénédict De Saussure, "Voyages dans les Alpes," 4 [1796], par. 2010.

[3] Théodore De Saussure, "Annales de Chimie et de Phys.," 44 [1830], p. 5.

[4] Fourcroy, "Syst. des Conn. Chim.," vol. i. [1801], p. 158.

[5] Humboldt, "Journ. de Phys.," 47 [1798], p. 202; "Gilbert's Annalen," 3 [1800], p. 77.

[6] Blochmann, "Liebig's Annalen," 237 [1887], p. 39.

[7] A. v. Humboldt, "Versuche über die chemische Zerlegung des Luftkreises," Brunswick, 1797.

method which was subsequently employed by Lewy[1] (1843–1850), De Luna[2] (1860), Frankland[3] (1861), and Macagno,[4] in spite of the fact that De Saussure, Thorpe, and others had pointed out that it was not capable of giving sufficiently accurate results with the minute quantities of carbonic anhydride present in air.

Thenard[5] appears to have been the first to devise a method giving fairly reliable and approximately accurate figures. This consisted in weighing the barium carbonate produced on allowing a known volume of air to remain in contact with baryta water, and because air contains so small a proportion of carbonic anhydride, he insisted that the volume of air thus treated must be considerable—the actual amount which he employed being no less than from 237–300 litres.

Théodore De Saussure[6] in his classic researches on atmospheric carbonic anhydride which extended over a period of more than twenty years made use of a somewhat similar method, of which the following are the essential particulars:—

A glass balloon of 35–45 litres capacity was employed, to the neck of which a copper ferrule was cemented provided with a stopcock. The balloon having been properly cleaned and dried, was exhausted by an air-pump, and the air to be examined slowly admitted. One hundred grms. of dilute baryta water (1 per cent.) previously saturated with barium carbonate, were next poured in through a long funnel, the balloon closed, and either agitated for an hour or left to itself during seven or eight days with occasional shaking. It was then again well shaken to distribute the barium carbonate throughout the liquid, and the mixture poured through a funnel into a stoppered bottle. The balloon was next rinsed out several times with water (saturated with barium carbonate) and the barium carbonate itself thoroughly washed by decantation. After this it was

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[1] Lewy, "Journ. f. prakt. Chem.," 30 [1843], p. 207.

[2] De Luna, "Estudios quimicos sobra el aire atmosferico." Madrid. 1860.

[3] Frankland, "Chem. Soc. Journ.," 13 [1860], p. 22.

[4] Macagno, "Chem. Centralblatt," 11 [1880], p. 225.

[5] Thenard, "Traité de Chimie," 5th ed., vol. i. [1813], p. 303.

[6] De Saussure, "Bibliothèque Univers. Sciences et Arts," 1 [1816], p. 124; also, "Annales de Chimie et de Phys.," 2 [1816; title-page date, 1830], p. 199; 3 [1816; title-page date, 1830], p. 170; 38 [1828], p. 411; 44 [1830], p. 5.

dissolved in dilute hydrochloric acid which had previously been employed for finally rinsing out the balloon (in order to dissolve any barium carbonate adhering to its sides). The solution was then precipitated with sodium sulphate and the resulting barium sulphate washed and dried on a sand bath. Throughout these operations no filter was used—all washings being by decantation.

To describe even in outline all the different processes which have been employed since De Saussure's time to determine atmospheric carbonic anhydride would not only be tedious but would scarcely serve any useful purpose. But, on the other hand, certain of these processes deserve notice, owing to the importance of the work performed by their aid. With the exception of one or two methods based on the physical properties of gases, such as absorption of heat,[1] rate of diffusion,[2] &c., all these processes depend in the first instance on the employment of an alkali or alkaline earth as absorbent; the amount of carbonic anhydride absorbed being arrived at subsequently by one or other of several methods, among which the more important are:—

(1.) Increase in the weight of the absorbing apparatus.
(2.) Determination of the excess of the absorbent.
(3.) Liberation and measurement of the absorbed carbonic anhydride.

Quite a number of observers have made use of the first method, which appears to have been inaugurated by C. Brunner[3]: his absorbing apparatus consisting of a tube filled partly with slaked lime, and partly with asbestos moistened with sulphuric acid to absorb any moisture which might be lost from the lime. Boussingault[4] employed pumice moistened with potash solution; Schlagintweit,[5] solid potash; Ch. Mène,[6] potash solution in Liebig's bulbs; Claësson,[7] barium hydrate.

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[1] Röntgen, "Ber. d. oberhessischen Ges. f. Natur. u. Heilkunde," 20 [1881] p. 52. Heine, "Wiedemann's Annalen," 16 [1882], p. 441.

[2] Schydlowski, "Zeitschr. f. anal. Chem.," 27 [1888], p. 720.

[3] Brunner, "Pogg. Annalen," 24 [1832], p. 569, and "Annales de Chimie et de Phys.," [3], 3 [1841], p. 305.

[4] Boussingault, "Annales de Chimie et de Phys.," [3], 10, [1844], p. 456.

[5] Schlagintweit, "Pogg. Annalen," 76 [1849], p. 446.

[6] Mène, "Compt. Rend.," 33 [1851], p. 39.

[7] Claësson, "Ber. d. deutsch. chem. Ges.," 9 [1876], p. 174.

"Hlasiwetz[1] had already shown experimentally the untrustworthy nature of Brunner's method. Apart from the fact that the quantity of carbonic anhydride to be determined was much too small in proportion to the bulky absorption vessels (whose surfaces Hlasiwetz estimated to amount to seven square metres) so that a sufficiently accurate weighing was impossible unless very large quantities of air were employed, Hlasiwetz demonstrated that the method of drying the air exercised an important influence on the determination. The sulphuric acid of the drying apparatus absorbs carbonic anhydride, a fact which the two Rogers[2] had already mentioned, and which had been traced quantitatively later by Setschenow.[3] Hlasiwetz condemned chloride of calcium after he had observed that silver solution is rendered turbid by air which had previously passed through a ten-foot tube containing it. Further he remarked that potash absorbs oxygen—a statement resting upon the authority of H. Rose. For pumice moistened with potash, this property was brought forward later by Reiset[4] who traced it to the presence of manganous and ferrous compounds in the pumice, and also experimentally verified by Müntz and Aubin,[5] who rejected on that account the methods involving direct weighing of the absorbing apparatus."[6]

Reiset,[7] whose work on the amount of atmospheric carbonic anhydride is most important, employed a portable laboratory containing an aspirator of 600 litres capacity, an absorbing apparatus, &c., which enabled him to make the determinations at the place where the air samples were collected. His method consisted in drawing the air first through a U tube containing pumice moistened with sulphuric acid (which enabled him to determine the moisture), then through an absorbing apparatus containing baryta water saturated with barium carbonate. In his earlier experiments the absorbing apparatus consisted of a train of three Geissler's potash bulbs, through which 600 litres of air passed in twelve hours, the completeness of the absorption being

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[1] Hlasiwetz, "Wien, Akad. Sitzber.," 20 [1856], p. 189.

[2] Rogers, "Amer. Journ. Science," [2], 5 [1848], p. 114.

[3] Setschenow, "Jahresber. f. Chem.," 29 [1876], p. 46.

[4] Reiset, "Annales de Chimie et de Phys.," [5], 26 [1882], p. 148.

[5] Müntz and Aubin, "Annales de Chimie et de Phys.," [5], 26 [1882], p. 228.

[6] Blochmann, *loc. cit.*

[7] Reiset, *loc. cit.*

indicated by the clearness of the fluid in the end bulbs nearest to the aspirator. Later he employed a different form of apparatus consisting of a tube half a metre long and about 4 cm. bore, containing three platinum plates shaped like the lid of a tin canister, but with flexible and slightly conical sides, causing them when pushed into the tube to retain their position; the lowest being at the bottom of the tube, the second at a distance of about 12 cm. above it, and the third at the same distance above the second. These plates were each perforated with 120 holes of $\frac{1}{2}$ mm. diameter. The tube with these plates in position was let into a wide-mouthed bottle provided with a second tubulure, and secured to its neck air-tight by a rubber collar. Above, the tube was closed by a cork through which a narrow tube passed communicating with a weighed U tube filled with pumice saturated with sulphuric acid. Into the wide tube 300 c.c. of baryta water were placed before each experiment.

The apparatus having been attached to the aspirator, air passed first through a weighed U tube containing pumice moistened with sulphuric acid, then through the second tubulure of the bottle containing the wide tube, and thence bubbled through the perforations of the platinum discs into the baryta water, which was thus divided into three portions, and the air very thoroughly washed. Finally it passed through the second drying tube, the increase in whose weight denoted the loss by evaporation of the baryta water (afterwards made good by adding distilled water to it). At the end of the experiment the contents of the wide tube were washed down into the bottle to which it was attached, with a known volume of distilled water—the mixture then syphoned off into a stoppered bottle, allowed to remain at rest for forty-eight hours until the barium carbonate had subsided, a portion then removed by means of a pipette into another bottle and there titrated with standard sulphuric acid (decinormal), with litmus as indicator.

Müntz and Aubin,[1] to whom we are also indebted for most valuable work on atmospheric carbonic anhydride, employed an entirely different method from Reiset's, the principle of which was to absorb the gas by a suitable medium, then to liberate it and to

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[1] Müntz and Aubin, "Annales de Chimie et de Phys.," [5], 26 [1882], p. 222.

measure its volume. This principle was originally suggested by H. Mangon, in 1875, to Tissandier,[1] who desired to investigate the upper regions of the air during balloon voyages, and was employed by the latter for the purpose, necessitating as it did only simple operations at the place of observation, and permitting the actual determinations to be made later in the laboratory. Müntz and Aubin employed as absorbing vessels, glass tubes about 90 cm. long and 2 cm. bore, drawn out at each end and filled with pumice moistened with strong caustic potash solution. A number of these tubes could be prepared on any convenient occasion, and when sealed up at their two ends were ready for use at any time. When a determination had to be made, the ends of a tube were broken off and a given volume of the air aspirated through it at a rate of about 3 litres per minute, the total volume being from 200–300 litres, after which the two ends of the tube were again sealed up.

The apparatus for liberating and measuring the absorbed carbonic anhydride was somewhat complicated, but the essential features were as follows:—The ends of the tubes having been broken off, one extremity was connected with a mercury pump and gas measuring apparatus and the other with a vessel containing dilute sulphuric acid, the junction with the latter being closed with a pinchcock. A vacuum having been established, acid was admitted into the tube (heated by a steam jacket), from which it flowed into a boiling flask connected with a Liebig's condenser, and the evolved carbonic anhydride, mixed with a little air, was drawn over into the measuring apparatus. Finally the actual volume of carbonic anhydride was determined by absorption with caustic potash.

Müntz and Aubin are among the very few observers who have tested their method by a blank experiment with a known quantity of carbonic anhydride. To do this they aspirated a definite volume of air freed from carbonic anhydride through a boiling flask containing acid, into which a measured volume of sodium carbonate solution of definite strength was gradually added—the experiment being so conducted that the resulting mixture of air and carbonic anhydride corresponded with ordinary "fresh" air. This

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[1] Tissandier, "Compt. Rend.," 80 [1875], p. 976.

mixture was then passed through one of their absorbing tubes, and the amount of absorbed carbonic anhydride eventually determined.

The result was 59·5 c.c. found as against 60·39 c.c. taken, or 98·5 per cent.

As a further check on the method, blank experiments were made with each series of the prepared absorbing tubes, one tube being taken from the beginning of the series, one from the middle, and one from the end, in order to determine any carbonic anhydride which their contents might contain. The average quantity thus found (amounting to about 1–1·2 c.c.) was deducted from the result of a determination. According to Müntz and Aubin it is to be traced to barium carbonate dissolved in the potash solution.[1] The great advantage of their method, in addition to its accuracy, is that the collection of samples does not require any special skill. The tubes can be preserved for an indefinite time before and after absorption, they can be readily transported, and eventually examined by a skilled experimenter. Hence, at the suggestion of Dumas, the method was employed by the expedition sent out to Central and South America by the French Academy of Sciences to observe the transit of Venus in 1882.[2]

Pettenkofer's process, from its simplicity, rapidity, and readiness with which it can be performed, is in one way still the standard method for determining atmospheric carbonic anhydride.

But as Angus Smith[3] says, "as with most other inventions its early and later years have not been spent in the same place. Dalton,"[4] he continues, "used a bottle filled with 102,400 grains (nearly 7 litres) of rain water," and says that "if it be emptied in the open air and 125 grains of strong lime water poured in, and the mouth then closed, by sufficient time and agitation, the whole of the lime water is just saturated by the acid gas it finds in that

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[1] This was specially prepared by dissolving 10 kilos. of caustic potash ("*potasse á la chaux*") in 14 kilos. water, adding 2 kilos. of barium hydrate, decanting the clear fluid, and further adding 200 grms. of barium hydrate.

[2] A method similar in principle to that of Müntz and Aubin was also employed by Lévy and Allaire at the meteorological observatory at Montsouris, at the suggestion of Marié-Davy, for daily determinations of atmospheric carbonic anhydride ("Compt. Rend.," 90 [1880], p. 32).

[3] "Air and Rain," [1872], p. 448.

[4] "Mem. Lit. and Phil. Soc. Manchester," [2], 1 [1805], p. 244. Paper read 1802.

volume of air. But 125 grains of the lime water used require 70 grain measures of carbonic acid to saturate it."

Later, Dalton appears to have employed a different method based on the same principle as Pettenkofer's, viz. absorption of the carbonic anhydride by a solution of an alkaline earth, and subsequent titration of the latter by a standard acid.

Hadfield,[1] a pupil of Dalton's who continued the latter's researches on atmospheric carbonic anhydride, gives the following particulars of the process:—

"Mr. Dalton considers a globe one-fifth the size[2] sufficiently ample, and uses lime water of a well-known strength instead of barytic, taking care to have more than enough to engage the acid gas; after the agitation and absorption the residue of lime water is poured out, and its reduced value is then ascertained, as it was before, by means of some test acid of known strength. Thus data are gained for the calculation of the carbonic acid engaged to the lime."

"In my investigations of this subject I have adopted Mr. Dalton's mode, and from December, 1828 to 1830, the experiments have been made in a glass bottle of a balloon shape of the capacity of 471 cubic inches (about 7¾ litres), fitted with a brass cap and stop-cock for the purpose. The experiments of the present year (1830) have been made in a larger bottle of the capacity of 498 cubic inches (about 8¼ litres). The method of filling the latter bottle with air was a little different from that of the former, for instead of filling the bottle with rain-water, as was the case with the first bottle to get the air in, the end of a bellows pipe was introduced into the latter and the air blown in."

Another of Dalton's pupils,[3] H. H. Watson, also worked on the same subject, and according to Blochmann, both he and Hadfield employed the same method of procedure, viz. after absorbing the carbonic anhydride with excess of lime water, they filtered and washed the precipitated chalk and titrated the excess of lime water

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[1] *Ibid.*, 6 [1842], p. 10.

[2] This refers to De Saussure's absorbing vessel, which Hadfield says had a capacity of one cubic foot or more.

[3] "Journ. f. prakt. Chem.," 6 [1835], p. 75; "Brit. Assoc. Reports," 3 [1834], p. 583. Communicated by Dalton.

in the filtrate and washings, with dilute sulphuric acid. (1 c.c. = 0·8 mgs. CO_2.)

These investigations of Dalton and his pupils were either not generally known or had been forgotten when Pettenkofer published his method in 1858[1]; and certainly he had no knowledge of them; but it is clear, from what has been said, that the principle of his method had been anticipated.

Pettenkofer employed glass flasks of from 3–3½ litres capacity, which, previous to a determination, were carefully cleaned and dried. To fill them with the air to be examined, a special form of bellows was employed with a tube attached to the inlet valve; the mouth of which tube was directed successively to all parts of the space from which the air was to be taken. From the bellows the air was driven through a glass tube to the bottom of the flask. As soon as the latter had been properly filled, it was closed by a rubber cap having two openings for the introduction of tubes. One of them was closed with a glass rod, the other with a kind of funnel tube, which entered the flask to a depth of about 2 inches. The upper part of the funnel-tube was a wider tube which could be closed by a cork.

30 c.c. of clear lime-water were next introduced into the flask through the funnel-tube from a pipette graduated for the purpose, and the funnel-tube closed with a cork. The flask was then agitated, so that the lime-water wetted the greater part of its surface, and the agitation continued for eight or ten minutes. Finally the excess of lime-water was determined with standard oxalic acid (1 c.c. = 1 mg. CaO), the acid being run directly into the flask from a burette, and the fluid tested from time to time with small strips of turmeric paper fastened to a stick, and passed through one of the openings in the rubber cap. The final point of neutralization was ascertained by removing portions of the liquid, and allowing them to drop on to turmeric paper.

Later Pettenkofer modified the process in some respects. A six-litre flask was employed instead of one of smaller capacity; baryta water was used as absorbing fluid instead of lime-water; and a period of two hours was allowed for absorption. After

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[1] "Abhandlungen der naturw.-tech. Commission bei der kgl. bayer. Akad. der Wissenschaften," 2 [1858], p. 1; also, "Chem. Soc. Journ.," 10 [1858], p. 292.

that interval a small narrow bottle was filled with the turbid absorbent, the barium carbonate allowed to subside, and an aliquot part of the clear liquid titrated with oxalic acid solution —1 c.c. = 1 mg. CO_2.

Pettenkofer pointed out that traces of caustic alkalies interfere with the delicacy of the titration, and recommended the addition of barium chloride to the baryta water, by which means barium hydrate and a corresponding quantity of alkaline chloride are formed, he says, and the delicacy of the reaction no longer interfered with.

. . . .

Since the introduction of Pettenkofer's process many modifications have been proposed and employed.

Angus Smith[1] in his work on air employed a confectioner's glass jar, instead of a flask, as absorbing vessel : the broad mouth of which permitted the hand to enter, so as to readily clean and dry the vessel ; and instead of blowing air into it he operated in the reverse manner, that is to say by extracting by means of a flexible bellow's pump, thus causing the air of the locality to enter in its place.

Schulze,[2] whose investigations on the amount of atmospheric carbonic anhydride extended over a considerable period, and are among the more important which have been made, modified the method of titration and introduction of the absorbent, so as to avoid access of breath or the air of the laboratory during the process. This he accomplished by binding a sheet of thin india-rubber over the mouth of the (4 litre) flask immediately after filling it with the air to be examined. This sheet was then pierced by the nozzle of the pipette delivering the baryta water and a second one bound on. After a suitable time for absorption, the latter was removed, and after the introduction through the pierced rubber sheet of a few drops of alcoholic turmeric solution, and about 25 c.c. of boiling water to wash down the baryta water adhering to the sides of the vessel—the nozzle of the burette was passed through the perforation, and the titration with (oxalic) acid proceeded with. Schulze controlled his results by parallel determinations with other methods.

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[1] "Air and Rain," p. 450.

[2] "Landw. Vers. Stat.," 9 [1867], p. 217 ; 14 [1871], p. 366.

Blochmann[1] was the first to suggest phenol-phthaleïn as indicator in Pettenkofer's process, and to that author we are also indebted for suggesting modifications in the latter, whereby several of its sources of error are avoided. In his very complete and valuable paper on the amount of carbonic anhydride in the air[2] the apparatus is fully described and figured. Here we can only indicate its essential features.

(1.) The bottle holding the stock of baryta water is permanently attached to a measuring pipette, and is so arranged that on withdrawing a portion of the fluid, its place is taken by air freed from carbonic anhydride. The titre of the solution is thus preserved.

(2.) The absorbing vessel is a clear glass bottle of a capacity of 5–6 litres closed by a glass stopper pierced with two holes, into which two glass tubes are ground. Both of these latter terminate externally in glass stopcocks, while within the bottle one reaches nearly to its bottom, the other barely passing through the stopper. To ensure air-tight junctions the space (purposely left) above the stopper in the neck of the bottle is filled with mercury, on to which a layer of paraffin wax is afterwards poured. These two tubes are employed for the ingress and egress of the air to be examined, and subsequently of the absorbing fluid also—the bottle being inverted for the removal of the latter.

(3). The titration of an aliquot portion of the absorbent (previously freed from barium carbonate by filtration through an asbestos plug) is performed *within* a burette of peculiar construction, so arranged that while its lower portion receives and measures off a charge of the fluid to be titrated, its upper part contains the standard acid (sulphuric), and communication between the two is established by a three-way cock. All contact with external air during the removal of fluid from the absorbing vessel and during the titration of the latter is avoided.

Lebedinzeff[3] more recently has taken up the subject, but as far as we can judge from the abstract of his work he has not introduced any important modifications into Pettenkofer's process. Following

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[1] "Ber. d. deutsch. chem. Ges.," 17 [1884], p. 1017.

[2] "Liebig's Annalen," 237 [1887], p. 39.

[3] "Zeitschr. f. anal. Chem.," 30 [1891], p. 267.

Blochmann, his store bottle for the baryta water and measuring pipette, form a closed system into which only purified air can enter. His absorbing vessel (7–12 litres capacity) is fitted with a hollow glass stopper carrying two stop-cocks. He, however, measures the baryta water into thin-walled pipettes (previously filled with purified air) which are then sealed. One of these tubes is placed in the absorbing vessel previous to filling it with the air to be examined. Air is then aspirated for a sufficient time, the stop-cocks closed, the baryta tube broken, and after shaking, the vessel is left for 24 hours. An aliquot portion of the clear fluid is then titrated with standard oxalic acid and phenol-phthaleïn as indicator, all due precautions being observed to avoid access of air containing carbonic anhydride during the process.

Section II.—The Authors' Experiments on Pettenkofer's Process as modified by them.

The experimental work we are about to describe originated in a set of determinations we had to make of carbonic anhydride in the air of a weaving shed in a linen factory at Belfast. For these determinations we employed a somewhat rough modification of Pettenkofer's process, in which the vessels serving for the collection of the air samples, the absorption of the carbonic anhydride, as well as for the subsequent titrations, were ordinary Winchester quart bottles of greenish-white glass. For the titration itself we used dilute hydrochloric acid, with phenol-phthaleïn as indicator.

Although no considerable degree of accuracy was necessary for the purpose we had in view in making the determinations, we were struck with the discrepancies in the results obtained with duplicate samples of air; and following the matter up we were gradually led into an inquiry regarding Pettenkofer's process, the extent of accuracy and delicacy of which it is capable, and the most suitable method of performing it and overcoming incidental errors.

We use the term "Pettenkofer's process" in a somewhat wide sense. The essence of the method we understand to be the enclosure of a relatively small volume of air in a glass vessel: the absorption of the carbonic anhydride by an alkaline fluid: and the subsequent titration of the excess of the latter with standard acid and a colour indicator.

As we have already said, the inception of the method was scarcely due to Pettenkofer, but yet his name has become so inseparably connected with it that no matter what modifications may have been introduced as regards the form of collecting vessel, the method of filling it with air, the nature and strength both of absorbing solution and standard acid, and the kind of colour indicator used, the process may still be properly spoken of as "Pettenkofer's."

Almost at the outset of our experiments a possible source of error suggested itself which it is true had been touched on by others, but did not appear to us to have been sufficiently investigated, viz. the action of the alkaline absorbent on the glass surface of the receiving vessel.

Preliminary experiments showed that very dilute baryta water exercised an appreciable action on glass, silica being dissolved and the titre of the solution affected.

Having satisfied ourselves on this point, it occrred to us that this source of error might be entirely avoided by coating the inner surface of the receiving vessels with a layer of some substance which the baryta could not act upon. Paraffin wax suggested itself as suitable for the purpose; and with receivers coated with that substance we at once obtained fairly satisfactory (*i.e.* concordant) results, as the following table shows:—

Series 1.—(Air.)

Determinations performed in paraffined bottles—which were also used as titrating vessels.

No. of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.	Capacity of Vessel.	Parts of CO_2 found in 10,000 of air.	Differences from mean.	Time of absorption.
1	70 c.c.	63·6 c.c.	0·64 c.c.	2570 c.c.	2·49	− 0·03	about 24 hrs.
2	,, ,,	63·7 ,,	0·63 ,,	2613 ,,	2·41	− 0·11	,,
3	50 ,,	43·4 ,,	0·66 ,,	2520 ,,	2·61	+ 0·09	4 hours.
4	,, ,,	43·6 ,,	0·64 ,,	2563 ,,	2·49	− 0·03	,,
5	,, ,,	43·6 ,,	0·64 ,,	2570 ,,	2·49	− 0·03	19 hours.
6	,, ,,	43·0 ,,	0·70 ,,	2613 ,,	2·67	+ 0·15	,,
				Mean =	2·52		

As our immediate object at this stage was only to ascertain to what extent agreement among the results was possible, with varying times for absorption, no corrections for temperature, pressure, &c., were made.

The receiving vessels were ordinary Winchester quart bottles of greenish-white glass, coated on the inside with paraffin wax. The absorbing solution was baryta water of the strength 1 c.c. = 0·1 c.c. CO_2 at N.T.P., the excess of which was afterwards titrated with dilute hydrochloric acid of corresponding strength, with phenol-phthaleïn as colour indicator.

Wishing, as we have said, to test the extent of the accuracy and delicacy of Pettenkofer's process, if carried out with all due precautions, we decided to experiment upon artificial mixtures of pure air and carbonic anhydride—the volume of the latter to correspond as nearly as possible with that usually present in "fresh" air, *i.e.* 3 in 10,000.

As regards the precautions we observed in the determinations, in addition to the specially prepared receiving vessels, we employed :—

(1). A stock bottle for the baryta water, coated on its inner surface with paraffin wax, and connected with a measuring pipette ; the whole forming a closed system, into which only purified air could enter.

(2). An apparatus for performing the titrations *in vacuo*, and for withdrawing the baryta water from the absorbing vessel in such a manner that access of carbonic anhydride from without was prevented.

(3). Burettes, for running in the acid, of special construction and very carefully graduated.

(4). Distilled water, free from all uncombined carbonic anhydride, for making up the standard solutions, and for washing out the receiving vessels.

Before passing to the actual determinations we made of carbonic anhydride both in artificial mixtures of that gas and purified air, and in ordinary air itself, it may be advisable to give some details regarding the above precautions.

Receiving Vessels.—These, as a rule, were ordinary Winchester quart bottles of greenish-white glass, coated with paraffin wax on their inner surface ; but occasionally we employed glass balloons of greater capacity, with the same coating. In practice we found it somewhat troublesome to coat the vessels properly, as a rather thick layer of the wax is necessary, or it becomes detached from the glass in course of time. This difficulty is avoided by proceeding as follows:—

Ordinary (white) paraffin wax is melted and allowed to cool until near its solidifying point. It is then poured into the *cold* vessel, and the latter rolled round until a uniform and sufficiently thick coating is obtained over all parts. A little practice is necessary to effect this properly, but the operation is not difficult.[1]

In our earlier determinations the titration of the excess of absorbent was performed, as we have said, within the receiving vessels, which were closed during the period of absorption by vaselined stoppers or india-rubber corks; but later, when the absorbent was drawn off into a vacuous vessel and there titrated, the receiving vessels were fitted as shown in the subjoined diagram.

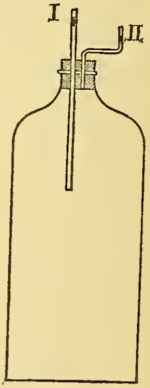

Fig. 1.
Paraffined Receiving Vessel.

Two glass tubes pass through either an india-rubber cork, or an ordinary cork well soaked in hot paraffin wax. These were closed when necessary by plugs, consisting of short glass rods attached to pieces of india-rubber tubing.

To fill one of these receivers with a sample of air, the method of exhaustion was employed, the operator being at a sufficient distance from the collecting area to avoid the possibility of breath contamination. For this purpose an air-pump, or rather exhausting syringe, was attached to one end of an india-rubber tube, about 12 feet long, while the other end of this tube was connected with I. or II. of the receiver. The pump removed about 200 c.c. of air at each stroke, and, as a rule, we gave 100 strokes in each filling, so that 20 litres of air passed through the receiver—a quantity we deemed more than sufficient to ensure complete displacement of that which was originally present by the

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[1] The receivers thus coated should be left for some time before their capacity is ascertained, otherwise, on filling with water for that purpose, the paraffin is liable to crack.

sample to be examined. The india-rubber tube was then removed and the receiver plugged.

Before adding the absorbent, the glass rod plugging I. was replaced by a soda-lime tube, the rubber junction being pinched between the finger and thumb during the operation, to prevent access of air. The rod attached to II. was then removed with the same precaution, and its rubber junction attached to the pipette for delivering the charge of baryta solution, which latter was then run in. The glass rods were then replaced with the same precautions as before, to prevent access of air; the receiver shaken with a rolling motion, so as to thoroughly wet all parts of its inner surface, and left on its side for some hours.

It may be mentioned that the capacity of the receiver was ascertained by measuring the volume of water required to fill both it and the attached tubes, and that it was of course necessary to subtract from this volume that of the absorbing solution added, in making the calculation of the amount of carbonic anhydride present in the air. It is scarcely necessary to add, that a reading of barometer and thermometer was made at the time of collecting the air sample.

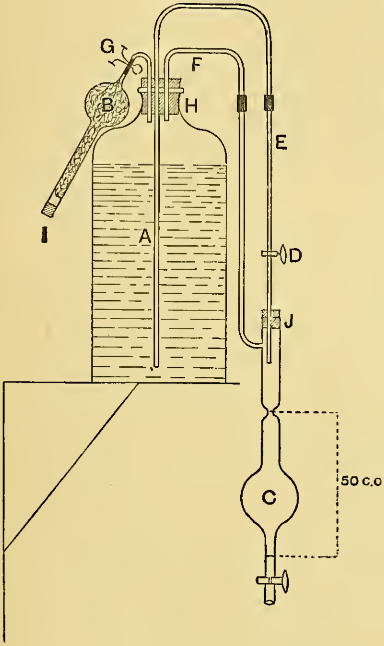

Fig. 2.—Baryta Stock Bottle.

A.—Paraffined bottle containing the baryta solution.
B.—Soda-lime tube.
C.—Pipette holding 50 c.c.
D.—Glass stop-cock connecting the syphon *E* with the pipette *C.*
F.—Air-tube.
G.—Pinch-cock.
H. I. J.—India-rubber corks.

Baryta stock-bottle and measuring pipette.—The stock-bottle for holding the supply of standard baryta solution contained about 1 litre, and was coated on the inside with paraffin wax in precisely the same way as the receivers—so also was the lower part of the glass siphon tube. Figure 2 (p. 123) explains the arrangement attached to it, for drawing off a charge of 50 c.c. in such a way that the air taking its place was first freed from carbonic anhydride. The mode of using the apparatus will be apparent at a glance. The stock of solution having been introduced into *A* and its rubber-cork *H*, and all attachments fastened in, the corks *I* and *J* (also of indiarubber) are removed, and the siphon tube *E* filled with the solution by suction. The pinch-cock *G* is now attached, and the cork *J* fastened in the position shown. Before filling the pipette *C* with a charge of the solution, we usually washed it out with a little of the liquid. The use of the soda lime tube *B* is obvious during the charging operation. It is of course corked when the apparatus is not in use, and also closed at the other end by the pinchcock *G*. The whole apparatus is conveniently kept on a somewhat high shelf.

The standard solutions.—These were made as dilute as was compatible with the delicacy of the colour indicator employed in the titrations. In all our determinations the indicator used was phenol-phthaleïn, as in addition to its extreme delicacy, it possesses another important advantage, viz. that the colour effect to be observed is no mere change of tint (as is the case with turmeric, litmus, methyl orange, &c.), but the production of colour in a colourless solution, or *vice versâ*. Hence this indicator is characterized by its sharpness. By employing acid and alkaline solutions of equivalent strength, and made so that 1 c.c. of either corresponded with 0·1 c.c. carbonic anhydride at N.T.P. and by only using a small quantity of phenol-phthaleïn, we found that the "end" reaction required an addition of less than $\frac{1}{10}$ c.c. This end reaction was, in our determinations, the final disappearance of the faint pink colour which remained when the baryta had been nearly neutralized by acid. As the total quantity of carbonic anhydride to be determined was usually about 1 c.c., it is obvious from the above that the limit of accuracy in titrations with solutions of the above strength was about $\frac{1}{100}$ c.c. of carbonic anhydride or 1 per cent. of the total amount to be determined.

Experience has shown us that these solutions are very suitable for the determinations as we conduct them, and they were employed in most of our experiments; but in a few cases where the extreme of accuracy was aimed at they were diluted to one quarter of the strength.[1]

The starting-point for the preparation of both the alkaline and acid standard solutions was decinormal hydrochloric acid, standardized with great care.

89·6 c.c. of this, when diluted with *pure* water to one litre, give a solution of which 1 c.c. = 0·1 c.c. CO_2 at N. T. P.[2]

To prepare the baryta solution, recrystallized barium hydrate was dissolved in distilled water and the solution filtered and diluted, or possibly strengthened finally, until a stock was obtained which was clear and exactly corresponded volume for volume with the acid. The preparation is easy to describe but is tedious to execute.

Titrating vessels.—In order to guard against the error arising from access of air, and especially of air charged with carbonic anhydride from the breath, we performed all the titrations except in our earlier experiments in vacuous vessels. These have the

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[1] Pettenkofer employed, in his earlier determinations ("Chem. Soc. Journ.," 10 [1858], p. 292), lime-water as absorbent, and titrated it with standard oxalic acid of the strength 1 c.c. = 1 mg. CaO., which is equivalent to about 0·4 c.c. CO_2 at N.T.P. The lime-water did not exactly correspond with the oxalic acid solution—30 c.c. of the former being equivalent to from 34–38 c.c. of the latter. He tells us that the turmeric paper (which he always used as indicator) "is so delicate that the addition of 4–6 drops of lime-water to the neutralized liquid is sufficient to reproduce this alkaline reaction." This quantity is equivalent to from 0·2–0·3 c.c., which would correspond with about 0·1 c.c. CO_2.

We have arrived at a similar result as regards the relative delicacy of phenol-phthaleïn and turmeric paper as indicators by independent experiments. The turmeric paper was prepared according to Pettenkofer's directions, *i.e.* by first washing turmeric with successive quantities of cold water, then extracting with alcohol, soaking pure filter paper in the extract, and allowing it to dry in the dark. Such paper is much more sensitive than ordinary turmeric paper, faint alkalinity being indicated when a drop of fluid is allowed to spread on it, by a transient brown ring, which rapidly disappears. Its delicacy, as compared with phenol-phthaleïn, was tested as follows:—

50 c.c. of distilled water, known to contain no free carbonic anhydride, and to be neutral, were placed in a flask, and the weak baryta (1 c.c. = 0.1 c.c. CO_2) added from a narrow burette, until the mixture showed an alkaline reaction with the turmeric paper. The point was somewhat uncertain; but independent experiments made by each of us gave from 0·4–0·5 c.c. as the quantity of baryta necessary.

To another 50 c.c. of the water in the same flask a droplet of phenol-phthaleïn was added, and the baryta solution run in until a distinct pink colour appeared. This required 0·05 c.c.

Phenol-phthaleïn is therefore from eight to ten times as sensitive as turmeric.

[2] Ordinary distilled water is by no means pure as regards carbonic anhydride. This

additional advantage that their use greatly facilitates the withdrawal of the charge of absorbent from the receivers, and also of the water employed subsequently to wash them out, in cases where that method was employed. Two different forms of these vessels were used at different times. The construction of one of them is shown in fig. 3. It was the one first used, and was intended not only for performing the titrations *in vacuo* with an aliquot part of the absorbent, but also for filtering the latter from barium carbonate. In using it, the space between *E* and *C* was first rendered vacuous by attachment of *E* to an air-pump and the two taps closed. The upper end *A* was next attached to the rubber junction II. of the receiver (the latter being clamped in an inverted position to a retort stand), and the stopcock *C* slowly opened, when the absorbent was drawn out of the receiver through the asbestos plug at *B*, serving as a filter, and thence into the measuring bulb *D*. When exactly 35 c.c. of clear fluid had thus been obtained, *C* was closed, the vessel inverted, and the burette attached to *E* by an india-rubber junction, both the end of *E* and the junction being first filled with the standard acid. In performing the operation both the vessel and burette were clamped to a retort-stand. The burette was then filled up to the zero-mark with acid, and the titration performed by opening *E*.

Fig. 3.
No. 1 Titrating vessel.

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is probably now well known, but it does not seem to have been taken into account by most of our predecessors in the subject under consideration.

We have found the following amounts in different samples of freshly-prepared distilled water used in the chemical laboratory of the Queen's College, Belfast:—

(1)	contained	2·475	c.c. CO_2	at N. T. P.	per litre.
(2)	,,	3·090	,,	,,	,,
(3)	,,	3·706	,,	,,	,,
(4)	,,	5·703	,,	,,	,,

The magnitude of the error which might thus be introduced into the determination

We eventually discarded filtration, which did not yield satisfactory results,[1] and employed a simpler form of vacuous vessel. We also titrated the whole of the absorbent, and not an aliquot part, and rinsed out the receiver with water free from uncombined carbonic anhydride. The construction of the apparatus shown in fig. 4 needs no special description, and the way in which it is used will be apparent from what has been said regarding the first vessel.

After it has been exhausted and the stopcock closed, the tube *B* is attached by its rubber junction to the tube II of the inverted receiver clamped to a retort-stand. A soda-lime tube having been attached to the tube I, the absorbent is withdrawn by cautiously opening the stopcock, care being taken that no air follows it before the stopcock is closed.

To rinse out the receiver and collect the rinsings in the titrating vessel the manipulation is as follows:—The titrating vessel is first removed and the glass rod plug substituted for it. The receiver is then unclamped and placed upright on a table. The nozzle of a measuring pipette filled with water free from carbonic anhydride is now inserted in place of the glass rod plug attached to II and the stopcock attached to this pipette opened, when water flows into the receiver. When sufficient has been added the pipette is removed and the glass rod plug attached. The receiver is then rolled round so that all parts of its inner surface are well washed, when it is once more inverted and the

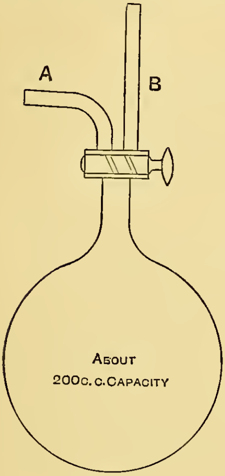

Fig. 4.

No. 2 Titrating vessel.

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when ordinary distilled water is used either for washing out the receiving vessels or in preparing the standard acid is therefore considerable.

The only reliable method for avoiding this source of error is to neutralize the distilled water with dilute baryta. Redistillation of water, even from an alkaline solution, does not give at any period of the distillation a distillate free from carbonic anhydride, owing to absorption of that gas from the atmosphere. Mr. W. Caldwell has, at our suggestion, investigated the amount thus absorbed, and, on an average, has found 0·5 to 0·6 c.c. of the gas at N.T.P. per litre of water.

[1] Possibly the asbestos absorbed baryta. That filter-paper does so has been proved by both Müller and Reiset.

wash-water drawn off into the titrating vessel in the same way as the absorbent. In most of our experiments the rinsing was repeated twice, but not more than 50 c.c. of water were used altogether. It should be added that during the removal of the glass rods plugging I and II, and their replacement by the soda-lime tube and titrating vessel respectively, or *vice versâ*, the rubber junctions were pinched between the finger and thumb to prevent access of air.

Fig. 5.
Burette.

Burettes.—In some of our earlier experiments ordinary burettes reading to $\frac{1}{20}$ c.c. were employed, but in the later series, where great accuracy was aimed at, special burettes were used of the form shown in the figure.

They were graduated only at the lower and narrow extremity, so that very accurate readings could be made of volumes of acid from 37–44 c.c. As we invariably used the same quantity of barium hydrate solution in all our later determinations, viz. 50 c.c., and the receiving vessels contained from $2\frac{1}{2}$ to about 3 litres, the quantity of acid required was always well within the above limits, where fresh air was concerned, or the corresponding artificial mixture. In a few of the later experiments, however, where more dilute solutions were used, or larger receiving vessels, another burette of similar construction was employed with a range of graduation from 27–40 c.c.

In our experiments with artificial mixtures of air and carbonic anhydride, it was necessary in the first place to remove the carbonic anhydride from ordinary air. This was done by precisely the same method as that employed in making an actual determination, *i.e.* by adding 50 c.c. of the standard baryta solution to a receiving vessel full of air: plugging the tubes, and after agitation allowing the vessel to remain at rest for about twelve hours. At the end of this time it was clamped in an inverted position to a tall retort stand, and the soda-lime tube and pinchcock attached to tube I, while the vacuous titrating vessel was attached to II. The absorbent was now drawn off, and the receiver washed out twice in succession with small quantities of neutralized distilled water—

due precautions being observed to prevent access of air during the operation. At first we thought this washing to be unnecessary, for owing to the greasy nature of the surface of the paraffin wax, only droplets of the absorbent remain behind. The extent of the error thus introduced is shown in Series 4, p. 133, compared with subsequent Series.

The receiver now contained air free from carbonic anhydride, and it was next charged with a definite volume of that gas—the operation being performed with the apparatus figured on following page.

By raising the reservoir *E* of the apparatus, and turning the stop-cock *C*, the measuring pipette *H*, and the tube *K* were completely filled with mercury (the cock *J* of the manometer tube being closed meanwhile). The receiver of purified air, clamped in an inverted position as shown, was next brought over *K*, and the latter attached to it by the rubber junction which with the short glass rod had served to plug the tube I. During the attachment and previous removal of the glass rod, the rubber tube was pinched between the finger and thumb to prevent entrance of the external air. *E* was next lowered so as to produce a vacuum in *H* and *F*, the tap *C* turned so that *A* communicated with *H*, and a stream of carbonic anhydride flowed into the apparatus. The pinchcock *G* was now opened, and a stream of gas allowed to flow into *I*, which contained strong caustic potash solution, and indicated eventually by the complete absorption of the bubbles that all air had been displaced from *A*, and that the measuring pipette *H* was full of pure carbonic anhydride. The stop-cock *C* was then closed and *E* raised, so that mercury flowed into *H* and *F*, and past *G*, which was closed. The stop-cock *J* of the manometer tube was next opened, and the stop-cock *C* and reservoir *E* so manipulated that a definite volume (usually 1 c.c.) of carbonic anhydride was enclosed in the measuring pipette at the existing atmospheric temperature and pressure—with due allowance for the capillary rise of mercury in its lower extremity.

A note having been taken of this volume as well as of the barometric height, and temperature of the air (as indicated by a thermometer placed in the neighbourhood of *H*), the stop-cock *J* was closed, the reservoir *E* raised, and *C* turned, so that the measured volume of carbonic anhydride passed slowly into the

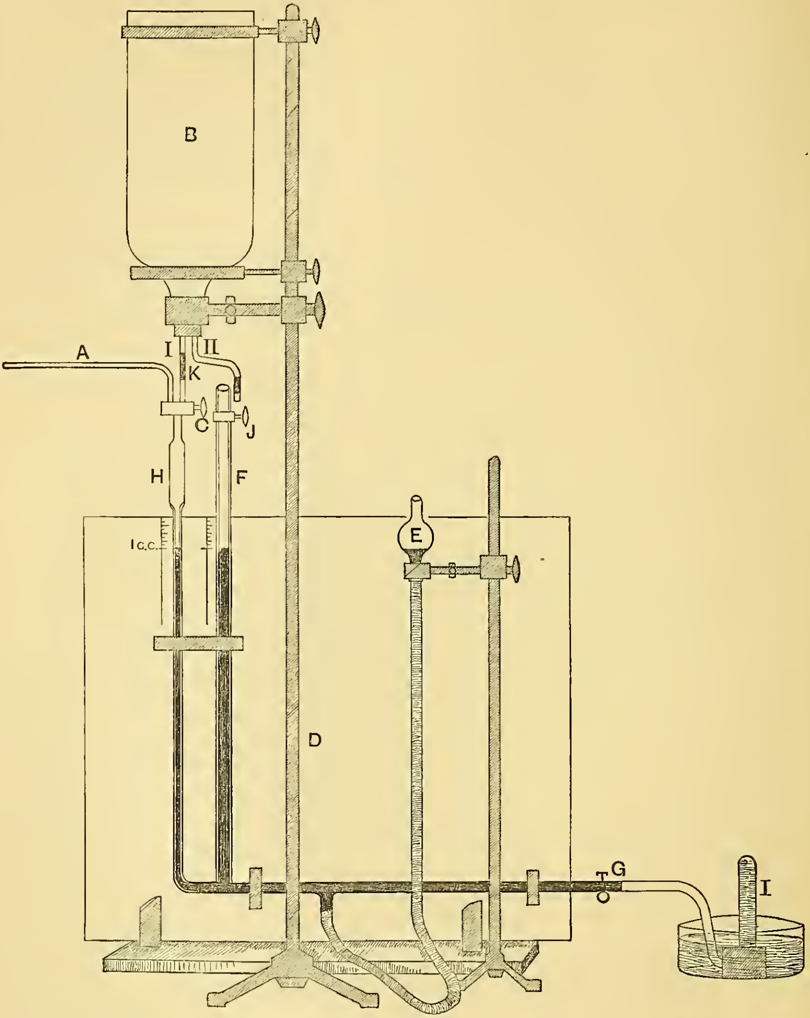

Fig. 6.

A. India-rubber tube leading to reservoir of dry carbonic anhydride.

B. Receiving vessel, containing air freed from carbonic anhydride.

C. Stop-cock, by turning which either *A* or *B* can be made to communicate with *H*.

D. Board fixed vertically on a stand, to which the gas pipette *H* and manometer *F* are attached.

E. Reservoir of mercury, which can be raised or lowered.

F. Manometer tube.

G. Pinchcock.

H. Pipette for measuring the carbonic anhydride, the lower part graduated into thousandths of a c.c. above and below the 1 c.c. mark.

I. Inverted vessel of caustic potash solution, for ascertaining when all air had been displaced from the apparatus by carbonic anhydride.

J. Stop-cock of manometer tube.

receiver, and the tube *K* was filled with mercury, when *C* was closed.

After an interval of about twenty-four hours to ensure diffusion of the carbonic anhydride into the air of the receiver, the rubber junction attached to I was pinched between the finger and thumb—removed from the measuring pipette by raising the receiver, and plugged with a glass rod. The receiver was then unclamped, and placed upright on a table. To add the charge of absorbent was somewhat troublesome.[1] For this purpose the glass rod plug was removed from the rubber junction attached to II (the junction being pinched during the operation), and in its place the nozzle of the measuring pipette containing the baryta solution introduced. The receiver was then held in a slanting position (to avoid drops of the absorbent running down I), and the charge allowed to run in. The india-rubber junction was then carefully pinched, while the nozzle of the measuring pipette was removed, and the glass rod plug inserted. The determination was then proceeded with, as already described, for the examination of a sample of ordinary air.

The following series of determinations of carbonic anhydride, both in artificial mixtures of purified air and that gas, and of air itself are given in chronological order.

Unless otherwise stated the solutions were of the strength 1 c.c. = 0·1 c.c. CO_2 at N. T. P. Hence the "carbon anhydride found" was obtained by subtracting the volume of acid required from that of the baryta solution originally taken, and dividing the difference by 10.

In the first of the series, with artificial mixtures, the capacity of the receivers is not given, as our aim was only to determine the actual volume of carbonic anhydride, while in the later series we sought also to ascertain the proportion of the gas in 10,000 volumes of air, in order to compare the results with those of the determinations made with air itself.

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[1] In some of the earlier determinations the absorbent was added to the receiver of purified air before adding the measured volume of carbonic anhydride: but, later, the method was abandoned, as it did not represent exactly the conditions met with in a determination with ordinary air.

SERIES 2.—(ARTIFICIAL MIXTURES).

Paraffined Winchester Quarts containing purified air and known volumes of carbonic anhydride. Titrations performed within the bottles.

Barometer = 758 mm. T. = 20° C.

1 c.c. CO_2 added = 0·929 c.c. at N. T. P.

No. of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.
1	50 c.c.	40·00 c.c.	1·000 c.c.
2	,, ,,	40·30 ,,	0·970 ,,
3	,, ,,	41·70 ,,	0·830 ,,
4	,, ,,	40·57 ,,	0·943 ,,

Carbonic anhydride taken, . . = 0·929 c.c.
,, ,, found (mean), . = 0·936 ,,
Error (mean), . . = + 0·007 ,,

SERIES 3.—(ARTIFICIAL MIXTURES).

Paraffined Winchester Quarts containing purified air and known volumes of carbonic anhydride. Titrations performed in vacuum apparatus, No. 1, with a portion only of the baryta solution, but without filtration.

0·935 c.c. CO_2 added at N. T. P.

No. of Experiment.	Baryta solution added.	Baryta solution titrated.	Acid required.	Acid calculated as being required for 50 c.c. of baryta.	Carbonic anhydride found.
1	50 c.c.	35 c.c.	29·30 c.c.	1·86 c.c.	0·814 c.c.
2	,,	,,	28·65 ,,	40·93 ,,	0·907 ,,
3	,,	,,	28·70 ,,	41·00 ,,	0·900 ,,
4	,,	,,	28·55 ,,	40·78 ,,	0·922 ,,
5	,,	,,	28·70 ,,	41·00 ,,	0·900 ,,
6	,,	,,	29·20 ,,	41·71 ,,	0·829 ,,

Carbonic anhydride taken, . . = 0·935 c.c.
,, ,, found (mean), . = 0·879 ,,
Error (mean), . . = – 0·056 ,,

SERIES 4.—(ARTIFICIAL MIXTURES).

Paraffined Winchester Quarts containing purified air and known volumes of carbonic anhydride. Titrations performed in vacuum apparatus No. 2 with the whole of the solution—sucked out as far as possible—but the receivers were not washed out.

0·935 c.c. CO_2 added at N. T. P.

No. of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.
1	50 c.c.	39·00 c.c.	1·100 c.c.
2	,,	40·90 ,,	0·910 ,,
3	,,	41·00 ,,	0·900 ,,
4	,,	41·90 ,,	0·810 ,,
5	,,	41·50 ,,	0·850 ,,
6	,,	41·00 ,,	0·900 ,,

Carbonic anhydride taken, . . = 0·935 c.c.
,, ,, found (mean), . = 0·911 ,,
Error (mean), . . = − 0·024 ,,

SERIES 5.—(ARTIFICIAL MIXTURES).

Paraffined Winchester Quarts containing purified air and known volumes of carbonic anhydride. Titrations performed in vacuum apparatus No. 2. Receivers washed out with about 50 c.c. of neutralized distilled water, the washings being added to contents of vacuum apparatus.

Barometer = 763 mm. T. = 20° C. 1 c.c. CO_2 added = 0·935 c.c. at N. T. P.

No. of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.
1	50 c.c.	40·40 c.c.	0·960
2	,, ,,	40·40 ,,	0·960
3	,, ,,	40·00 ,,	1·000
4	,, ,,	40·50 ,,	0·950
5	,, ,,	Spoilt.	—
6	,, ,,	40·55 ,,	0·945

Carbonic anhydride taken, . . = 0·935 c.c.
,, ,, found (mean), . = 0·963 ,,
Error (mean), . . . = + 0·025 ,,

Series 6.—(Artificial Mixtures).

Paraffined Winchester Quarts containing purified air and known volumes of carbonic anhydride. All operations as in Series 5, but with the greatest possible care.

Barometer = 759 mm. T. = 21° C. 1 c.c. CO_2 added = 0·927 c.c. at N.T. P.

No. of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.	Capacity of receiver.	Parts of CO_2 added in 10,000 of air.	Parts of CO_2 found in 10,000 of air.	Error in parts per 10,000.
1	50 c.c.	40·80 c.c.	0·920 c.c.	2589 c.c.	3·58	3·55	– 0·03
2	,, ,,	40·90 ,,	0·910 ,,	2598 ,,	3·56	3·50	– 0·06
3	,, ,,	40·90 ,,	0·910 ,,	2614 ,,	3·54	3·48	– 0·06
4	,, ,,	40·80 ,,	0·920 ,,	2942 ,,	3·15	3·12	– 0·03
5	,, ,,	40·80 ,,	0·920 ,,	3010 ,,	3·08	3·05	– 0·03
6	,, ,,	spoilt.	—	2656 ,,	—	—	—

The results of this last series may be summoned up as follows:—

Carbonic anhydride taken, ... = 0·927 c.c.
,, ,, found (mean), ... = 0·916 ,,
Error (mean), ... – 0·011 ,,

Mean error in parts per 10,000 of air taken, . . . = – 0·04 ,,
Greatest ,, ,, ,, . . . = – 0·07 ,,
Least, ,, ,, ,, . . . – 0·02 ,,

In the following series of determinations of carbonic anhydride in air, paraffined receivers were also employed with the same titrating vessels, burettes, etc., as were employed in the experiments with artificial mixtures.

The first of this series (No. 7) was made merely for the purpose of comparing the differences in the amount of carbonic anhydride found in parts per 10,000 of air under the same conditions of experiment, and no corrections for temperature and pressure were made. In the series which follow, these corrections were made, and the proportion of carbonic anhydride in air at N. T. P. are given.

SERIES 7.—(AIR).

Determinations of carbonic anhydride in air collected in the grounds of Queen's College, Belfast. Weather fine, but gusty.

No. of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.	Capacity of receiver.	Parts of CO_2 found in 10,000 of air.	Differences from mean.
1	50 c.c.	42·25 c.c.	0·775 c.c.	2539 c.c.	3·052	− 0·121
2	,, ,,	42·00 ,,	0·800 ,,	2548 ,,	3·139	− 0·034
3	,, ,,	42·10 ,,	0·790 ,,	2564 ,,	3·081	− 0·092
4	,, ,,	40·65 ,,	0·935 ,,	2892 ,,	3·233	+ 0·060
5	,, ,,	40·25 ,,	0·975 ,,	2960 ,,	3·293	+ 0·120
6	,, ,,	41·55 ,,	0·845 ,,	2606 ,,	3·242	+ 0·069
				Mean	= 3·171	

[SERIES 8.—(AIR).

Series 8.—(Air).

Determinations of carbonic anhydride in air collected in a large unused room in Queen's College, Belfast, with open windows and free circulation.

Barometer = 740 mm. Temperature = 17° C.

Number of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.	Capacity of Receiver.	Without correction for moisture.			With correction for moisture.		
					Volume of air in receiver at N. T. P.	Parts of CO_2 found in 10,000 of air.	Differences from mean.	Volume of air in receiver at N. T. P.	Parts of CO_2 found in 10,000 of air.	Differences from mean.
1	50 c.c.	42·05 c.c.	0·795 c.c.	2539 c.c.	2327·2 c.c.	3·416	– 0·114	2282 c.c.	3·483	– 0·116
2	,, ,,	41·75 ,,	0·825 ,,	2548 ,,	2335·5 ,,	3·532	+ 0·002	2290 ,,	3·602	+ 0·003
3	,, ,,	41·70 ,,	0·830 ,,	2564 ,,	2350·1 ,,	3·531	+ 0·001	2302·8 ,,	3·601	+ 0·002
4	,, ,,	40·40 ,,	0·960 ,,	2892 ,,	2650·8 ,,	3·621	+ 0·091	2599·2 ,,	3·692	+ 0·093
5	,, ,,	40·50 ,,	0·950 ,,	2960 ,,	2713·1 ,,	3·501	– 0·029	2660·3 ,,	3·570	– 0·029
6	,, ,,	41·45 ,,	0·855 ,,	2606 ,,	2388·6 ,,	3·579	+ 0·049	2342·2 ,,	3·650	+ 0·051
					Mean	= 3·530		Mean	= 3·599	

Mean result, with correction for moisture, ... 3·599
,, ,, without ,, ,, ,, ... 3·530

Difference, . . . 0·069

SERIES 9.—(AIR).

Same as Series 8, but on a different day. New baryta solution was used, 1 c.c. = 0·025 c.c. CO_2, and corresponding solution of acid, also a new burette of narrow bore, graduated for 24 c.c.

Barometer = 756 mm. T. = 18° C.

No. of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.	Capacity of receiver.	Volume of air in receiver at N. T. P.	Parts of CO_2 found in 10,000 of air.	Differences from mean.
1	50 c.c.	15·375 c.c.	0·8656 c.c.	2539 c.c.	2369·4	3·653	– 0·019
2	,, ,,	14·625 ,,	0·8844 ,,	2548 ,,	2377·8	3·719	+ 0·047
3	,, ,,	14·750 ,,	0·8812 ,,	2564 ,,	2392·7	3·682	+ 0·010
4	,, ,,	11·250 ,,	0·9687 ,,	2892 ,,	2698·8	3·589	– 0·083
5	,, ,,	9·500 ,,	1·0125 ,,	2960 ,,	2762·2	3·665	– 0·007
6	,, ,,	13·750 ,,	0·9062 ,,	2606 ,,	2431·9	3·726	– 0·054
					Mean	= 3·672	

Mean, with correction for moisture, ... 3·747
,, without ,, ,, ... 3·672

Difference, . . . 0·075

SERIES 10.—(AIR).

Same as Series 9, but on a different day. Barometer = 756 mm. T. = 18° C.

No. of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.	Capacity of receiver.	Volume of air in receiver at N. T. P.	Parts of CO_2 found in 10,000 of air.	Differences from mean.
1	50 c.c.	Spoilt.	—	—	—	—	—
2	,, ,,	17·313 c.c.	0·8172 c.c.	2548 c.c.	2377·8	3·436	+ 0·017
3	,, ,,	17·250 ,,	0·8187 ,,	2564 ,,	2392·7	3·421	+ 0·002
4	,, ,,	13·563 ,,	0·9109 ,,	2892 ,,	2698·8	3·375	– 0·044
5	,, ,,	11·938 ,,	0·9515 ,,	2960 ,,	2762·2	3·444	+ 0·024
6	,, ,,	14·813 ,,	0·8797 ,,	2606 ,,	2431·9	spoilt.	—
					Mean	= 3·419	

Mean, with correction for moisture, ... 3·491
,, without ,, ,, ... 3·419

Difference, . . ·072

SERIES 11.—(AIR).

Same as Series 9 and 10, but with the stronger baryta solution (1 c.c. = 0·1 c.c. CO_2 at N. T. P.) and a different burette.

Barometer = 752 mm. T. = 17° C.

No. of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.	Capacity of receiver.	Volume of air in receiver at N. T. P.	Parts of CO_2 found in 10,000 of air.	Differences from mean.
1	50 c.c.	42·25 c.c.	0·775 c.c.	2539 c.c.	2365·0 c.c.	3·276	− 0·031
2	,, ,,	42·10 ,,	0·790 ,,	2548 ,,	2373·3 ,,	3·328	+ 0·021
3	,, ,,	42·10 ,,	0·790 ,,	2564 ,,	2388·2 ,,	3·307	− 0·000
4	,, ,,	41·00 ,,	0·900 ,,	2892 ,,	2693·8 ,,	3·341	+ 0·034
5	,, ,,	40·95 ,,	0·905 ,,	2960 ,,	2757·1 ,,	3·282	− 0·025
					Mean	= 3·307	

Mean, with correction for moisture, . . . 3·370

,, without ,, ,, . . . 3·307

Difference, . . . ·063

SERIES 12.—(AIR).

Same as Series 11, but on a different day. The receivers were, however, large paraffined flasks.

Barometer = 759 mm. T. = 19° C.

No. of Experiment.	Baryta solution added.	Acid required.	Carbonic anhydride found.	Capacity of receiver.	Volume of air in receiver at N. T. P.	Parts of CO_2 found in 10,000 of air.	Difference.
1	50 c.c.	33·38 c.c.	1·662 c.c.	5345 c.c.	4990·6 c.c.	3·330	0·030
2	,, ,,	33·23 ,,	1·677 ,,	5442 ,,	5081·2 ,,	3·300	
WITH CORRECTION FOR MOISTURE.							
1	—	—	—	—	4883·4 c.c.	3·397	0·025
2	—	—	—	—	4972·0 ,,	3·372	

The preceding results—and especially those made with artificial mixtures—show, we venture to think, that Pettenkofer's method, if carried out with the precautions we have described, is one of greater accuracy and delicacy than is generally supposed.

Although smaller receiving vessels were employed than were used by Pettenkofer himself, and by most of the observers who have since used the method—the results obtained by us vie in point of accuracy with those obtained by the elaborate and tedious methods of Reiset, and Müntz and Aubin, in which *hundreds* of litres of air were operated on.

As regards the degree of absolute accuracy very few observers appear to have tested the point in the various methods which they have used, so that it is difficult to compare our results with analogous figures obtained by others.

Müntz and Aubin, as we have already stated, are an exception to this rule, as they describe one experiment on similar, but not exactly the same, lines as our own, in which they found 98·5 per cent. of the added carbonic anhydride, or in parts per 10,000, 2·98 instead of 3·03 (see p. 113).

A word ought, perhaps, to be said regarding the correction for aqueous vapour present in air. Probably from the minuteness of such a correction (relative to the magnitude of the incidental errors attending the determinations) very few observers appear to have taken it into account. In all determinations involving extreme accuracy it is, however, a factor which, no doubt, should not be neglected.

In the eighth series we have calculated for each determination the extent of the correction, on the assumption that the air-sample was saturated with moisture at the given temperature—an assumption which is probably not strictly accurate, owing to the greasy surface of the paraffin wax which localized the moisture, and also to the short interval of time which elapsed between adding the absorbent and the collection of the air-sample. But at any rate it is the maximum correction. In the succeeding tables we have omitted the details of the correction, but give the mean.

We shall conclude this part of our Paper by giving the results of duplicate determinations made on 23 days, with air collected in the grounds of Queen's College, Belfast, in 1897, during the months of March, April, May, June, and July.

We may draw attention to the fact that, with two exceptions, the differences in the duplicate samples are *in parts per million.*

SERIES 13. (AIR.)—Collected in the grounds of Queen's College, Belfast.

Date.	Direction of Wind.	Kind of Weather.	Height of Barometer.	Temperature in °C.	Without correction for moisture.		With correction for moisture.	
					CO_2 in 10,000 vols. of air.	Differences in Duplicate Samples.	CO_2 in 10,000 vols. of air.	Differences in Duplicate Samples.
1897. March 24	W.	Gale, with rain, ...	mm. 752·5	13	2·804 2·772	0·032	2·846 2·813	0·033
,, 25	W.	Calmer and dry, ...	760·6	14	2·838 2·784	0·054	2·883 2·828	0·055
,, 26	S.–S.W.	Strong wind and showers, . . .	739·7	11·5	2·745 2·838	0·093	2·780 2·877	0·097
,, 29	N.	Moderate wind, ...	751·2	11	2·971 2·995	0·024	3·010 3·034	0·024
,, 31	N.E.	Calm, cloudy, ...	746·8	8	2·035 2·975	0·060	3·067 3·007	0·060
April 14	W.	Showery and gusty, ...	751·6	11	2·785 2·808	0·023	2·821 2·845	0·024
,, 27	N.E.	Calm, ...	761·5	13	2·803 2·852	0·049	2·843 2·894	0·051
,, 29	S.W.	Gusty, clear, with sunshine, . .	758·0	13	2·496 2·582	0·086	2·533 2·620	0·087
,, 30	N.W.	Calm, showery, ...	753·2	12·5	2·543 2·493	0·050	2·580 2·529	0·051
May 3	W.	Calm, showery, ...	756·8	11	2·500 2·568	0·068	2·532 2·601	0·069
,, 7	S.	Calm, sultry, mist and rain, . .	760·9	11	2·574 2·534	0·040	2·607 2·567	0·040
,, 10	N.	Calm, cloudy, with sunshine at times,	763·0	11·5	2·748 2·970	0·222	2·784 3·009	0·225

,,	12	N.W.–W.	Calm, overcast, ...	767·8	9·8	2·941 2·974	0·033	2·976 3·010	0·034
,,	14	W.–S.W.	Calm, overcast, ...	767·5	12	2·753 2·799	0·046	2·790 2·837	0·047
June	3	E.	Calm, hazy, sunshine, . . .	767·8	16	2·977 2·926	0·051	3·030 2·978	0·052
,,	4	E.	Calm, hazy, sunshine, . . .	765·4	19·5	2·473 2·431	0·042	2·528 2·485	0·043
,,	9	S.E.	Calm, gloomy, inclined to rain, . .	758·0	12·8	3·082 3·125	0·043	3·129 3·171	0·042
,,	10	S.	Cloudy, calm, ...	765·0	15·5	2·993 3·146	0·153	3·045 3·200	0·155
,,	11	S.W.–W.	Overcast, sultry, inclined to rain, .	765·5	19	3·172 3·100	0·072	3·241 3·167	0·074
,,	14	N.W.	Stormy, cloudy, ...	765·0	18·5	3·060 3·117	0·057	3·124 3·182	0·058
,,	18	N.	Stormy, but bright, ...	753·0	14	3·259 3·240	0·019	3·311 3·292	0·019
,,	21	W.	Windy, sunshine, ...	761·8	18	3·158 3·104	0·054	3·222 3·167	0·055
July	7	N.W.	Fine, but some showers, ...	757·3	17	3·024 3·036	0·012	3·082 3·094	0·012

Mean of 46 determinations, with correction for moisture, ... 2·912
,, ,, ,, without ,, ,, ... 2·867

Difference, ... ·045

Mean of differences in 23 duplicate determinations, with correction for moisture, ... ·061
,, ,, ,, ,, ,, without ,, ,, ... ·060

Difference, ... ·001

SECTION III.—THE AUTHORS' EXPERIMENTS ON THE ACTION OF BARYTA WATER ON GLASS AND ON SILICA, AND THE DISTURBING EFFECT OF SOLUBLE SILICATES ON THE DELICACY OF THE PHENOL-PHTHALEÏN COLOUR REACTION.

Action of Dilute Baryta Water on Glass.—At the outset of the investigation just described, two sets of experiments were made which satisfied us that a weak baryta solution has an appreciable action on glass, and that this action has a disturbing effect on the titer of the solution. They were as follows:—

(1). A measured volume of the baryta solution was placed in a weighed platinum dish, and evaporated with excess of the standard hydrochloric acid solution, and the residue heated until of constant weight.

Residue obtained, . . 0·518 grm.

(2). The same volume of the baryta solution was placed in a stoppered Winchester quart, the latter was then well shaken and placed on its side for 48 hours. The solution was next poured into a weighed platinum dish, the bottle washed out with distilled water, and the washings added. The whole was then treated as in the first experiment.

Residue obtained, . . 0·534 grm.

(3). The experiment was performed as in the preceding case, but the baryta solution remained for 72 hours in the bottle.

Residue obtained, . . 0·560 grm.

(4). 50 c.c. of the baryta solution (1 c.c. = 1 c.c. of standard acid) were allowed to remain in a Winchester quart, full of air, from which the carbonic anhydride had been removed (as described on p. 128) for 65 hours, and then titrated in the vacuum apparatus.

Standard acid required, . . 48·9 c.c.

(5). Duplicate experiment to (4), but in another bottle.

Standard acid required, . . 49·1 c.c.

We now proceed to describe in detail the additional experiments we made to decide definitely as to the extent and nature of the action which a weak baryta solution exercises on glass, and especially on the glass of which the greenish-white Winchester quart bottles used in our experiments are made.[1] We may, however, first draw attention to the fact that the actual quantities involved both in the experiments we made in the past and in those we are about to describe, were very small. Thus—

(A.) Strength of baryta water used, 1 c.c. = 0·1 c.c. CO_2 at N. T. P.

(B.) Actual volume of carbonic anhydride to be determined in a Winchester quart of air, about 1 c.c.

(C.) Theoretical residue left on evaporating 10 c.c. of the baryta water with hydrochloric acid, 0·0093 grm.

We are, therefore, dealing with quantities which so far as weights are concerned involve single milligrammes, while as regards volumes, any disturbing influence affecting *hundredths* of a c.c. of carbonic anhydride would sensibly affect the determinations.

Repetition of Previous Experiments.—Quantities of 50 c.c. of the baryta solution were exposed as already described in Winchester quart bottles of light-green glass, which had been carefully cleaned, rinsed with distilled water, and well drained. The bottles contained ordinary air, as for the purpose we had in view we did

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[1] This action cannot, of course, occur in our modification of Pettenkofer's process, and we should not have gone any further into the matter but for the fact that our statement that glass is attacked by weak baryta solution was challenged. It was contended that Reiset and others had already investigated the subject, but had found no such "extraordinary action" as that indicated by our experiments; and it was further contended that the method adopted in the first of these was unreliable, owing to the fact "that it was impossible to obtain accurate weighings of the barium chloride owing to the rapidity with which it rehydrates itself."

If this objection had any solid foundation in fact, then it would obviously be impossible to determine the water of crystallization in barium chloride. This was a simple point to test, and was easily decided experimentally. Two determnaitions were made by heating quantities of the crystallized salt in platinium crucibles to 150° C., covering the crucibles with their lids, and allowign them to cool in a dessicator, the heating, &c., being repeated until their weights were constant. With large crystals the loss was slightly too *great* (15·02 and 15·32 per cent.), but with small crystals—obtained by shaking a hot saturated solution in a corked vessel, cooled rapidly by immersion in a current of cold water—the correct amount was obtained, viz. 14·66 and 14·67 per cent. in duplicate experiments, the theoretical quantity being 14·75.

not consider it necessary to remove the carbonic anhydride previous to the experiment.

After certain intervals of time, the contents of each bottle were transferred to a large platinum crucible (of 115 c.c. capacity, and provided with a tightly-fitting lid) and the bottle rinsed out with 60 c.c. of the weak hydrochloric acid solution in three separate portions, which were also added to the contents of the platinum crucible. The latter was then heated on a water bath until its contents were dry, next transferred to an air bath heated to 150 °C., and after some time covered, placed in a dessicator for ten minutes and weighed, the heating, &c. being repeated until a constant weight was obtained.

No. of Experiment.	Conditions.	Weight of Ba Cl_2 &c.	Difference in weight of residue	
			From Blank A.	From Blank B.
1	Blank A.	0·0487 grm.	—	+ 0·0003 grm.
2	Blank B.	0·0484 ,,	– 0·0003 grm.	—
3	After 48 hours.	0·0508 ,,	+ 0·0021 ,,	+ 0·0024 ,,
4	,, 72 ,,	0·0512 ,,	+ 0·0025 ,,	+ 0·0028 ,,
5	,, 72 ,,	0·0537 ,,	+ 0·0050 ,,	+ 0·0053 ,,
6	,, 98 ,,	0·0549 ,,	+ 0·0062 ,,	+ 0·0065 ,,
7[1]	,, 98 ,,	0·0585 ,,	+ 0·0098 ,,	+ 0·0101 ,,

These results prove a very decided action, increasing on the whole with the time of exposure. They bear out and amplify our previous work on the subject.

We did not expect to find that the duplicate experiments would show exactly the same results, as the extent of the action probably depends upon variable conditions, such as the amount of the carbonic anhydride in the air of the bottle, the temperature of the room, the extent to which the bottle was agitated so as to expose fresh surfaces of glass, &c., and the duplicate experiments were not performed at the same time.

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[1] This result is possibly too high, as we noticed during the evaporation a speck of some foreign substance in the otherwise clear liquid.

It was suggested to us that it might be possible to demonstrate the action of weak baryta water on glass objectively by separating and collecting the products. Acting on this suggestion we have found it easy to separate and even to determine one such product, namely, silica. The following plan was adopted:—

Four Winchester quarts, similar to those we used in our previous experiments, were carefully cleaned, rinsed with distilled water and drained. Each was then charged with 50 c.c. of the baryta solution, stoppered, and placed on its side for a certain time, with occasional rolling and shaking. The contents of all four were then transferred to a platinum dish, and each bottle separately rinsed out with 60 c.c. of the dilute acid in three separate portions, these washings being added to the contents of the platinum dish. The latter was then heated on a water bath until its contents were quite dry; 1 c.c. of strong hydrochloric acid next added, and finally the insoluble residue either washed into a filter and weighed (after complete washing and ignition) or rinsed into tubes which were sealed up.

The *same* bottles were used in all our experiments, conducted in this way. The blank experiments were made by evaporating 200 c.c. of the baryta water with 240 c.c. of the acid in the same platinum dish, the subsequent treatment being as above described.

No. of Experiment.	Time of Exposure.	Appearance of residue in tube, or weight of silica.
1	42 hours.	Considerable flocculent deposit.
2	Blank experiment.	Minute deposit.
3	72 hours.	0·0066 grm.
4	Blank experiment.	0·0006 ,,
5	72 hours.	Heavy deposit.

A similar experiment made with a glass flask also yielded silica, so that the action is not confined to the glass of which Winchester quarts are made.

The action of alkalies upon glass has been repeatedly investigated, and, in connection with this matter, we may refer to the work done by Fresenius,[1] Emmerling,[2] Weber and Sauer,[3] and Förster.[4] Fresenius and Emmerling experimented with boiling solutions, while Förster, as well as Weber and Sauer, investigated the action at ordinary temperatures also.

Emmerling's results are instructive in showing that a very considerable action is induced even by exceedingly weak solutions. Thus, on boiling about 400 c.c. of a solution of caustic potash in a flask of 600–700 c.c. capacity, he found that the latter experienced a loss in weight per hour for different concentrations of the potash solution, as follows:—

	Per Cent.	Per Cent.	Per Cent.
Concentration, ...	0·25	0·025	0·005
Loss of weight of vessel per hour, .	0·0115	0·0070	0·0027

Förster proved that at ordinary temperatures a weaker alkaline solution may exercise an actually greater effect on glass than a stronger one, while the relative action of a weaker solution appears to be always greater than that of a stronger, as the following table of his results show:—

Grms. NaOH in 100 c.c. solution.	Loss in mgs per 100. sq. cms. of surface.			
	I.	II.	III.	IV.
45	1·8	1·7	2·0	3·7
10	5·2	6·3	6·1	6·6
1	3·9	4·5	5·1	5·5

In the above experiments the Roman numerals refer to different kinds of glass, which were exposed to the solution at ordinary temperatures for fifty days in each case.

The only experiments on the action of baryta water on glass of which we have been able to find an account are those of Weber and Sauer, who employed a saturated solution, which was kept in 100 c.c. flasks of different varieties of glass for a period of two

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[1] "Quantitative Analysis," II., p. 798.

[2] "Liebig's Annalen," 150 [1859], p. 257.

[3] "Berichte d. deutsch. chem. Ges.," 25 [1892], pp. 70 and 1814.

[4] *Ibid.*, p. 2494.

months. The loss in weight in mgs. which each experienced was found to be as follows:—

Glass, . .	1	2	3	4	5	6	7	8	9	10	11
Loss, . .	14	$10\frac{1}{2}$	$8\frac{1}{2}$	6	$5\frac{1}{2}$	5	5	5	5	$4\frac{1}{2}$	4

It seemed to us to be of some importance to ascertain, if possible, the exact nature of the action of baryta water on glass. Is a soluble silicate of barium formed or an insoluble one, which in our experiments was eventually dissolved by the dilute acid? Does the glass dissolve as such, or are certain of its constituents alone removed?

Before, however, describing our experiments on these points we may mention that other chemists have drawn attention to the action of baryta water on glass as a possible source of error. Thus, Reiset[1] says, "en effet les vases en verre dans lesquels on conserve de l'eau de baryte perdent généralement leur transparence. Le verre parait attaqué et comme décomposé: les boules des barboteurs, en verre soufflé, présentent souvent de nombreuses stries blanchâtres qui ne disparassent pas après un lavage avec l'acide nitrique faible." He, however, did not find that the titer of the solution was disturbed.

Blochmann,[2] quoting Ebermayer's results, says that the latter observer abandoned the "flask" method in favour of the "aspiration" method, in consequence of the high results he obtained with the former (see Appendix, p. 225). Ebermayer attributed the error of the flask method chiefly to the removal of baryta from the solution, and its fixation by the silica of the glass.

The following experiments were made by us in order to ascertain the precise nature of the action of baryta water on glass:—

(1). Four Winchester quart bottles of greenish glass were each charged with 50 c.c. of the baryta solution (1 c.c. = 0·1 c.c. CO_2 at N. T. P.), then closed with stoppers, well shaken, and placed on their sides for eight days, during which time they were occasionally shaken. Their contents were then filtered into a platinum dish, the bottles rinsed out two or three times with distilled water, and the rinsings poured through the same filter. 1 c.c. of strong hydrochloric acid was then added, and the dish heated on a water-

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[1] "Annales de Chimie et de Phys." [5], 26 [1882], p. 175.

[2] *Loc. cit.*, p. 88.

bath until its contents were completely dry. To the dry residue another c.c. of strong hydrochloric acid was added, the mixture heated for a minute or two on the water-bath, and then washed through a small filter—the washing being continued until no residue was left on evaporating a drop on a slip of glass. The filter and its contents were then dried, ignited, and weighed.

Crucible, *plus* SiO_2	21·9181 grms.
,, alone, ...	21·9124 ,,
SiO_2 =	·0057 ,,

The washings were mixed with 1 c.c. of dilute sulphuric acid (1 : 3), and evaporated to small bulk on the water-bath. The sulphate of barium was then filtered off and washed, first with strong hydrochloric acid, and finally with distilled water, until a drop left no residue on evaporation. Dilute ammonia was now added to the filtrate and washings until the mixture was faintly alkaline, when it was evaporated to dryness, re-dissolved in water, one drop of dilute ammonia added, and the ferric oxide and alumina filtered off, washed, ignited, and weighed.

Crucible, *plus* Fe_2O_3 and Al_2O_3, . .	21·9136 grms.
,, alone, ...	21·9122 ,,
Fe_2O_3 and Al_2O_3 =	·0014 ,,

To the filtrate a drop or two of ammonium oxalate was added, and it was then evaporated to small volume, but no precipitate appeared, so the absence of lime was concluded. Finally, the solution was evaporated to dryness and calcined, the residue re-dissolved, filtered, and once more evaporated to dryness with a few drops of dilute sulphuric acid, and again calcined at a bright red heat, and afterwards weighed.

Crucible, *plus* alkaline sulphates, . .	21·9160 grms.
,, alone, ...	21·9120 ,,
Alkaline sulphates,	·0040

The action of the baryta water on the glass of the Winchester quarts was thus shown to consist (partly at all events) in the removal from it of silica, alumina, and ferric oxide, together with alkalies,[1] all of which passed into solution.

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[1] The original barium hydrate had been twice recrystallized, and all evaporations were performed in platinum vessels.

(2.) A duplicate experiment conducted in the same manner as (1), but the baryta water was $2\frac{1}{2}$ times as strong. The following quantities were obtained:—

Silica,	0.0106 grm.
Alumina and ferric oxide,	0·0017 ,,
Alkaline sulphates,	0·0025 ,,

(3.) Seven of the Winchester quart bottles previously used for experiments (1) and (2) were each rinsed with 60 c.c. of the dilute hydrochloric acid (1 c.c. = 0·1 c.c. CO_2) in several portions: these washings were united, evaporated to dryness in a platinum dish, and further treated as (1) and (2), when the following quantities were obtained:—

Silica,	0·0020 grm.
Alumina and ferric oxide,	0·0008 ,,
Lime (CaO),	0·0020 ,,
Alkaline sulphates,	0·0030 ,,

Thus baryta water exercises a second action on glass, whereby substances are formed which are insoluble in water but soluble in dilute hydrochloric acid.

(4.) A control experiment, in which 200 c.c. of the weak baryta water and 240 c.c. of the dilute hydrochloric acid were evaporated together to dryness in a platinum dish, and the residue treated as in the preceding experiments, using as far as possible the same quantities of wash-water in the different filtrations, when the following results were obtained:—

Silica,	0·0012 grm.
Alumina and ferric oxide,	0·0005 ,,
Lime (CaO),	0·0003 ,,
Alkaline sulphates,	0·0016 ,,

In the following table we have collected the results of the preceding experiments, after deducting the quantities obtained in the blank determinations. It also contains the mean results of analyses made of the glass itself—for which we are indebted to Messrs. Caldwell & Hawthorne, the honorary demonstrators of the chemical department, Queen's College, Belfast.

Experiment.	Glass treated with	SiO_2.	Al_2O_3 and Fe_2O_3.	CaO.	Alkaline sulphates.	Remarks.
1	Weak baryta solution,	0·0045	0·0009	None.	0·0024	Dissolved by the baryta solution.
2	Stronger " "	0·0094	0·0012	None.	0·0009	
3	Both baryta solutions,	0·0008	0·0003	0·0017	0·0014	Insoluble in the baryta solution, but soluble in weak hydrochloric acid.
	Percentage composition of the glass,	69·95	2·57	17·21	Alkalies as Na_2O. 10·27	

Although from the minuteness of the quantities involved the results of the determinations are somewhat uncertain, we are of opinion that our experiments warrant the following conclusions :

(1.) A weak baryta solution acts with relative rapidity on the glass of the Winchester quarts (and probably exercises an appreciable action on most varieties of glass), dissolving silica and alkalies, and smaller quantities of alumina and ferric oxide, but *no* lime.

(2.) A stronger solution dissolves *more* silica but *less* alkalies, about the same amount of alumina and ferric oxide, and also, as in the previous case, no lime.

(3.) The baryta water also exercises another action whereby substances are produced which adhere to the glass, and are unsoluble in the baryta solution. They dissolve (in part at all events) in weak hydrochloric acid, and the resulting solution contains a small quantity of silica, practically no alumina or ferric oxide, but appreciable quantities of lime and alkalies.

We may mention that Cossa and G. Lavalle[1] found on the sides of a glass vessel containing baryta water, and closed for twenty-seven years, transparent columnar crystals which when analysed gave—

	Per cent.
SiO_2, . . .	18·56
BaO, . . .	48·23
H_2O, . . .	33·33
	100·12

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[1] Zeitschr. f. Kryst. u. Min., 11., p. 399 ; also Chem. Soc. Journ. (Abs.), 50 [1886], p. 594.

Disturbing effects produced in the titration of baryta water after it has remained in contact with glass.—On page 142 we describe two preliminary experiments which indicated that the titer of a baryta solution was affected by contact with glass in such a manner that its alkalinity was *reduced.* The experiments we have just described on the quantitative effects produced by such contact, might very naturally be supposed to confirm the result of those experiments, and we were therefore not a little surprised to find on repeating them, with every possible precaution, that instead of growing weaker owing to partial neutralization by silica dissolved, or at all events removed from the glass, the baryta water actually experiences a slight *increase in alkalinity* which augments with the time of exposure. The experiments were made by allowing the weak baryta water to remain in receivers consisting of Winchester quart bottles with corks and attached tubes, as in fig. 1, p. 122, the air in them having been previously freed from carbonic anhydride, and the baryta water used for that purpose carefully washed out with water freed from carbonic anhydride. After a suitable interval the baryta water was drawn off into the vacuous titrating vessel, the receiver carefully washed out with purified water, the washings being also drawn off into the titrating vessel.

Immediately before or after the titration a blank determination was made of the alkalinity of the same quantity of baryta solution which had not been in contact with glass.

No. of Experiment.	Conditions.	Baryta solution employed.	Acid required.	Difference in acid required = increase in alkalinity.
			c.c.	
1	Blank, ...	50 c.c.	49·95	+ 0·40
	In contact with glass 70 hours, .	,, ,,	50·35	
2	Blank, ...	,, ,,	49·95	+ 0·40
	In contact with glass 72 hours, .	,, ,,	50·35	
3	Blank, ...	,, ,,	49·95	+ 0·65
	In contact with glass 118 hours, .	,, ,,	50·60	
4	Blank, ...	,, ,,	49·29*	+ 2·01
	In contact with glass 15 days, . .	,, ,,	51·30	

* Fresh acid solution.

Before discussing the cause of increase in the alkalinity of the baryta solution, we pass to the consideration of another effect produced by the action of baryta water on glass, whereby the delicacy of the phenol-phthaleïn colour reaction is not only interfered with but practically destroyed for all accurate determinations.

Effect of the presence of alkaline or soluble silicates on the delicacy of the phenol-phthaleïn colour reaction during titration with an acid.—We noticed repeatedly in the preceding experiments that the final decolorization of the phenol-phthaleïn by acid occurred quite differently in the baryta water before and after the latter had been in contact with glass.

In the former case a single drop or at most two drops of acid were sufficient to discharge the faint pink shade of colour which experience had taught us indicated the near approach of neutrality. Whereas, in the latter case a much larger quantity of acid was necessary, and the colour faded away almost imperceptibly as it was added, rendering the observation of final decolorization very difficult and uncertain.

It occurred to us that this effect was very possibly due to the presence of dissolved silicates; and to decide the question the following experiments were made:—

(1.) *A*. A weak solution of caustic potash was titrated, after the addition of a drop of phenol-phthaleïn solution, with dilute hydrochloric acid until a certain faint pink colour remained.

B. A weak solution of silicate of soda was mixed with the same quantity of phenol-phthaleïn and titrated with the same acid, and in a vessel of the same size, until the same tint was obtained.

A then required 5 drops of acid for complete decolorization.

B required 40 drops, and even then a trace of pink remained.

(2.) Pure unignited silica was rotated by a turbine in a paraffined bottle with baryta water for five days.

A. 10·0 c.c. of the original baryta water were mixed with a drop of phenol-phthaleïn solution, and the standard hydrochloric acid added until a faint pink colour resulted.

B. 10·0 c.c. of the solution after contact with silica and filtration were treated in the same way until the same shade of pink remained.

A now required 2 drops more acid for decolorization. Total acid used 26·6 c.c.

B required 16 drops. Total acid used 7·4 c.c.

The remainder of the weak baryta solution and silica were rotated in the paraffined bottle for an additional period of three days.

A. 10·0 c.c. of the original baryta treated as before required an addition of 2 drops of acid for final decolorization.

B. 10·0 c.c. of the silicated solution required 22 drops. Total acid used 6.75 c.c.

After rotating for three more days—

A still required 2 drops for decolorization.
B required 26 drops. Total acid used 6·55 c.c.

(3.) 0·212 grm. anhydrous carbonate of soda and 0·12 grm. anhydrous silica, quantities equivalent to $Na_2CO_3 + SiO_2$ were fused in a platinum crucible until all action was over. The resulting metasilicate of soda was then dissolved and titrated with decinormal acid, with phenol-phthaleïn as indicator. The colour faded so slowly that the exact point of decolorization was very hard to determine. At first it was judged that 37 c.c. of acid had effected it, but after a time a faint pink shade seemed to have returned. Finally 37·9 c.c. of the standard acid were added. 0·212 grm. of carbonate of soda would, if converted into caustic soda, require 40 c.c. of the acid.

Thus metasilicate of soda, when titrated with phenol-phthaleïn as indicator *behaves almost like caustic soda.*[1]

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[1] It is, perhaps, superfluous to state, when phenol-phthaleïn is used neutralization is indicated when the reaction

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$

has occurred.

The quantity of carbonate of soda employed in the above experiment requires 20 c.c of decinormal acid for this reaction. Metasilicate of soda is, therefore, nearly twice as strong in alkaline effect as the carbonate.

It is thus proved that, in titrating an alkali or an alkaline solution with phenol-phthaleïn as indicator, the indications of the latter are altogether interfered with, and the sharpness of the reaction destroyed, if soluble silicates are present. As baryta water acts on glass with the formation of such compounds, our employment of vessels coated with paraffin wax in Pettenkofer's process is amply justified, for that reason alone, if not for others; for it is almost unnecessary to say that when such vessels are used no disturbance of the colour reaction occurs.

Further we have, in the preceding experiments a clue to the explanation of the increased alkalinity of the baryta solution after it has been in contact with glass. Whatever the exact mechanism of the reaction may be, it seems probable that the dissolved constituents of the glass function on the whole as alkalies, and after our experiment with metasilicate of soda, such an explanation does not appear improbable.

What then, it may be asked, was the reason for our finding *diminished* alkalinity in our first experiments? We believe that the explanation is a simple one, viz. that we used ordinary distilled water for washing out the contents of the absorbing vessel, and that the carbonic anhydride of the former accounts for the weakening of the baryta solution.[1] That this is probable the following consideration will show.

The decrease in alkalinity observed correspond with about 1 c.c. of the solution, which was equivalent to 0·1 c.c. of carbonic anhydride. According to our determinations in ordinary distilled water, 0·1 c.c. of that gas would be contained in from 22–40 c.c. of the water, and in our later determinations made with air, 50 c.c. were employed for washing out the receivers.

Action of weak baryta solution on silica.—We thought it of interest to pursue this matter, with the object, if possible, of ascertaining what substance or substances are formed when silica and baryta water remain in contact. Therefore, at the close of the titration experiment described on p. 153, we filtered a quantity of the silicated solution, and determined in the filtrate SiO_2,

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[1] For at this time, the fact that distilled water contains carbonic anhydride had escaped our attention.

and BaO by the usual methods. The following quantities were obtained :—

Silica, . . .	0·0575 grm.
Barium oxide, .	0·0586 ,,

The ratio 5 SiO_2 : 2 BaO requires the proportion 575 : 586. Not being satisfied that the baryta had remained in contact with the silica sufficiently long for complete action, the following experiment was performed :—Excess of pure silica dried at 100° C., but not ignited, was placed in a paraffined bottle, and the latter filled completely with the weak baryta solution (1 c.c. = 0·1 c.c. CO_2 at N.T.P.). The bottle and its contents were rotated with a turbine for three days. A portion of the liquid was then filtered off and titrated with dilute hydrochloric acid (of equivalent strength to the baryta water). As in previous experiments the point of final decolorization of the phenol-phthaleïn used as colour indicator was difficult to determine. 20 c.c. required 6·3 c.c. of the acid. On determining SiO_2 and BaO in some of the clear fluid we obtained :—

Silica, . . .	0·0446 grm.
Barium oxide, .	0·055 ,,

The ratio 2 SiO_2 : BaO requires 0·0446 : 0·0568.

This experiment was unsatisfactory, as, for some reason which we cannot explain, the silica obtained was quite black after ignition, even in oxygen, and the colour did not change on boiling with aqua regia. A final experiment conducted like the preceding one gave the following results after seven days rotation of the vessel containing the baryta water and silica. 20 c.c. required 2·7 c.c. of standard acid. A portion of the solution contained—

Silica, . . .	0·0275 grm.
Barium oxide, .	0·0150 ,,

The ratio 4 SiO_2 : BaO requires 0·0275 : 0·0175.

Quite different and very curious results were obtained by allowing the silica to remain in contact with a stronger baryta solution, viz. decinormal.

On analyzing such a solution which had been in contact with silica for a year in a paraffined bottle, the following results were obtained :—25 c.c. when titrated with standard acid and phenol-phthaleïn required 18·1 c.c. decinormal acid.

50 c.c. contained 0·0085 grm. SiO_2 and ·2811 grm. BaO, giving the ratio of about $SiO_2 : 13\,BaO$.

The residue left in the paraffined bottle was washed with distilled water until the washings no longer showed an alkaline reaction, and it was then treated at ordinary temperatures for twenty-four hours with decinormal hydrochloric acid. The resulting solution was filtered, and a determination made of the silica and baryta which it contained. The silica amounted to 0·0102 grm., and the baryta (BaO) to 0·8370 grm., quantities which about correspond with the ratio $SiO_2 : 20\,BaO$.

Since writing this paper our attention has been called to the interesting work both of Kohlrausch[1] and of Kahlenberg and Lincoln[2] on solutions of alkaline silicates.

The former by conductivity determinations, and the latter by both conductivity and cryoscopic measurements, have shown that when such solutions are sufficiently diluted, hydrolytic decomposition of the dissolved salt occurs, yielding alkaline hydrate and colloidal silicic acid.

This would explain the result obtained by us on titrating a solution of metasilicate of soda, but on the other hand it renders an explanation of the fact observed by us, that a very dilute solution of barium hydrate dissolves amorphous silica with partial neutralization, extremely difficult. For Kahlenberg and Lincoln tell us that "silicates of the general formulae M_2SiO_3, and $MHSiO_3$, are practically hydrolytically dissociated when 1 gram molecule is contained in 48 litres. Silicates of the general formula $M_2Si_5O_{11}$ are practically decomposed by water when 1 gram molecule is present in 128 litres." As our baryta water was weaker than centinormal it is not easy to see how it should have any solvent action on silica if the above statement is true, and much less that it should become practically neutralized in the process.

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[1] Kohlrausch, "Zeitschr. f. phys. Chem.," 12 [1893], p. 773.

[2] Kahlenberg and Lincoln, "Journ. Phys. Chemistry," vol. ii., p. 77.

PART II.

Section I.—The Amount.

Atmospheric carbonic anhydride plays such an important *role* in nature, that the question of its amount, whether in the past, present, or future, is one of very great interest, not only to the chemist, but also to the biologist, geologist, meteorologist, the agriculturist, and hygienist, and to the student of nature generally.

The reciprocal action of plants and animals on air may be said to fulfil three functions :—(1) to provide each with an important food stuff—viz. carbon and oxygen respectively; (2) to regulate the condition of the atmosphere for their respective well-being; and (3) to keep in "circulation" the supply of carbon which is essential to the existence of both, and in which each generation of either may be said to have a life interest only.

If from any cause the amount of atmospheric carbonic anhydride should be largely increased, the existence of animals would be threatened, while, if the reverse occurred, that of vegetables would be jeopardized; and animals would also stand in danger of eventual annihilation from the want of food which in the long run they derive from the synthetic processes of the vegetable kingdom.

While the chief operations of plants and animals, as regards their mutual welfare, act in the sense of maintaining a state of balance or equilibrium in the amount of atmospheric carbonic anhydride, certain well recognized agencies are at work tending to increase its quantity. These have been called "sources of evolution," and the most important are combustion, putrefaction, and decay, and also fermentation—all of which in one way are unimportant, because, even including the combustion of coal, all can be traced back ultimately to the operations of the organic kingdom. They are therefore, more or less, temporary agencies.[1]

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[1] The combustion of petroleum may be an exception however. If petroleum has been formed from carbon, originally present in the interior of the earth, the carbonic anhydride evolved by its combustion is of course of subterranean origin and must be classed in the second category, *i.e.*, among the sources of evolution tending to permanently increase the amount of atmospheric carbonic anhydride.

The only agency of a different kind, *i.e.* one tending to permanently increase the amount of aerial carbonic anhydride (and so to disturb the balance maintained by the organic world) is to be found—so far as we are aware—in volcanic or subterranean sources, which in the past may have been of enormous importance, but of which the record only remains geologically.

We shall allude presently to the curious theory of Ebelmen, Sterry Hunt, and Winchel, who supposed that vast quantities of carbonic anhydride have reached the earth from inter-planetary space.

Opposed to the sources of evolution are those agencies acting in the opposite direction, *i.e.* as "sources of absorption." These have acted in the past, are still active, and will, no doubt, continue in action—not only tending to remove carbonic anhydride from the atmosphere, but also to permanently withdraw it from the sphere of organic action. The first of these consists in the weathering of rocks, whereby broadly speaking, silicates become replaced by carbonates. To this action the production of soil is due, and to it also may be traced the gradual disintegration of mountain peaks and the general levelling of the earth's surface which is no doubt occurring. While this action is of a purely mineral nature, the second source of absorption is of a totally different kind, and is the work of the animal kingdom. Animals having a calcareous coating or skeleton, such as mollusks, corals, foraminifera, &c., have in all probability derived the carbonic anhydride of their calcareous material, if not immediately, at least ultimately, from the air. The vast geological strata of cretaceous substances which owe their origin to this cause are silent but impressive witnesses to the enormous quantities of carbonic anhydride thus locked up, and, as far as can be judged, permanently removed from the sphere of organic action.[1]

Three distinct sets of actions are thus occurring in nature which affect the amount of atmospheric carbonic anhydride. First come those sources of evolution tending to permanently increase it; next, those of absorption causing the opposite effect; and, lastly, regulating actions in which evolution and absorption occur

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[1] Broadly speaking, at all events as some slight evolution may occur by the action of the acids present in vegetable soil on the carbonates contained in it.

alternately or together, and a condition of balance or equilibrium is maintained.

Regarding the first of these it seems to us that subterranean and volcanic action is alone of importance. Cotopaxi, according to Boussingault, evolves more carbonic anhydride annually than a whole city like Paris, while Lecoq has calculated that of the mineral springs, those of Auvergne alone give off in the same time 7,000,000,000 cubic metres of the gas, an amount rather less than $\frac{1}{10}$ the volume produced by the annual combustion of the coal employed throughout the whole of Europe.[1]

Therefore it may be assumed that even at the present time considerable quantities of carbonic anhydride are being poured into the air from the interior of the earth, while in the past, when volcanic action was so much more active, it is only reasonable to suppose that the amount was vastly larger.

The remarkable theory of Sterry Hunt[2] supposes another source of augmentation in the amount of atmospheric carbonic anhydride. According to his calculations, "the carbonic anhydride absorbed in the process of rock decay during the long geological ages, and now represented in the form of carbonates in the earth's crust, must have probably equalled two hundred times the entire volume of the present atmosphere. This amount could not, of course, exist at any one time in the air: it would at ordinary temperatures be liquified at the earth's surface. Whence came this vast quantity?" he asks; and, having dismissed de Beaumont's hypothesis, which supposed a reservoir of carbonic andydride in the interior of the earth, and also the idea that the gas was of volcanic origin, he came to the conclusion that it has reached us from celestial sources—a theory which is not new, he says, "but was put forth by Sir William Grove in 1843, and developed by Matthieu Williams in 'The Fuel of the Sun,' and has lately been noticed by Dr. P. M. Duncan in its geological bearings."

Could it be definitely proved that the subterranean sources of carbonic anhydride are to be traced to carbonates produced in previous ages, as Sterry Hunt believed, then, undoubtedly, colour would be given to his theory; but, in the absence of any over-

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[1] See Varigny, "Air and Life." Smithsonian Miscellaneous Collections.

[2] British Assoc. Reports [1878], p. 544.

whelming evidence to this effect, we venture to think that it must be received with extreme caution, as the *Deus ex machinâ* argument does not appeal to the scientific mind.

Let us next glance at the "regulating agencies."

In addition to the reciprocal action of plants and animals, Schlœsing maintains that the oceans are not only gigantic reservoirs of carbonic anhydride, but function also as automatic regulators of its amount in the atmosphere.[1] He found that sea-water[2] contained a constant amount of carbonic anhydride, and that practically the whole of it was present in the form of bicarbonates.[3] Having previously shown that pure water in contact with an earthy carbonate, and an atmosphere containing carbonic anhydride, becomes charged with bicarbonate—the amount of the latter varying according to a definite law—he proved that when a neutral sodium salt, chalk, and magnesia, are added to water, the amount of bicarbonate also increases with the quantity of carbonic anhydride in the atmosphere; and that although this quantity may differ from that observed in the previous case, a condition of equilibrium is nevertheless reached between it and the tension of the carbonic anhydride.

"This state tends to occur incessantly in sea-water, which for thousands of years has been in contact with the earthy carbonates at its bottom, its shores, and with the silt washed down by rivers

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[1] "Compt. Rend.," 90 [1880], p. 1410.

[2] That of the English Channel.

[3] The probable regulating effect of water in removing from the atmosphere the carbonic anhydride evolved from volcanic and subterranean sources, the combustion of petroleum, &c., so as to maintain the state of equilibrium necessary for the welfare of animals and plants, was pointed out by Peligot in 1855 (Annales de Chimie et de Phys., [3] 44 [1855], p. 257), in a paper which does not appear to have received the attention it deserves. Peligot was led to form his theory on the subject from the relatively high proportion of carbonic anhydride he found in solution in the waters of the Seine. Rain-water, he says, according to Bunsen's calculations, should contain a fairly high proportion of carbonic anhydride; the gases it is capable of dissolving from the atmosphere at 0° C. containing 2·92 per cent. of that body. Now rain-water, Peligot goes on to argue, on coming into contact with the soil, dissolves a further quantity of carbonic anhydride from the ground air, together with carbonates from the soil itself; so that eventually all the dissolved carbonic anhydride exists in the form of bicarbonates, and these latter make their way eventually into the ocean. As to the fate of the carbonic anhydride thus continually introduced into sea-water, he remarks, that in default of direct observation it is impossible to say whether it accumulates, or remains in constant quantity under the influence of of sub-marine life, or by its absorption by the alkaline elements of rocks in process of disintegration.

(*apports des fleuves*). The equilibrium cannot be realised absolutely, as perfect equilibrium is not compatible with either atmospheric or ocean currents. Continuous exchanges ought to occur between the two *media*, provoking either disengagement of carbonic anhydride from sea-water, and consequent precipitation of carbonate of calcium (diminution in tension of atmospheric carbonic anhydride), or absorption of carbonic anhydride, and consequent solution of carbonate of calcium (increase in tension of atmospheric carbonic anhydride)."

Schlœsing then calculates the respective quantities of marine and aerial carbonic anhydride on the basis (1) of his determination of the amount of the gas in sea-water, and (2) that air contains on an average three volumes in 10,000, and comes to the conclusion that "the oceans hold in reserve a disposable quantity of carbonic anhydride, for exchanges with air, ten times greater than the total quantity contained in the atmosphere, and *a fortiori* very much larger than the variations in this quantity."[1]

Schlœsing's theory is certainly ingenious, but it seems to us that it requires further investigation and is open to criticism. For instance, according to it, ought not the air of the tropics to be richer in carbonic anhydride than that of Polar regions, and ought not great ocean currents like the Gulf Stream to exercise a perceptible absorbing action as they pass from warmer to colder regions, leaving the atmosphere poorer in carbonic anhydride? But no such effects have been observed with certainty.[2] Even allowing that in the main Schlœsing is correct, oceans would at best only exercise a limited action as regulators, for suppose a gradual but constant source of increase in the amount of atmospheric carbonic anhydride to exist, oceans would only partially diminish it, and a gradual but perceptible increase would still occur.

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[1] "It is admitted," he says, "that the sea, if spread over the whole surface of the globe, would have a depth of 1000 metres. The quantity of carbonic anhydride contained in a vertical prism of this layer having 1 square metre for a base is 98·3 kilos, forming bicarbonates: the half is 49 kilos, and this is the quantity disposable for the regulating action, the other half being retained by the bases. In supposing that our atmosphere has a uniform composition, and contains $\frac{3}{10000}$ of its volume of carbonic anhydride—a vertical prism of this atmosphere, having for a base 1 square metre, contains only 4·7 kilos of carbonic anhydride."

[2] See p. 179.

May not the permanent regulators of atmospheric carbonic anhydride in the past, at all events, be found in those mineral and animal agencies which have led to the absorption of the gas and the formation of calcareous deposits?

No doubt the reciprocal action of plant and animal life on air and the regulating action of the oceans may possibly be adequate instruments for maintaining a state of balance or equilibrium in the amount of atmospheric carbonic anhydride, and for the circulation of the carbon necessary for the existence of the organic world, *provided that no additional and considerable sources of absorption or evolution are active.* But such is not the case as we have seen. Therefore we suggest that the chief permanent source of evolution, viz. volcanic or subterranean action, is met and compensated by the chief permanent sources of absorption, *i.e.* the weathering of rocks with the formation of earthy carbonates, and the eventual absorption of these by "cretaceous" organisms, while a certain proportion of carbonic anhydride remains free in the air to be dealt with by plants and animals.

The production of coal may point to an effort of nature in the past to reduce the proportion of atmospheric carbonic anhydride by thus temporarily locking up the carbon, the amount of the former having become excessive with a correlative preponderance or luxuriance of vegetable life.

May we not be entering upon a period when the reverse is occurring with absorption and diminution of aerial carbonic anhydride, in spite of our unconscious efforts to increase its amount by the combustion of coal and petroleum—a period which may foreshadow the complete extinction of life on our globe?

Several memoirs bearing on the subject just discussed deserve mention.

In a series of papers, published in the "Chemical News," T. L. Phipson[1] discusses the question of the primeval atmosphere, and the changes which have subsequently occurred in its composition.

He bases his views on a theory propounded, he says, by Kœne, according to which the carbonic anhydride and nitrogen of the air have never ceased diminishing since the origin of living creatures

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[1] Phipson. Chemical News, vols. 67, 68, 70.

(? organisms), whilst the relative proportion of oxygen has gone on increasing. "In the more remote geological ages there could have been no free oxygen at the high temperatures to which all combustible bodies were exposed, and we can only conceive the atmosphere when the earth had evolved sufficiently to have been composed of nitrogen, carbonic acid, and water. Such is the starting point of Kœne's doctrine . . . The next point to which the theory refers is that an immense amount of carbon is fixed in the earth by the remains of plants and animals, and never returns to the air . . . Oxygen alone remains in relatively larger and larger proportions . . . As for carbonic acid, it has almost entirely gone."

Phipson then describes his own experiments on the growth of plants in pure carbonic anhydride (and water vapour), and found that it did not kill them at once, but that they lived in it for some time.

Then he exposed his plants to Kœne's primitive atmosphere (nitrogen, carbonic anhydride, and water vapour), and found that their vegetation was remarkably healthy and even luxuriant for a lengthened period. Next he argues that the primeval atmosphere consisted of nitrogen alone (and water vapour also ?), and that into this with the dawn of plant-life (which preceded that of animals) free oxygen first made its appearance in the atmosphere, and that since then plants have continued thus to pour oxygen into the air. As to the source of the carbonic anhydride from which the oxygen resulted he attributes it to volcanic action "which continued to be intense until after the coal period, and appears to have gradually diminished from that period to the present time, though it is still very active . . . The oxygen of the atmosphere has thus gone on increasing in quantity from the earliest ages of the earth's history until the present time; and when it had attained to a certain amount animal life became possible and duly appeared. At the same time carbonic anhydride has diminished, since the strata of the earth reveal immense deposits of carbon which was originally present as carbonic anhydride."

Meunier,[1] in criticising Sterry Hunt's theory, is of opinion that the chief permanent source of carbonic anhydride evolution

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[1] Meunier, Compt. Rend., 87 [1878], p. 541.

is volcanic, and that the gas has not reached us from interplanetary space at all, because in that case the moon would have an atmosphere.

He seeks to account for the vast quantities of carbonic anhydride of volcanic origin by the action of water trickling through the earth's crust on to materials in its interior, of the nature of cast iron, thus giving hydrocarbons, which by their combustion produced the gas.

Dittmar[1] has made an important contribution to the subject of the carbonic anhydride of sea water. From his exceedingly careful researches on its amount he came to the following conclusions:—

(1.) That free carbonic anhydride in sea water is the exception. As a rule, it is less than the proportion corresponding to bicarbonates.

(2.) In surface waters the proportion of carbonic anhydride increases when the temperature falls, and *vice versâ.*

(3.) Within equal ranges of temperature it seems to be lower in the surface water of the Pacific than it is in the surface water of the Atlantic Ocean.

He also made experiments to determine the dissociation pressure of the bicarbonates in sea water, but with an artificial sea water. He found the tension to be about 0·0005 atmospheres, at temperatures which from recollection he fixed at 18-21° C., and considered that at 0° C. it would be 0·0003, which would correspond with the pressure of the gas in the air.

[We gather from the memoir that this was a preliminary experiment of an investigation he proposed to continue, but we have not been able to find any account of further work, which was probably cut short by his death a few years later.]

"I think," he says. "that he (Schlœsing) is right, but if so then the proportion of carbonic anhydride in the atmosphere should be more in the tropics than in the temperate zones and polar regions."

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[1] Dittmar, Challenger Reports, vol. i., Physics and Chemistry. See summary, p. 209.

Having quoted Thorpe's researches on the atmospheric carbonic anhydride over the Irish Sea, the Atlantic, and tropical Brazil, in support of this, he then mentions Sterry Hunt's theory (which had in the meantime been elaborated by Winchel), and says, regarding the extraordinary supplies of carbonic anhydride, which, according to that theory, came from interplanetary space:—"I see no reason for this hypothesis, which I suspect is not in accordance with what we know of the constancy in the rate of rotation of the earth, all the immense mass of carbonic anhydride sought to be accounted for may have come out of the bowels of the earth, whence this gas is still being emitted in enormous quantities. The difficulty I apprehend lies in the other direction. Our atmosphere would long have become unfit for respiration if the volcanic carbonic anhydride were not constantly being removed by the bases of disintegrating silicates, chiefly as carbonate of lime, of which a considerable proportion goes down the rivers into the ocean. This latter will 'soon' (in the geologist's sense) have arrived at a state of saturation in regard to this component."

Dittmar's views thus coincide with our own up to a certain point; but we have gone a step further, and show how "the state of saturation" he speaks of is being checked.

. . . .

As regards the actual amount of carbonic anhydride present in the atmosphere, we have in the following table collected the results of all the more important work which has been done on the subject since it first received attention, and these we have arranged in chronological order. The table contains the work of some fifty observers, and embraces several thousand determinations. All the results have been verified as far as possible from the original memoirs. In some cases it was necessary to compile them from the authors' figures, which we have done on our own responsibility. As regards the columns headed "Variations," we have followed Wollny's example. The absolute variation is the difference between the maximum and minimum amount of each observer, while the percentage variation refers to the ratio of the minimum to this excess.

The Amount of Carbonic Anhydride in the Atmosphere.

Date of Observation.	Observer.	Locality.	No. of Observations.	CO_2 in 10,000 vls. of Air.			Variation.		Authority.
				Mean.	Maxm.	Minm.	Absolute.	Percentage	
—	—	—	—	600	—	—	—	—	Gehlers. Phys. Wörterb.
—	Girtanner, . . .	—	—	100	—	—	—	—	v. Arnim.
—	Fourcroy, . . .	—	—	—	200	100	—	—	Fourcroy.
1797	Humboldt, . . .	Paris (and elsewhere), ...	—	150	180	50	—	—	v. Arnim.
1802	Dalton, . . .	Manchester, ?	1	6·83	—	—	—	—	Dalton.
1812	Thenard, . . .	Near Paris, ...	1	3·97	—	—	—	—	Thenard.
1809–1815	De Saussure, . .	Geneva, ...	6	5·96	7·79	4·57	3·22	70	De Saussure.
*1827	,, ,, . . .	,, ...	23	5·06	5·78	3·58	2·20	61	,, ,,
1828	,, ,, . . .	,, ...	53	4·47	5·74	3·20	2·54	79	,, ,,
1829	,, ,, . . .	,, ...	101	4·03	5·35	3·15	2·20	70	,, ,,
1830	,, ,, . . .	,, ...	2	3·73	3·76	3·71	0·05	1	,, ,,
1832	Watson, . . .	Bolton, ...	19	5·30	8·62	4·20	4·42	105	Watson.
,,	,, . . .	Country near Bolton, ...	12	4·13	4·74	3·61	1·13	31	,,
1839–1840	Boussingault, . .	Alsace, ...	19	3·65	4·94	2·57	2·37	92	Boussingault.
1840–1841	,, . .	Paris, ...	142	4·00	6·66	2·16	4·50	208	,,
1840	Verver, . . .	Gröningen, ...	90	4·20	5·10	3·50	1·60	46	,,
†1847	Lewy, . . .	Atlantic, ...	11	4·63	5·77	3·34	2·43	73	Lewy.
,,	,, . . .	Havre, ...	3	3·59	3·60	3·57	0·03	1	,,
		Paris	3	5·14	5·23	5·10	0·13	2	,,

1848	,, . . .	New Granada (normal air), . . .	8	4·01	4·99	3·07	1·92	62	,,
,,	,, . . .	,, ,, (abnormal air), . . .	11	7·28	24·47	3·07	21·40	697	,,
1850	,, . . .	Bogota (normal air), ...	14	4·90	7·65	3·61	4·04	112	,,
,,	,, . . .	,, (abnormal air), ...	22	11·39	49·04	3·61	45·43	1259	,,
1848	A. & H. Schlagintweit,	Alps, ...	6	4·47	5·80	3·20	2·60	81	A. & H. Schlagintweit.
1851	A. Schlagintweit .	Berlin, ...	3	4·22	4·53	3·90	0·63	16	A. Schlagintweit.
,	,, ,, . .	Monte Rosa, ...	10	7·88	9·51	5·94	3·57	60	,, ,,
,,	,, ,, . .	St. Jean de Gressoney, ...	1	4·97	—	—	—	—	,, ,,
,,	,, ,, . .	Zermatt, ...	1	4·80	—	—	—	—	,, ,,
,,	,, ,, . .	Bödemié, ...	1	4·75	—	—	—	—	,, ,,
1848–1850	Marchand, . . .	Halle (Saxony), ...	150	3·10	—	—	—	—	Marchand.
1857	v. Gilm, . . .	Innsbruck, ...	—	4·15	4·60	3·80	0·80	21	Ebermayer & v. Fodor.
1859–1860	Frankland, . . .	London, ...	10	8·65	11·00	4·20	6·80	162	Frankland.
1861	,, . . .	Mont Blanc (summit), ...	1	6·1	—	—	—	—	,,
,,	,, . . .	Chamounix, ...	1	6·3	—	—	—	—	,,
,,	,, . . .	Grand Mulets, ...	1	11·1	—	—	—	—	,,
1860	De Luna, . . .	Madrid (inside walls), ...	12	5·2	8·00	3·00	5·00	166	Angus Smith.
,,	,, ,, . . .	,, (outside walls), ...	12	4·5	9·00	2·00	7·00	350	,, ,,
1864 ?	Roscoe, . . .	London and Manchester, ...	161	3·95	—	—	—	—	Thorpe.
1864	Angus Smith, . .	London, ...	23	3·41	4·28	2·80	1·48	53	Angus Smith.
,,	,, ,, . .	Manchester (suburbs), ...	14	3·69	4·67	2·91	1·76	60	,, ,,

* Compiled from the Tables given in De Saussure's original paper in the "Annales de Chimie."

† Compiled from Lewy's Tables in the "Annales de Chimie."

The Amount of Carbonic Anhydride in the Atmosphere.

Date of Observation.	Observer.	Locality.	No. of Observations.	CO_2 in 10,000 vls. of Air.			Variation.		Authority.
				Mean.	Maxm.	Minm.	Absolute.	Percentage	
—	—	—	—	600	—	—	—	—	Gehlers. Phys. Wörterb.
—	Girtanner,	—	—	100	—	—	—	—	v. Arnim.
—	Fourcroy,	—	—	—	200	100	—	—	Fourcroy.
1797	Humboldt,	Paris (and elsewhere),	—	150	180	50	—	—	v. Arnim.
1802	Dalton,	Manchester, ?	1	6·83	—	—	—	—	Dalton.
1812	Thenard,	Near Paris,	1	3·97	—	—	—	—	Thenard.
1809–1815	De Saussure,	Geneva,	6	6·96	7·79	4·57	3·22	70	De Saussure.
*1827	,, ,,	,,	23	5·06	6·78	3·58	2·20	61	,, ,,
1828	,, ,,	,,	53	4·47	5·74	3·20	2·54	79	,, ,,
1829	,, ,,	,,	101	4·03	5·35	3·15	2·20	70	,, ,,
1830	,, ,,	,,	2	3·73	3·76	3·71	0·05	1	,, ,,
1832	Watson,	Bolton,	19	5·30	8·62	4·20	4·42	106	Watson.
,,	,,	Country near Bolton,	12	4·13	4·74	3·61	1·13	31	,,
1839–1840	Boussingault,	Alsace,	19	3·65	4·94	2·57	2·37	92	Boussingault.
1840–1841	,,	Paris,	142	4·00	5·66	2·16	4·50	208	,,
1840	Verver,	Gröningen,	90	4·20	5·10	3·50	1·60	46	,,
†1847	Lewy,	Atlantic,	11	4·53	5·77	3·34	2·43	73	Lewy.
,,	,,	Havre,	3	3·69	3·60	3·67	0·03	1	,,
,,	,,	Paris,	3	6·14	6·23	5·10	0·13	2	,,
1848	,,	New Granada (normal air),	8	4·01	4·99	3·07	1·92	62	,,
,,	,,	,, ,, (abnormal air),	11	7·28	24·47	3·07	21·40	697	,,
1850	,,	Bogota (normal air),	14	4·90	7·65	3·61	4·04	112	,,
,,	,,	,, (abnormal air),	22	11·39	49·04	3·61	45·43	1259	,,
1848	A. & H. Schlagintweit,	Alps,	6	4·47	5·80	3·20	2·60	81	A. & H. Schlagintweit.
1851	A. Schlagintweit	Berlin,	3	4·22	4·53	3·90	0·63	16	A. Schlagintweit.
,,	,, ,,	Monte Rosa,	10	7·88	9·61	5·94	3·67	60	,, ,,
,,	,, ,,	St. Jean de Gressoney,	1	4·97	—	—	—	—	,, ,,
,,	,, ,,	Zermatt,	1	4·80	—	—	—	—	,, ,,
,,	,, ,,	Bödemié,	1	4·76	—	—	—	—	,, ,,
1848–1850	Marchand,	Halle (Saxony),	160	3·10	—	—	—	—	Marchand.
1857	v. Gilm,	Innsbruck,	—	4·15	4·60	3·80	0·80	21	Ebermayer & v. Fodor.
1859–1860	Frankland,	London,	10	8·65	11·00	4·20	6·80	162	Frankland.
1861	,,	Mont Blanc (summit),	1	6·1	—	—	—	—	,,
,,	,,	Chamounix,	1	6·3	—	—	—	—	,,
,,	,,	Grand Mulets,	1	11·1	—	—	—	—	,,
1860	De Luna,	Madrid (inside walls),	12	6·2	8·00	3·00	5·00	155	Angus Smith.
,,	,, ,,	,, (outside walls),	12	4·5	9·00	2·00	7·00	350	,, ,,
1864 ?	Roscoe,	London and Manchester,	161	3·95	—	—	—	—	Thorpe.
1864	Angus Smith,	London,	23	3·41	4·28	2·80	1·48	53	Angus Smith.
,,	,, ,,	Manchester (suburbs),	14	3·69	4·67	2·91	1·76	60	,, ,,

* Compiled from the Tables given in De Saussure's original paper in the "Annales de Chimie."

† Compiled from Lewy's Tables in the "Annales de Chimie."

The Amount of Carbonic Anhydride in the Atmosphere.

Date of Observation.	Observer.	Locality.	No. of Observations.	CO_2 in 10,000 vls. of Air.			Variation.		Authority.
				Mean.	Maxm.	Minm.	Absolute.	Percentage	
1864	Angus Smith,	Manchester (streets, usual weather),	75	4·03	—	—	—	—	Angus Smith,
,,	,, ,,	,, (,, during fogs),		6·79	—	—	—	—	,, ,,
,,	,, ,,	,, (,, about middens),		7·74	—	—	—	—	,, ,,
,,	,, ,,	,, (all the town specimens),		4·42	—	—	—	—	,, ,,
,,	,, ,,	,, (do., fogs excepted)		4·24	—	—	—	—	,, ,,
,,	,, ,,	,, (do., fogs & middens excepted),		4·03	—	—	—	—	,, ,,
1865	,, ,,	Scotland (country),	92	3·36	3·61	3·00	0·61	20	,, ,,
,,	,, ,,	,, (towns) Perth,	10	4·14	5·73	3·24	2·49	77	,, ,,
,,	,, ,,	Glasgow,	32	5·02	7·16	3·14	4·02	128	,, ,,
,,	Thorpe,	Irish Channel,	26	3·08	3·32	2·66	0·66	25	Thorpe.
1866	,,	Atlantic,	51	2·95	3·36	2·66	0·70	26	,,
,,	,,	Tropical Brazil (rainy season),	31	3·28	3·49	3·07	0·42	14	,,
,,	Moss,	Arctic Regions,	3	5·53	6·42	4·83	1·59	33	Moss.
1869	Angus Smith,	London,	34	4·39	5·28	3·52	1·76	50	Angus Smith.
1863–1864	F. Schulze,	Rostock,	431	3·64	—	—	—	—	Blochmann.
1868	,, ,,	,,	1034	2·89	3·44	2·25	1·19	53	Wollny & Ebermayer.
1869	,, ,,	,,		2·86	3·40	2·45	0·95	39	,, ,,
1870	,, ,,	,,		2·90	3·33	2·59	0·74	29	,, ,,
1871	,, ,,	,,		3·01	3·50	2·67	0·83	31	,, ,,
1872	Henneberg.	Weende (near Göttingen),	17	3·20	3·38	3·03	0·35	11	Henneberg.

,, ,,	Reiset,	Near Dieppe,	92	2·94	3·14	2·80	0·34	12	Reiset.
1874–1875	Fittbogen & Hässelbarth	Dahme (Holstein),	347	3·34	4·17	2·06	2·11	102	Fittbogen & Hässelbarth.
,, ,,	Farsky,	Tabor (Bohemia),	295	3·43	4·07	3·02	1·05	35	Farsky.
,, ,,	Wolffhügel,	Munich (at ground level),	205	3·68	14·50	1·80	12·70	705	Wolffhügel.
,, ,,	,,	,, (4·3 metres from ground),	205	3·75	7·10	1·50	5·60	373	,,
1875	Claësson,	Lund (Sweden),	31	2·79	3·27	2·37	0·90	38	Claësson.
,,	Truchot,	Clermont-Ferrand,	50–60	4·09	—	—	—	—	Truchot.
1876	,,	,, ,, (winter; good weather),	—	3·30	4·60	2·10	2·50	119	Wollny.
,,	,,	,, ,, (rainy weather),	—	4·60	5·10	4·20	0·90	21	,,
,,	,,	,, ,, (snow-fall),	—	5·60	8·70	4·40	4·30	98	,,
1877–1878	—	Glasgow,	—	3·66	—	—	—	—	—
1877	v. Fodor,	Buda-Pesth,	1200	4·14	4·68	3·79	0·89	23	v. Fodor.
1878	,, ,,	,, ,,		3·74	4·15	3·34	0·81	24	,, ,,
1879	,, ,,	,, ,,		3·79	4·46	3·47	0·99	28	,, ,,
,,	Macagno,	Palermo,	—	3·60	7·60	2·00	5·60	280	—
,,	Armstrong,	Grasmere (day observations),	53	2·96	3·26	2·71	0·55	20	Armstrong.
,,	,,	,, (night ,,),	62	3·30	4·08	2·86	1·22	42	,,
1879	Reiset,	Near Dieppe,	91	2·98	3·41	2·74	0·67	24	Reiset.
1880	,,	,, ,,	37	2·97	3·52	2·77	0·75	27	,,
*1876	Lévy	Montsouris,	—	2·76	3·13	2·49	0·64	—	—
1877	,,	,,	—	2·84	3·44	2·67	0·77	29	Wollny.
1878	,,	,,	—	3·45	3·59	3·22	0·37	11	,,

* The figures given under "mean," "maximum," and "minimum" are on the *monthly* results. The observations have been continued to the present date, but want of space prevents us from giving the remainder.

The Amount of Carbonic Anhydride in the Atmosphere.

Date of Observation.	Observer.	Locality.	No. of Observations.	CO_2 in 10,000 vls. of Air.			Variation.		Authority.
				Mean.	Maxm.	Minm.	Absolute.	Percentage	
1879	Lévy,	Montsouris,	—	3·29	3·58	2·45	1·13	46	Wollny.
1880	,,	,,	—	2·70	2·92	2·43	0·49	20	,,
1881	,,	,,	—	2·77	2·97	2·66	0·31	12	,,
1882	,,	,,	—	2·86	3·11	2·58	0·53	20	,,
1883	,,	,,	—	2·85	3·17	2·68	0·49	20	,,
1884	,,	,,	—	2·95	3·12	2·59	0·53	20	,,
1885	,,	,,	—	2·95	3·08	2·85	0·23	8	,,
1886	,,	,,	—	2·77	2·91	2·62	0·29	11	,,
1887	,,	,,	—	2·83	3·03	2·65	0·38	14	,,
1880–1881	Müntz & Aubin,	Paris (winter),	28	3·19	4·22	2·88	1·34	46	Müntz & Aubin.
1881	,, ,,	Plain of Vincennes,	35	2·84	3·17	2·70	0·47	17	,, ,,
,,	,, ,,	Pic du Midi,	14	2·86	3·01	2·69	0·32	12	,, ,,
,,	,, ,,	Pyrennean Valleys,	3	2·81	3·00	2·66	0·34	13	,, ,,
,,	,, ,,	Farm of the Agricultural Institute,	12	2·98	3·29	2·73	0·56	20	,, ,,
1882	,, ,,	Florida (day and night observations),	14	2·92	3·05	2·84	0·21	7	,, ,,
,,	,, ,,	Martinique (day and night observations),	10	2·80	3·08	2·68	0·40	15	,, ,,
,,	,, ,,	Mexico (day and night observations),	6	2·73	2·86	2·52	0·34	13	,, ,,
,,	,, ,,	Chubut, Patagonia (day and night obs.),	4	2·95	3·12	2·79	0·33	12	,, ,,
,,	,, ,,	Santa Cruz (day and night observations),	20	2·66	2·97	2·58	0·39	15	,, ,,
,,	,, ,,	Chili (day and night observations),	10	2·69	2·82	2·59	0·23	9	,, ,,

,, ,,	,, ,, (Hyades)	Cape Horn,	39 ?	2·56	—	—	—	—	,, ,,
,, ,,	,, ,,	Northern Hemisphere (general mean),	—	2·82	—	—	—	—	,, ,,
,, ,,	,, ,,	Southern ,, ,, ,,	—	2·72	—	—	—	—	,, ,,
*1882–1884	Russell,	London (during fogs),	37	7·05	14·10	4·50	9·60	213	Russell.
,, ,,	,,	,, (ordinary weather),	156	4·13	6·40	3·00	3·40	113	,,
1883–1884	Ebermayer,	Bavaria (forest air),	84	3·29	5·49	2·65	2·84	107	Ebermayer.
,, ,,	,,	,, (plains and mountains),	28	3·18	4·50	2·52	1·98	78	,,
,, ,,	Spring and Roland,	Liége,	266	3·35	5·25	2·67	2·58	96	Spring and Roland.
1885	Blochmann,	Königsberg,	40	3·10	3·26	2·91	0·35	12	Blochmann.
†1885–1886	Marcet & Landriset,	Malagny (near Geneva),	25	3·80	4·96	3·25	1·71	52	Marcet & Landriset.
,, ,,	,, ,,	Summit of Le Dole,	25	3·57	4·34	2·67	1·67	62	,, ,,
1887	Van Nuys and Adams,	Bloomington, U. S. A.,	18	2·82	2·90	2·73	0·17	6	Van Nuys & Adams.
,, ?	Dragendorff,	Dorpat (Russia),	366	2·66	3·60	1·90	1·70	90	—
1887–1888 ?	v. Frey,	,, ,,	566	2·62	—	—	—	—	—
1888 ?	Uffelmann,	Rostock,	—	3·18	—	—	—	—	—
1889–1891	Petermann & Graftiau,	Gembloux (Belgium),	525	2·94	3·54	2·60	0·94	36	Petermann & Graftiau.
1891	Lebedinzeff,	Odessa,	—	3·04	3·34	2·88	0·46	16	Lebedinzeff.
‡1896–1897	Carleton Williams,	Sheffield (city),	22	3·90	6·22	2·80	3·42	122	Carleton Williams.
,,	,, ,,	,, (suburbs),	142	3·32	5·19	2·21	2·98	134	,, ,,
1897	Letts & Blake,	Belfast,	46	2·91	3·31	2·48	0·83	33	Letts & Blake.

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* These figures are not exactly the same as Russell gives in his summary, but they have been very carefully compiled from his results published *in extenso* in the "Monthly Weather Reports," 1884.

† Compiled from the Tables given in the original paper (Quart. Journ. Roy. Meteor. Soc., 1887). The mean figures, however, slightly differ from those given there, and there would appear to have been a miscalculation.

‡ Compiled from the Tables given in the original paper (Commemoration Vol. Univ. Coll. Sheffield, 1897).

It will be seen that the earliest workers obtained an amount which was vastly too high: nor need any surprise be felt at this, as their method was eudiometric, and therefore not sufficiently delicate for the purpose.

Dalton, in 1802, was the first to correct the extravagant figures of Humboldt, and by employing a different method to obtain results which were only about twice as large as the correct value.

Thenard, in 1812, originated a different method, by which he obtained results which were surprisingly near the truth.

De Saussure, whose researches extended over the period 1809–1830, and who made some hundreds of observations, did not materially reduce Thenard's figure—but it is interesting to notice, as Blochmann has pointed out, that his figures almost steadily decreased as his work progressed.

From this time until about the year 1870, the normal amount of atmospheric carbonic anhydride appears to have been taken as 4 in 10,000 vols., and we fancy that many chemists are inclined to quote this figure even at the present day.

Later researches have, however, made it clear that a reduction on that amount of at least 25 per cent. must be made for the quantity in the "fresh air" of most localities, with the exception of towns.

It is difficult to say exactly to what observers we are indebted for this revision. In 1848–1850 Marchand, at Halle, had found an average of 3·10 in 150 determinations; and, in 1865, Angus Smith an average of 3·36 in 92 determinations on the air of the country in Scotland. Thorpe, in 77 experiments made in 1865–1866 on ocean air, had found 3·0, and F. Schulze, a yearly average from 1868–1871, at Rostock, varying between 2·86 and 3·01. Marchand's determinations do not appear to have been generally known, and the lowness of the other figures was at first attributed to the proximity of the places of observation to the sea; but the very careful work of Reiset partly at Paris, and of Müntz and Aubin, not only in France, but in various localities visited by the French expeditions sent out to observe the Transit of Venus, in 1882, and subsequently, the results obtained by most other observers have shown that the true amount oscillates about an average of 3 in 10,000, or according to Müntz and Aubin, 2·82 for the northern hemisphere, and 2·72 for the southern.

SECTION II.—CAUSES OF VARIATION.

In attempting to review and criticise the subject of the variations in the amount of atmospheric carbonic anhydride many difficulties are encountered, and perhaps not the least of these is to correctly appraise and estimate the value of the evidence brought forward in support of the different contentions which have been raised from time to time in this matter.

We have seen that it took at least seventy years for chemists to arrive at a correct estimate of the average amount, and that during that time the figure has dwindled down from 100 to 200 vols. in 10,000, to about 3.

As most of the later authorities agree that the variations in this amount which are caused by natural agencies are small—the resources of the most reliable of our present methods of determination are taxed to their utmost, and therefore it is not surprising to find a conflict of opinion among those who are entitled to speak with authority on the subject, not only as regards the causes of the variations but as to their extent also.

Two opposite views have been maintained, of which De Saussure, and Gay Lussac were the respective authors. According to the first of these, considerable variations in the amount of atmospheric carbonic anhydride occur, of a more or less lasting or permanent nature, caused by natural agencies such as the seasons, influence of vegetation, the direction and force of the wind, humectation and desiccation of the soil, day and night, &c.

Gay Lussac, on the other hand, was of opinion that owing to the continuous movements of the air, both horizontally and vertically, practically uniform distribution or diffusion of the carbonic anhydride occurs. It must be at once granted, from the evidence which has since been forthcoming that Gay Lussac's opinion is correct to the extent that the variations are much less than De Saussure and others of his school believed and that the *average* amount of atmospheric carbonic anhydride is much the same under the most diverse conditions of weather, locality, season, &c.

But on the other hand, there can be no doubt that variations in the amount do occur; that, to a certain extent, they are lasting and that they owe their origin to natural agencies. These variations, if small in actual amount, are *relatively* large, and correspond with fluctuations of at least 10 per cent. of the total quantity, and according to some observers to a much higher figure.

Thus the oscillations in the amount of atmospheric carbonic anhydride must be admitted, even by those who take the lowest estimate, to be comparable in extent with the variations which occur in atmospheric pressure, and they may have a significance quite as important as these latter.

But in attempting to unravel the separate effects of those natural agencies which influence the proportion of atmospheric carbonic anhydride, very great difficulty is experienced, and indeed the task appears to be almost impossible in some cases with the material at present available for discussion.

This is due in great measure to the fact that many of the natural agencies are antagonistic in their effect, and that several of them may be acting at the same time, thus giving a mixed result. Then, too, a difficulty arises as to the trustworthiness of the work of some of the observers—the fact that they have in many cases employed different methods of determination, and that very few of these have been tested as regards their degree of absolute accuracy—and also that the observers have collected their air samples at different heights above the ground.

In our opinion, the subject is an important one, and is worthy of a systematic re-investigation by a number of skilled observers, working in different localities and employing the same method of determination, which shall have been proved to give results which do not vary from the true amount by more than two or three parts per million of air.

In the following pages we propose merely to collect and review the evidence which has been brought forward regarding the extent and the causes of variation of the amount of atmospheric carbonic anhydride.

Locality and Local Effects.

The influence of locality is, as might be expected, well marked in the air of towns compared with that of their suburbs, or of country and sea-side places, and abundant evidence is forthcoming as to an excess of carbonic anhydride in the former. The main cause of increase is no doubt to be found in the combustion of fuel and illuminants, but the respiration of men and animals, the decay of refuse, &c., are also important sources of evolution.

Boussingault, in a paper published in 1844,[1] calculated that the following quantities of carbonic anhydride in cubic metres were thrown into the air of Paris every twenty-four hours:—

By the population,	336,777
,, horses,	132,370
,, wood burnt,	855,385
,, charcoal burnt,	1,250,700
,, pit coal burnt,	314,215
,, wax burnt,	1,071
,, tallow burnt,	25,722
,, oil burnt,	28,401
Total,	2,944,641

(giving the ratio of carbonic anhydride produced by combustion to that owing its origin to respiration of about 5 : 1). He then goes on to calculate that if this amount was suddenly thrown into the air of Paris it would form a layer nearly $\frac{1}{10}$ metre deep.

It is interesting to carry this calculation further.

Boussingault found 4·0 parts of carbonic anhydride per 10,000 in the air of Paris, and we now know that the average for country air is about 3·0. If Boussingault was correct, Paris air (like London air) contains $\frac{1}{3}$ more carbonic anhydride than fresh air, or we may state the case this way:—

1 cubic metre of "fresh" air contains	0·3 litres CO_2
,, ,, ,, ,, Paris ,, ,,	0·4 ,, ,,
Difference,	0·1 ,, ,,

But if all the carbonic anhydride generated in Paris were thrown suddenly on to the surface of the ground each cubic metre of the air there would contain 100·0 litres; but as the actual increase is 0·1 litres per cubic metre, it follows that the total average effect is the dilution of the carbonic anhydride thrown into the Paris atmosphere 1000 times by fresh air, the latter receiving an addition of 33·3 per cent. in the process.

It is possible that Boussingault's estimate of the carbonic anhydride in Paris air is too high, and that the difference between

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[1] Annales de Chimie et de Phys. [3], 10 [1844], p. 461.

it and the amount in fresh air is less than 1 in 10,000 (though Russell has shown that this is the difference between London air and fresh air).

If we take Müntz and Aubin's figures for the Plain of Vincennes and Paris respectively, the mean difference is 0·35, or about $\frac{1}{3}$ of the amount taken in the above calculation, which would give a dilution of the carbonic anhydride thrown into Paris air of 3000 times.

These figures will give some idea, at all events, of the extent of the diluting effects occurring in a town by natural agencies.

In the following table we have collected some typical examples of the differences between the air of towns and country.

THE AMOUNT OF ATMOSPHERIC CARBONIC ANHYDRIDE IN TOWN AND COUNTRY.

Observer.	Town.	CO_2 in 10,000 of air (mean).	Country.	CO_2 in 10,000 of air (mean).
A. Smith, . . .	Manchester streets,	4·03	Manchester (suburbs)	3·69
,, ,, . . .	London, . .	4·39	2 mls. from Clapham,	3·45
,, ,, . . .	Perth, . .	4·14	Scotland (country), .	3·36
,, ,, . . .	Glasgow, . .	5·02	,, ,, .	,,
Müntz & Aubin, .	Paris, . . .	3·19	Plain of Vincennes,	2·84
Spring & Roland, .	Liége (Belginm), .	3·35	—	—
Petermann & Graftiau,	—	—	Gembloux (Belgium),	2·94
Carleton Williams, .	Sheffield (town),	3·85	Sheffield (suburbs),	3·26

As examples of the effects of purely local conditions the following may be mentioned.

The average amount of atmospheric carbonic anhydride found by Russell during an investigation of London air extending over two and a-half years (January, 1882, to May, 1884), was, excluding fogs, 4 in 10,000 volumes, compared with 3 in pure country air. "The smallest amount of carbonic acid found in the city air was 3·0, and this was on a Bank Holiday, August 7th, 1882. In fact it appears that the amount is usually low on these holidays, for on both Whit Monday and the August Bank Holiday of last year the carbonic acid only amounted to 3·3 parts."[1]

During Reiset's investigations of the air near Dieppe, he says:—"The presence of a flock of three hundred sheep in the neighbourhood of the apparatus during a fine calm day was revealed by a notable augmentation in the proportion of the carbonic anhydride: 3·178 volumes were obtained in 10,000." (Average for Dieppe, 2·963.)

Another very remarkable case of the effects of purely local conditions has been recorded by Lewy (in 1847).[2]

"The analyses," he says, "of the abnormal air of New Granada present us with results not less interesting. From time to time once or twice in the year the atmosphere of New Granada contains an extraordinary proportion of carbonic anhydride, which coincides with an appreciable decrease of oxygen, and consequently alters the composition of the atmosphere in a very marked manner. The great number of volcanos which exist in the New World, and the clearing of forests which is effected every year in this country, may cause the alteration. It is, in fact, during these clearances that the constitution of the atmosphere experiences the extraordinary changes I have mentioned.

"These clearings, which are effected by vast conflagrations, called in the country *las quemas*, produce considerable quantities of carbonic anhydride, which, mixing with the atmosphere, alter its composition. The amount of carbonic anhydride which I found in this air rose in some analyses to 49 in 10,000, diminution in oxygen sometimes to 0·68 (per cent.). Instead of 21·01 I found only 20.33."

In the examples noticed above the conditions may be said to be artificial. The question however arises whether locality itself, apart from such conditions, has any distinct influence, and we think that the answer must be given in the affirmative. At least it would seem that there is a fair agreement in the results of a number of different investigators, that the air of inland localities is richer in carbonic anhydride than that of districts either situated at the seaside itself or near it, or even in the neighbourhood of

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[1] Russell: Monthly Weather Reports Met. Council, April, 1884, p. 15.

[2] Lewy, "Journ. prakt. Chem.," 54 [1851], p. 253, and Phil. Mag., [4] 2 [1851], p. 500.

large freshwater surfaces. The following table (from which large cities have been purposely excluded) will show this :—

Near Sea or Lake.			Inland.		
Observer.	Locality.	CO_2 in 10,000 of Air (mean).	Observer.	Locality.	CO_2 in 10,000 of Air (mean).
De Saussure, .	Lake of Geneva	4·39	De Saussure, .	Chambeisy, .	4·60
Reiset, . .	Dieppe, .	2·96	Risler, . .	Calèves, .	3·03
Schulze, . .	Rostock, .	2·92	Henneberg, .	Weende, .	3·20
Thorpe, . .	Atlantic, .	2·95	A. Smith, .	Scotland (country), .	3·36
Claesson, .	Lund, . .	2·79	Farsky, . .	Tabor, . .	3·43
			Thorpe, . .	Para, . .	3·28
Dragendorff, .	Dorpat, .	2·66	Fittbogen and Hässelbarth,	Dahme, .	3·34

Some exceptions may be found to this rule, but they are not numerous. Thus Macagno, as the mean of his determinations at Palermo (sea side), found 3·60, while against this figure where excess of carbonic anhydride appears, we have that of Petermann and Graftiau at Gembloux (inland), viz. 2·94, and of Müntz and Aubin for the Plain of Vincennes (inland) 2·84—quantities even lower than those found at some of the seaside localities. Considering that the chief sources of evolution of carbonic anhydride are confined to land surfaces, it is not at all surprising to find that as a rule a slight excess of the gas appears in the air over them, and in this connection it may be mentioned that Spring and Roland attribute the high figure at Liége (3·35) as partly due to evolution of carbonic anhydride from the ground, the soil there overlying coal strata, and emitting large quantities of that gas.

According to Müntz and Aubin, another effect of locality is to be found in the slightly larger amount of carbonic anhydride in the air of the northern hemisphere compared with that of the southern. The figures they give for these two, as the general mean, being 2·82 and 2·72 respectively ; and they attribute the difference to the fact that the larger water surfaces of the southern hemisphere are cooler than those of the northern, where land surface predominates ; hence, according to Schlœsing's theory, the pressure of carbonic anhydride is greater in the second than in the first. A further consequence of Schlœsing's theory should be that the amount of atmospheric carbonic anhydride—especially over or near the sea—should vary with the temperature of the ocean, and therefore with latitude, and it might also be expected that ocean currents like the Gulf Stream would have an effect.

Unfortunately, however, the experimental data available for the discussion of this point are scarcely sufficient to warrant any very definite conclusions. We have, however, collected in the subjoined table what we consider to be the most reliable figures bearing on the subject.

Latitude.	Locality.	Observer.	No. of Observations.	CO_2 in 10,000 Vls. of Air.		
				Mean.	Maxm.	Minm.
58° 27′ N.	Dorpat,	Dragendorff,	366	2·66	3·60	1·90
55 20 N.	Lund,	Claesson,	31	2·79	3·27	2·37
54 42 N.	Königsberg,	Blochmann,	40	3·10	3·26	2·91
54 36 N.	Belfast,	Letts & Blake,	46	2·91	3·31	2·48
54 27 N.	Grasmere,	Armstrong,	53	2·96	3·26	2·71
54 21 N.	Irish Sea,	Thorpe,	26	3·08	3·32	2·66
54 0 N.	Rostock,	Schulze,	1034	2·92	3·50	2·25
50 34 N.	Gembloux,	Petermann & Graftiau,	525	2·94	3·54	2·60
49 55 N.	Dieppe,	Reiset,	104	2·90	3·24	2·74
48 49 N.	Plain of Vincennes,	Müntz & Aubin,	32	2·83	3·17	2·70
29 54 N.	Florida,	,, ,,	8	2·90	2·97	2·87
19 10 N.	Mexico,	,, ,,	4	2·66	2·81	2·52
18 0 N.	Haiti,	,, ,,	10	2·70	2·86	2·60
14 36 N.	Martinique,	,, ,,	4	2·73	2·76	2·71
1° 27′ S.	Para (Brazil),	Thorpe,	31	3·28	3·49	3·07
33 16 S.	Chili,	Müntz & Aubin,	8	2·66	2·76	2·59
43 18 S.	Chubut,	,, ,,	2	2·79	2·79	2·79
50 0 S.	Santa Cruz,	,, ,,	14	2·66	2·97	2·58
55 58 S.	Cape Horn,	Hyades, ,,	39	2·56	—	—

If we accept Thorpe's figures for tropical Brazil as representing the amount of carbonic anhydride in the air of the tropics, and omit Müntz and Aubin's figures for central and southern America, then the Table undoubtedly indicates a diminution for higher latitudes in the northern hemisphere, which, with a few exceptions, would appear to be progressive and to hold good both for the mean and minimum amounts.

Müntz and Aubin's figures are somewhat puzzling, whether taken alone, or in conjunction with those of the other observers. The mean amount found at Florida (2·90) is, it is true, higher than the mean for the Plain of Vincennes (2·83) or on the Pyrennean mountains (2·86); but at Mexico a sudden drop occurs, and at Martinique the figure (2·73) is actually lower than at the Plain of Vincennes. Again, in the southern hemisphere they found a larger proportion at Chubut (2·79) than at Chili (2·66), where a surprisingly low amount was obtained. But further south the results are certainly in harmony with Schlœsing's theory: thus, at Santa Cruz a mean of 2·66 was found, and it is interesting to note that Dragendorff found precisely the same amount at Dorpat. Lastly, at Cape Horn 2·56 was found as a mean—the lowest mean figure we believe recorded by any of the observers. Here the interesting observation was made that the amount of atmospheric carbonic anhydride varied with the temperature of the sea water, 2·530 being obtained as the mean volume for temperatures below 5° C. and 2·598 for temperatures above 5° C.

Thorpe made determinations of carbonic anhydride in the air of the Atlantic almost daily (after Madeira was reached) during a voyage from Liverpool to South America. He was thus working under very favourable conditions for tracing variations dependent on latitude. Unfortunately, he does not specifically state the latitudes corresponding with the different observations, but a study of the numbers obtained by him reveals no steady increase as the equator was reached. The variations were irregular, but the lowest figure of all (2·69) was obtained when he must have been near the equator. He himself says the amount "is sensibly the same in different latitudes." Thus, there is evidence both for and against variations in the amount of atmospheric carbonic anhydride depending on latitude, but the experimental data are altogether insufficient to enable a definite conclusion either, one way or the other, to be arrived at. As the question is both interesting and important it is to be hoped that it will be further investigated, and will not be lost sight of by future scientific expeditions, as it has been by the past, with the solitary exception, we believe, of the French Transit of Venus expedition.

Day and Night.

As plants decompose carbonic anhydride only in presence of sunlight, it was to be anticipated that in the air over land surfaces there would be a diminution in the amount of that gas during day time, and an increase in the night. That such variations do occur, and are quite appreciable, there is abundant evidence to prove, and in the following table we have endeavoured to collect it :—

INFLUENCE OF DAY AND NIGHT ON THE AMOUNT OF ATMOSPHERIC CARBONIC ANHYDRIDE.

	Date of Observation.	Observer.	Locality.	Number of Observations.		CO_2 in 10,000 Vols. of Air. Mean Results.		Excess.			
								Absolute.		Percentage.	
				Day.	Night.	Day.	Night.	Day.	Night.	Day.	Night.
SEA.	1847	Lewy,	Atlantic,	7	4	5·30	3·46	1·84	—	53	—
	1865	Thorpe,	Irish Sea,	14	12	3·08	3·085	—	·005	—	·16
	1866	,,	Atlantic,	25	26	2·97	2·94	·03	—	1	—
LAND.	1827–1830	De Saussure,	Geneva,	52	52	3·98	4·32	—	·34	—	8
	1840–1841	Boussingault,	Paris,	?	48	3·90	4·20	—	·30	—	8
	1875	Truchot,	Clermont Ferrand,	—	—	3·53	4·03	—	·50	—	14
	,,	Wolffhügel,[1]	Munich,	35	35	3·93	4·04	—	·11	—	3
	1877	v. Fodor,	Buda-Pesth,	—	—	4·18	4·26	—	·08	—	2
	1879	Armstrong,	Grasmere,	53	62	2·96	3·30	—	·34	—	11
	,,	Reiset,	Near Dieppe,	42	31	2·89	3·08	—	·19	—	7
	1882	Müntz & Aubin,	Florida,	8	6	2·90	2·95	—	·05	—	2
	,,	,, ,,	Martinique,	4	6	2·73	2·85	—	·12	—	4
	,,	,, ,,	Mexico,	4	2	2·66	2·86	—	·20	—	7
	,,	,, ,,	Chili,	8	2	2·66	2·82	—	·16	—	6
	,,	,, ,,	Chubut (Patagonia),	2	2	2·79	3·12	—	·33	—	12
	,,	,, ,,	Santa Cruz, ,,	14	6	2·66	2·67	—	·01	—	·37
	1882–1883	,, ,,	Haiti,	10	6	2·70	2·92	—	·22	—	8
	,, ,,	,, ,, (Hyades),	Cape Horn,	—	—	2·563	2·556	·007	—	·27	—
	1885 ?	Wollny,	Munich,	—	—	3·30	4·25	—	·95	—	29

Thorpe gives no separate summaries as regards the day and night determinations in the air over the Irish Sea and Atlantic respectively, but collects them into a single table (Chem. Soc. Journ. Trans., 5 [1867], p. 197), and gives details from which the above figures were obtained. As regards these details, he tells us that in the Irish Sea, determinations were made at 4 a.m. and 4 p.m. respectively, and he gives two columns, headed "Expt. 1" and "Expt. 2." These, however, do not refer to results obtained at 4 a.m. and 4 p.m. respectively; and this introduces an element of confusion into the calculations. But when we get to the Atlantic air definite mistakes in his Table (so far, at least, as appears from the printed account of his work) have crept in. Under column headed "Day," Nos. 14, 42, 44, and 47 refer, we are elsewhere told (on p. 196), to 11.38 p.m., 9 p.m., 9 p.m., and 8 p.m. respectively; while under column headed "Night," Nos. 43, 45, and 46 refer to 11.15 a.m., 7.30 a.m., and 10.45 a.m.

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[1] Compiled from Wolffhügel's Tables. Only those day and night observations have been taken which immediately succeed each other.

On the other hand, the cause for this variation no longer exists over the ocean, and according to Levy's observations, not only does the variation itself cease, but it is actually reversed. Thorpe also found a minute excess in Atlantic air during the day time. This may be explained, as Levy supposed, by the evolution of the dissolved gases from the surface layers of the sea as they become heated by the sun, and a corresponding absorption as the temperature falls at night. From Thorpe's observations of the air over the Irish channel it would appear that there was practically no variation owing to night and day, which is very interesting, as the light ship on which his determinations, were made was only seven miles distant from land (the Isle of Man), hence the air which he examined was subject to both land and sea influences.

Hyades also, at Cape Horn, found a slight excess in day air. This may be explained by the almost complete absence of vegetation there, and also by the fact that the Cape is virtually surrounded by the ocean, the temperature of which is higher during the day than at night.

v. Fodor, Wollny,[1] and others explain the increase in the carbonic anhydride of night air over land surfaces as being due, not to the cessation of vegetable activity, but to ground air, which is very rich in carbonic anhydride. As night approaches, and the temperature falls, the ground air, which is then warmer than the atmosphere, escapes in considerable quantities, and, mingling with the latter, increases the amount of its carbonic anhydride.[2]

Considering the difficulty which has been experienced in tracing any considerable variation in the amount of atmospheric carbonic anhydride caused by vegetation, and also bearing in mind v. Fodor's observations on air at different heights above the surface of the ground, showing what an important influence ground air exercises on the amount of atmospheric carbonic anhydride, we are inclined to believe that v. Fodor's explanation is in the main the true one, more especially as the vegetation theory, while possibly explaining diminution during the day time, fails to account for the increase at night.

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[1] v. Fodor, "Luft, Boden, und Wasser," p. 53, and Wollny, "Forschungen a. d. Geb. d. Agrikultur-Physik," 8 [1885], p. 417.

[2] See Appendix on Ground Air, p. 214.

As additional evidence, he gives the amounts of carbonic anhydride he found in air taken at the surface of the ground during September, 1877. The mean quantities for thirty day, and the same number of night, determinations were 6·41 and 7·00 respectively—thus showing the very considerable variation of 0·59 which could scarcely be due to anything else than ground air, as his experiments were made within the town of Buda Pesth, and presumably the air was collected above a surface on which no grass was growing.

Whether we take the view that the variations are caused by vegetation or by ground air, the seasons should have an influence, and according to v. Fodor this is actually the case. He gives figures from which the following mean variations have been deduced—

	Excess :—	
	At Night.	During the Day
March,	——	0·12
April,	——	0·39
September,	0·72	——
October,	0·18	——
November,	——	0·02

His explanation of these is as follows :—That the nightly carbonic anhydride is so high in autumn, while in spring more of the gas is found during the day, depends upon the fact that it is in autumn especially that the nights are cool, and consequently it is then that the atmosphere can most readily drive out the warm ground air. In the early part of the year, on the contrary, very little ground air streams out, and indeed at this time the atmosphere will gain carbonic anhydride from the soil by day rather than by night, for it is during the day time that the superficial layers of the soil get warmed through, and processes of decay are active. Some observers have maintained that variations also occur during the day time, and among them were Mène and Truchot. Their figures, however, we agree with v. Fodor in thinking, are quite unreliable, and therefore we do not give them.

As we have mentioned elsewhere, Fittbogen and Hässelbarth found in the summer a sudden decrease shortly after sunrise, and a general decrease from then until mid-day, which they attribute to the action of the awakened and refreshed vegetation.

v. Fodor has investigated this matter, and, as the result of numerous and careful determinations, came to the conclusion that the amount is fairly constant during the day, but experiences a considerable increase in the evening—the excess observed at night time being poured into the atmosphere from the ground, chiefly during the evening hours.

Influence of Vegetation.

It is somewhat remarkable that very few details are to be found in the numerous memoirs which we have studied which bear on this point. Truchot found a marked *increase* in the quantity of atmospheric carbonic anhydride in the neighbourhood of vegetation, varying during the day from 0·40 vols. per 10,000 (sun) to 1·01 (cloud).

Reiset's results are somewhat conflicting. He tells us that the mean of 27 observations made of the air in a well-wooded coppice gave 2·917, while that obtained at the "field station" (with samples taken at the same hours) amounted to 2·902, showing, therefore, a slight excess in the former. On the other hand, five samples taken over a field of red clover in full flower in June showed an appreciable diminution (mean = 0·017) from that taken at the "normal station"; and also that in a barley field planted with lucern in full vegetation a larger diminution (mean = 0·104) was found.

Müntz and Aubin, without making any special experiments on the influence of vegetation, explain the fact that atmospheric carbonic anhydride is at its minimum when the sky is clear and the air agitated, by the increased activity of vegetables, and the rapid diffusion (by wind) of the carbonic anhydride produced at the surface of the soil.

Fittbogen and Hässelbarth found during observations made in the summer that a decrease was apparent from sunrise to mid-day, and all their experiments showed a sudden decrease shortly after sunrise, which they attribute to the action of the awakened and refreshed plants.

Simultaneous observations made by Wollny in calm weather over fallow land, and land clothed with vegetation, gave the following results :—

	0.2 Metres above—		Difference.
	Fallow Land.	Clover.	
Mean of 4 determinations in 1880, . .	3·72	3·45	0·27
,, ,, ,, ,, . .	4·43	3·88	0·55

	2.0 Metres above—		Difference.
	Fallow Land.	Clover.	
Mean of 4 determinations in 1881, . .	3·24	3·06	0·18
,, ,, ,, ,, . .	3·82	3·60	0·22

One would naturally expect that forest air, especially in summer, when the trees are in full vegetation, would contain less carbonic anhydride than the air outside the forest, but Ebermayer, who made a very complete investigation on this point during 1883–1884,[1] found that this was not the case, at all events as regards the air near the surface (1½ metres from ground level).

Rejecting the results obtained by the ordinary Pettenkofer process, which he considered were too high,[2] and taking only those obtained by the aspiration method, he found as a mean of eighty-four experiments on the air of Bavarian forests of different descriptions of wood, of different ages, &c., 3·29 of carbonic anhydride in 10,000 volumes of air, which he contrasts with the amount found by other observers in various parts of the world in ordinary air, and with those obtained by himself on the Bavarian plains (Hochebene), (3·20–mean of 19 determinations), and on the Bavarian mountains (3·16–mean of 9 determinations), from which he concludes that on the whole the amount in forest air is not different from that in ordinary air.

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[1] After a preliminary inquiry with Swappach in 1877–1878.

[2] See p. 225.

One paragraph, however, in his pamphlet, "Die Beschaffenheit der Waldluft" is of peculiar interest.

"To obtain a complete insight into the nature of forest air, it is necessary that the air should be examined during the time of vegetation, not only over the ground but also among the leafy tree crowns on clear and dull days."

"In the Karsten forest, in a plantation of sixty-year-old pine-trees, several experiments were conducted in such a way that a leaden tube was attached to a tree 25 metres high, reaching from the bottom to the middle of the crown. The lower end was attached to a baryta tube, and 10 litres of the 'crown' air were drawn by an aspirator through the baryta. There resulted, however, in these experiments always so little carbonic anhydride, that possibly some of it combined, during its long passage through the tube with the lead which had become moist. Therefore I shall not regard the result of these troublesome determinations as decisive, but propose to repeat them in such a way that the baryta tube, shall be fastened within the tree crown, and a large quantity of air aspirated from below. At the same time I propose to examine the 'crown' air for its content of oxygen."

Unfortunately, however, we can find no account of the results of these proposed experiments which would have been of very great interest, in view of the fact that there is such slight experimental evidence of any definite effect of vegetation in reducing the amount of atmospheric carbonic anhydride.

The want of this evidence is very probably due to the fact that all the observers have experimented close to the surface of the ground, and as a consequence their results have been affected by ground air.

The following considerations have occurred to us and may be of interest:—

Assuming that 1 square metre of leaf surface decomposes 1 litre of carbonic anhydride per hour,[1] and also assuming that air contains 3·3 part of the gas per 10,000, the litre is contained in an air space 1 square metre in area, and 3 metres high. A tree

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[1] Ostwald ("Outlines of General Chemistry," 1890) gives 0·000,000,0537 grm. as the amount of starch formed, according to Pfeffer, by one square centimetre of oleander leaf per second, which corresponds with an absorption of about 1·6 litres of carbonic anhydride per hour for each square metre of leaf surface.

in full foliage should, we imagine, expose more than 1 square metre of leaf surface to every square metre of land surface it covers. Suppose, then, a tree 3 metres high, in full vegetation, it would decompose all the atmospheric carbonic anhydride in its immediate neighbourhood in an hour, or, if it were 36 metres high, in a day.[1]

Therefore, in still air and in sunshine, the influence of vegetation on the amount of atmospheric carbonic anhydride ought to be very perceptible, especially in the neighbourhood of leafy tree crowns well above the soil, and consequently not subjected to the immediate effects of ground air. But wind will play a very important part in marking this action. Even, however, on a moderately breezy day we think it ought to be possible to trace an action by comparing the air at the weather and lee sides, respectively, of a forest or large plantation.

Suppose this imaginary case: namely, a forest twenty miles long, enclosed in a perfectly transparent air-tight, rectangular box, 36 metres high, open at the weather and lee sides, and so arranged that while the tree trunks project through its bottom, no ground air can gain admission. Then, with a gentle to moderate breeze of force 3–4 on Beaufort's scale, or velocity of twenty miles to the hour, air would remain in contact with the forest for one hour, and supposing equal admixture of all its parts, would contain on emerging $\frac{1}{12}$ less of its original amount of carbonic anhydride—a diminution say of 0·25 parts per 10,000 of air, a variation which could readily be detected. Of course, on the lee side of a forest under the actual conditions nothing like this reduction could be expected, owing to vertical movements of the air currents, evolution of carbonic anhydride from the soil, &c., which may account for Ebermayer's results.

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[1] Since writing the above, Horace T. Brown, in his very interesting address as President of the Chemical Section of the British Association (1899), has described the results of experiments on the rate of absorption of atmospheric carbonic anhydride by the leaves of growing plants, contained in transparent vessels, through which a current of ordinary air passed. In one such experiment the air, before entering the vessel, contained 2·80 parts CO_2 per 10,000, and on leaving 1·74, showing therefore a loss of 1·06, which corresponded with a rate of assimilation of 412 c.c. CO_2 at N.T.P. per square metre of leaf surface per hour. He also found that under constant illumination *the intake was directly proportional to the tension of the gas.* (See "Nature," 60 [1899], p. 479.)

Any diminution of atmospheric carbonic anhydride by the action of vegetation should correspond with an increase of atmospheric oxygen, of precisely the same amount, and it is therefore of interest to enquire into the variations which have been observed in the quantity of atmospheric oxygen. That variations do occur, has been recognized by all who have undertaken analyses of air; but, as in the case of atmospheric carbonic anhydride, the older observers found a larger variation than actually occurs. Some of their more important results were as follows[1]:—

	Percentage of Oxygen.		Variation.
	Maximum.	Minimum.	
Gay Lussac and Humboldt, ...	21·20	20·90	0·30
De Saussure, ...	21·15	20·98	0·17
Regnault, ...	21·00	20·90	0·10
Bunsen, ...	21·18	20·80	0·38

Coming to more recent work on the subject we have—

Date.	Observer.	Percentage of Oxygen.		Variation .
		Maximum.	Minimum.	
1875–76	Jolly, ...	20·960	20·470	0·490
1877	,, ...	21·010	20·530	0·480
1883–84	Kreusler, ...	20·991	20·867	0·124
,,	,, (deducting exceptional amounts),	20·940	20·880	0·060
1885	Hempel, ...	20·971	20·877	0·094

In 1886, the excellent idea occurred to Hempel of inviting the cooperation of several observers in different parallels of latitude, to collect samples of air at the same time (making due allowance for differences in longitude), for the purpose of oxygen determinations.

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[1] The figures are taken, partly from Roscoe and Schorlemmer's "Treatise on Chemistry," and partly from Angus Smith's "Air and Rain."

Morley, at Cleveland, U.S.A., and Kreusler, at Bonn, collected and analysed their own samples by two different methods, namely, explosion with hydrogen (Morley), and ignition with copper (Kreusler). Air samples from Tromsö in Norway, and from Para in Brazil, were collected by local scientific men and sent to Hempel, at Dresden, for analysis, in sealed tubes, where he also collected samples. All of these he analysed by absorption with caustic potash and pyrogallic acid. Unfortunately, he did not attempt to determine the carbonic anhydride separately, but contented himself with determinations of its joint amount with oxygen, from which he deducted 0·03 per cent. in all cases, to arrive at the percentage of oxygen.

In the subjoined table, we give the mean figures appearing in Hempel's memoir,[1] but the maxima and minima and the resulting variations we have ourselves collected from the figures, as they are not specifically stated in his summary :—

Latitude.	Locality.	Analyses made by—	Percentage amount of Oxygen.			Variation.
			Mean.	Maxm.	Minm.	
69° 40′ N.	Tromsö (Norway), .	Hempel,	20·92	20·97	20·87	0·10
51 30 N.	Dresden (Saxony), .	,,	20·90	20·93	20·85	0·08
50 50 N.	Bonn (on the Rhine), .	Kreusler,	20·92	20·94	20·90	0·04
41 27 N.	Cleveland (United States)	Morley,	20·93	20·95	20·90	0·05
1 27 S.	Para (Brazil), . .	Hempel,	20·89	20·96	20·83	0·13

We may therefore assume that the total variation is about 0·08 per cent. (mean of the above variations), or probably about eight times that of the atmospheric carbonic anhydride.

Kreusler gives the following table, indicating seasonal variations :—

January, . . .	20·910	July, . . .	20·918
February, . .	20·911	August, . . .	20·920
March, . . .	——	September, . .	20·913
April, . . .	20·910	October, . . .	20·909
May, . . .	20·910	November, . .	20·905
June, . . .	20·917	December, . .	20·906

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[1] Hempel, "Berichte d. deutsch. chem. Ges.," 20 [1887], p. 1864.

from which it would appear that the amount of atmospheric oxygen does perceptibly increase during the period of vegetable activity, and decrease when vegetation is dormant.

Influence of Atmospheric Precipitates—(1) *Fog and Mist.*

The first observer to draw attention to the influence of fog and mist on the amount of atmospheric carbonic anhydride was, we believe, Angus Smith.[1]

In his summary of the results of his examination of the air of Manchester he gives the figures :—

During fogs, ...	6·79
Ordinary weather, ...	4·03

Since then, Russell[2] has published a series of investigations on the amount during London fogs, and has contrasted it with the quantity found under normal conditions. His experiments extended from January, 1882, to April, 1884, during which period he recorded twenty-nine observations made in fogs of different degrees of density, and one hundred and thirty under normal conditions. His results may be summarised as follows :—

	During Fogs.	Vols. of CO_2 in 10,000 air.	Ordinary weather.	Vols. of CO_2 in 10,000 air.
Maximum,	Dec. 11th, 1882, 5 p.m. Thick, white fog,	14·1	Oct. 23rd, 1882. Fine,	6·4
Minimum,	Oct. 10th, 1882, and Jan. 18th, 1884. Slight fog,	4·5	Aug. 7th, 1882. Very fine (Bank Holiday),	3·0
Mean, .	(29 observations), . .	7·2	(130 observations), . .	4·0

The table he gives, showing several instances of the rapid

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[1] Angus Smith, "Air and Rain," p. 52.

[2] Russell, (1) Monthly Weather Report of the Meteorological Office for April, 1884 ; (2) Meteorological Council Report, ending March, 1884.

change in the composition of the air with the clearing off of a fog, is also of interest :—

Date.	CO_2 in 10,000 Vols. air during fogs.	CO_2 in 10,000 Vols. air when fog has cleared.
October 26, 1882.	9·9	5·0 (2 hours after).
November 18, 1882.	9·6	5·0 (1½ ,, ,,).
December 1, 1882.	5·5	4·1 (4½ ,, ,,).
December 20, 1882.	8·1	5·2 (1½ ,, ,,).
October 11, 1883.	7·6	5·1 (5 ,, ,,).
April 27, 1884.	5·3	4·6 (2½ ,, ,,).

In both London and Manchester fogs the conditions may be said to be artificial, and, no doubt, the combustion of coal is mainly responsible for the very high proportion of carbonic anhydride. But Reiset proved that even in country districts a marked increase occurs during misty and foggy weather. "Twelve experiments," he says, "made under these conditions, in 1879, have given a mean of 3·166. In 1880 (mean of five experiments), 3·233[1] during calm nights with fogs or mists. . . . One remarks, with interest, that in series 2 of the determinations the absolute maximum 3·415, on the 3rd of September, was succeeded, after twenty-four hours of an interval, by a minimum of 2·743, obtained on a bright sunshiny day. An intense fog, with northerly wind, had brought about this sudden perturbation in the proportion of the carbonic gas." His explanation of the cause is as follows :— "The vesicular vapour which constitutes fog can without doubt condense a small proportion of carbonic anhydride in a determinate volume of air; but I have not been able to establish any relationship between the hygrometric condition of the air and the proportion of carbonic acid. It would be more rational, perhaps, to admit, that during the calm which accompanies fog, the air, which so to speak is confined, is submitted to the direct influence of emanations from the earth, and of phenomena due to the

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[1] The mean amount of atmospheric carbonic anhydride found by him, in 1879–1880, at Dieppe, was 2·985.

action of plants, or of masses of organic matter in a state of decomposition."

In commenting on the work of Reiset and of Müntz and Aubin, Dumas goes so far as to say—"La seule cause que semble propre à faire varier la quantité géologique d'acide carbonique de l'atmosphère consiste dans la formation du brouillard. La vapeur d'eau en se condensant, ramasse l'acide carbonique, et l'air brumeuse se montre généralement plus chargé de ce gaz que l'air ordinaire."

It seems to us that foggy weather ought to occasion an increase in the amount of atmospheric carbonic anhydride, for the following reasons:—

A fog, or mist, usually occurs during an anti-cyclonic period, when the conditions are a complete calm and a gentle descenscional flow of air from the upper regions.

Emanations of carbonic anhydride, either from the soil or from the smoke of fires, are thus kept stationary, or are even depressed, and an accumulation of the gas occurs—very possibly this is aided by the screen of minute water-drops forming the mist or fog, which may prevent diffusion, and even dissolve the carbonic anhydride.

We have collected in the following table a number of determinations bearing on the effects of fog and mist on the amount of atmospheric carbonic anhydride:—

THE AMOUNT OF ATMOSPHERIC CARBONIC ANHYDRIDE DURING FOGS.

Locality.	Date.	Observer.	Ordinary Weather. CO_2 in 10,000 Vols. Air.			During Fogs. CO_2 in 10,000 Vols. Air.			Mean Increase during Fogs.	
			Mean.	Maxm.	Minm.	Mean.	Maxm.	Minm.	Absolute.	Percentage.
London, . . .	1882–1884	Russell, . . .	4·00	6·40	3·00	7·20	14·10	4·50	3·20	80
Manchester, . .	1864	Angus Smith, . .	4·03	6·04	3·11	6·79	7·34	5·23	2·76	68
Sheffield (Suburbs), .	1896–1897	Carleton Williams,‡ .	3·28	5·19	2·21	3·99	4·92	3·24	0·71	22
Buda-Pesth, .	1877–1879	v. Fodor, . . .	3·74†	?	?	3·76	?	?	0·02	0·6
Paris, . . .	1880–1881	Müntz & Aubin,‡ .	3·19*	4·22	2·88	3·55	3·61	3·49	0·36	11
Liége, . . .	1883–1884	Spring & Roland, .	3·35*	5·25	2·67	3·57	4·28	2·93	0·22	7
Tabor, . . .	1874–1875	Farsky,‡ . . .	3·43*	4·07	3·02	3·48	3·75	3·20	0·05	1
Dieppe, . . .	1880	Reiset, . . .	2·97*	3·52	2·77	3·23	3·52	2·94	0·26	9
,, . . .	1879	,, . . .	2·98*	3·41	2·74	3·17	3·41	3·00 ?	0·19	6
Gembloux, . .	1889–1891	Petermann & Graftiau,	2·94*	3·54	2·60	3·13	?	?	0·19	6

* General mean—fogs included.

† Mean for days preceding fogs.

‡ Results have been calculated from the original Memoirs by ourselves.

The observations naturally fall into two groups—(*a*) town, and (*b*) country fogs, respectively. As regards the first of these, London fogs appear to be pre-eminent for the extraordinary proportion of carbonic anhydride they contain, and those of Manchester are not far behind them, it would seem.

The fogs of continental towns show a remarkable difference in this respect—clearly seen in the case of Liége (where the observations extended over a long period)—and the conditions as regards intensity of manufacturing operations would, we presume, be comparable with those of Manchester. Paris, perhaps, should be ignored, as only two fog observations are recorded in Müntz and Aubin's work, and the total number of observations is small.

Buda-Pesth is at the foot of the list for towns, and practically no difference in atmospheric carbonic anhydride can be traced there to fog.

Coming now to the country, we still find that fog or mist causes an increase, but the extent of this increase as might be expected is very different from that found in towns. The effect, however, is apparent, but from the table, at all events, its magnitude would appear to diminish as the sea coast is left and inland districts are reached.

(2) *Rain and Snow.*

The precipitation of rain, snow, &c., has been considered by many observers to exercise an important influence on the amount of atmospheric carbonic anhydride.

Thus De Saussure says:—" One of the causes which has most influence on the variations of carbonic anhydride in different seasons, or in the same seasons of different years, is the accidental humectation of the soil by rain which probably diminishes this gas either by absorbing it or by causing the earth to absorb it. In order to judge of the influence of rain, it is necessary to compare in summer or autumn a season or a month of drought with a rainy season or month. Insignificant results are obtained by comparing two or three consecutive days without rain with two or three rainy days; rain acts but slowly on the air; a strong shower (*averse*), after a dry season, does not appear to immediately diminish the carbonic anhydride. . . . The action of rain does not appear able to make itself manifest in winter or spring in the climate of

Geneva, because it is modified by congelation and thaw (of the ground), which produces a diminution of the acid even when rain does not fall."

As evidence in favour of the above views De Saussure gives the following figures:—

Date.	Rainfall in Millimetres.	CO_2 in 10,000 vols. air.	Date.	Rainfall in Millimetres.	CO_2 in 10,000 vols. air.
June, 1828, . .	10	4·79	June, 1829, . .	77	4·07
July, 1827, . .	9	5·18	July, 1828, . .	173	4·56
——	—	—	July, 1829, . .	52	4·32
Aug., 1827, . .	75	5·01	Aug., 1828, . .	128	4·28
——	—	—	Aug., 1829, . .	116	3·8
Sept., 1827, . .	30	5·1	Sept., 1828, . .	104	4·18
——	—	—	Sept., 1829, . .	254	3·57
Oct., 1828, . .	75	3·94	Oct., 1829, . .	113	3·75
Nov., 1828, . .	81	4·11	Nov., 1829, . .	138	3·39
Dec., 1828, . .	9	4·14	Dec., 1829, . .	34	3·72

Fittbogen and Hässelbarth were also of opinion that rain generally caused a decrease.

Lewy says, as regards the air of S. America: "During the fine season *normal* air contains always a little more both of oxygen and carbonic anhydride than during the rainy season."

v. Fodor, at Buda-Pesth, during observations extending over three years (1877–1879), compared the amount of atmospheric carbonic anhydride on days before rain with that on the days when rain fell, with the following results:—

	Mean vol. CO_2 in 10,000 of air on—	
	Days before rain.	Days on which rain fell.
1877, . .	4·61 . .	4·15
1878, . .	3·86 . .	3·53
1879, . .	3·68 . .	3·60

Thus confirming the statement that rain causes a diminution.

Further, he compared fifty-three days on which rain fell after dry weather with three day spells immediately after each, with the following results:—

	Mean vol. CO_2 in 10,000 of air— Rainy days.	3-day spells after rain.
Winter [Nov.–April], .	3·78	3·68
Summer [May–October], .	3·68	3·90

and concluded that the lowering effect on the carbonic anhydride observed after rain is lasting in winter, but that in summer there follows a considerable increase after such diminution. Petermann and Graftiau give the following figures for Gembloux:—

General mean [525 observations], . .	2·94
Rainy weather [120 ,,], . .	2·93

and do not consider that rain has any perceptible influence.

As regards the nature of the effects produced by rain, it has been suggested that it may itself act as absorbent of atmospheric carbonic anhydride (which is improbable, in view of the fact that by the law of partial pressures 1 litre of distilled water should dissolve only about 0·3 c.c.), or that it may induce changes in the soil causing either evolution or absorption.

v. Fodor, Wollny, and others who consider that ground air plays the chief rôle in the variations of atmospheric carbonic anhydride, lay stress on the latter explanation, *i.e.* the influence of the rain on the soil and ground air. Thus warmth and moisture will promote decomposition of the organic matter of the soil, and consequently augment the amount of carbonic anhydride in the ground air, and eventually that of the external air also, whence the increase noticed by v. Fodor in the air after rainy weather in summer. On the other hand, in winter, where putrefactive changes are not active, absorption of carbonic anhydride by the wet soil will occur without any overbalancing evolution and hence the explanation of v. Fodor's results concerning the air after rain in winter.[1]

As regards snow, there seems to be an agreement among the observers that atmospheric carbonic anhydride is in excess when it is falling.

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[1] See p. 215.

F. Schulze says, that snow fall is often associated in a strongly marked manner, with sudden increase in carbonic anhydride, and gives the following examples—

Before snow-fall.	After fall of—	
2·56	50 grm. snow.	2·71
2·69	400 ,, ,,	2·81
2·80	250 & 750 ,, ,,	3·37
2·96	240 ,, ,,	3·15
2·77	250 ,, ,,	3·04
2·75	500 ,, ,,	3·03

at the same time he remarks that there are exceptions to the rule.

Spring and Roland found the average amount of carbonic anhydride on eight days during which snow fell to be 3·761, which is considerably above the average for Liége, viz. 3·352, and even above the average for fog and mist viz., 3·571, in that town.

Farsky's results at Tabor, in Bohemia, similarly point to an increase during snowy weather, the mean amount for twenty days on which snow fell during the period of his observations (calculated by us) being 3·60, while that for Tabor generally was found by him to be 3·43. The following figures which we have collected from his results are also of interest, as tending to show not only that an increase in carbonic anhydride occurs during snow fall, but that with continued snow, a further increase takes place as a rule—

Day before snow.	Snowy day.	Following day.
3·57	3·72	3·75 (snow).
3·45	3·69	3·91 (snow).
3·47	3·52	3·49 (snow).
3·37	3·39	3·51 (snow).
3·53	3·61	3·75 (snow).
3·39	3·28	3·59 (bright).
3·41	3·75	3·62 (rain).
3·65	3·75	3·41 (fine).
3·41	3·59	3·60 (snow).

Carleton Williams also found an increase in the air of the suburbs of Sheffield during snowy weather, and gives the figures:—

Snow (average of 32 experiments), . . .	3·58
No snow (average of 110 experiments), . .	3·24

v. Fodor, at Buda-Pesth, in an extended series of observations, obtained results confirming the above, and gives the following averages—

Mean for 23 days, previous to snow fall, .	3·75
Mean for 30 days, on which snow fell, . .	3·81

Puchner, in the town of Munich, found an increase with snow fall and attributes it to a mechanical action of the snow flakes in carrying down the gaseous products of combustion into the lower atmosphere. He also observed an increase during snowy weather both in the air of the suburbs and surrounding country districts.

Lastly, we may give the results of Petermann and Graftiau's observations at Gembloux (Belgium). They found, as a mean of seventeen days on which snow fell, 3·10; the general mean for Gembloux being 2·94, and the mean for foggy weather 3·13—the highest figure representing the effect of any single meteorological factor.

The explanation which they give is that snow (and fog) augment the amount by covering the earth with a thick curtain of the vapour of water, either vesicular or crystalline, which hinders diffusion of carbonic anhydride from the soil into the superior layers of the atmosphere.

It appears to us that such an explanation of the effect of snow is improbable, for if it were true, diminution and not increase should be the result of snow fall: the layer of snow resting on the surface of the ground hindering the diffusion of carbonic anhydride into the air.

Influence of Wind.

A number of observers have maintained that the amount of atmospheric carbonic anhydride is influenced by wind in one or both of two ways, viz. by its direction and by its force.

Thus De Saussure (at Geneva) gives 3·98 as the average proportion present with strong winds, and 3·78 when the air was only feebly agitated, the observations being made at mid-day.

Reiset (at Dieppe) says:—"The great S.W. wind, which prevails in our country, often brings with it rain or tempests: it usually leads to a regime of *minima*."

Schulze (at Rostock) was of the opinion that N.E. winds from the continent increased the amount, while S.W. winds decreased it—the latter effect being due to absorption by the sea.

Farsky (at Tabor in Bohemia) also maintained that an increase occurred with N.E. winds, and with northerly winds also, while those from the N.W. and S.W. lowered the amount.

Hässelbarth and Fittbogen (at Dahme) state that the figures obtained by them show an intimate connection between the force and direction of the wind, and the amount of atmospheric carbonic anhydride. According to them, an increase in force, no matter from what direction, invariably decreases the amount. After high winds and storms the quantity almost always increases. When this does not occur it is due to the maintenance of higher winds than usual or a change in their direction.

Spring and Roland (at Liége) also considered that the amount of carbonic anhydride varied with the direction of the wind, the variations being caused by the nature of the districts traversed by the latter. Maxima were observed with N. and N.W. winds, which carried air from the town to the laboratory, while a third maximum was observed with the S.S.W. wind, which brought air from the great industrial centre of Seraing. On the other hand, the minimum was found with a N.N.W. wind coming from the elevated plateau of Hervè, celebrated for its pasturage, and a second minimum, but not so low as the first, with the S.E. wind from the elevated plateaus of Spa and Stavelot; this wind, however, passing over a manufacturing centre before arriving at the laboratory. As to the effects of force of wind, Spring and Roland were of opinion that the amount of carbonic anhydride decreased with strong winds, and increased with stagnation of the air. Petermann and Graftiau, in a series of observations (at Gembloux in Belgium) extending continuously over a period of two years (May, 1889, to April, 1891), were unable to trace any decided effect of direction of the wind. Neither a *régime* of continental air currents nor one of maritime winds, they say, influences the amount of carbonic anhydride when the air is analysed at a station removed from local influences. As to the effects of force, they considered it an unimportant factor under ordinary conditions, but from the table which they give distinct diminution appears to be the rule with high winds from all directions except N., S.W., W.N.W., and possibly W., but the average diminution for all high winds is not large.

v. Fodor, at Buda-Pesth, gives the following figures for 1877–1879 :—

	("Passat"), N., N.E., E.	("Anti-passat") S., S.W., W.
CO_2 in 10,000 air mean,	3·76	3·90
,, ,, ,, winter,	3·84	3·94
,, ,, ,, summer,	3·69	3·87

		Yearly Mean.	Mean of Windy Days.
CO_2 in 10,000 air,	1877–1878	3·935	3·891
,, ,, ,,	1879	3·788	3·656

Mention may also be made of the view held by Marié-Davy, that the oscillations in the amount of atmospheric carbonic anhydride depend upon the changes in direction of the great aerial currents, and that the former may be employed in weather forecasting—a view which we believe to be incorrect.

As regards the theoretical aspect of the question of the influence of winds, it seems almost useless to discuss it without taking into consideration other meteorological factors, such as the type of weather prevalent and the movements of the barometer and thermometer.

The anti-cyclonic type of weather is characterised by calms, high pressure, and radiation, the general movement of the atmosphere being descensional. The probable effects of such a system on the amount of atmospheric carbonic anhydride are somewhat difficult to forecast. The cold at night, coupled with high pressure, should lead to a *régime* of minima. During the day, however, solar radiation and calm might have an important influence in reversing this effect on land surfaces, the imprisoned gases of the soil escaping as the ground becomes heated by the sun's rays and rising. This movement would, however, be checked by the descenscional air current, especially towards evening, and a fog or mist result. Fogs and mists are, as is well known, prevalent in the anti-cyclonic type of weather, and all observers agree that the carbonic anhydride of the atmosphere is then at its maximum.

The effects which are likely to be produced by the cyclonic type of weather are perhaps even more difficult to forecast. In the centre of the system the air currents are ascensional, and an inrush occurs along the adjacent surfaces. Hence the amount of carbonic anhydride present in the air, at a given spot on the latter, should depend upon the nature of the surface which the wind has previously traversed. If this happens to be water, less carbonic anhydride might be expected than with land, as the latter contains the chief sources of evolution, both natural and artificial. Theoretically, diminution of pressure should lead to an increase of atmospheric carbonic anhydride over both land and sea surfaces: on the former by liberating the gases of the soil, and on the latter by causing decomposition of the bicarbonates, according to Schlœsing's theory.

Moreover, the advent of a low pressure system is usually attended with an increase in temperature, the effects of which should augment those occasioned by the diminished pressure. Therefore, in that portion of the front of an advancing cyclone, which is characterized not only by fall of pressure, but by increase of temperature and calm—and which appeals to our senses by the warm, muggy feel of the air, the smell from sewers, and the capping of hills with cloud—an increase in the amount of atmospheric carbonic anhydride should occur. But in other parts of the system this effect might be altogether destroyed by the force of the wind.

For no matter what type of weather may happen to prevail, an increase in the wind's force ought, we think, to lead to a diminution of the amount, owing to the agitation of the different air strata and the resulting rapid admixture of the pure with the impure. Very few of the observers who have studied the question of atmospheric carbonic anhydride appear to have considered their results in relation to the prevalent type of weather, and their position at the time of observation on a synoptic chart, though the subject is worthy of attention; and here, of course, the method of determination is of importance, for it is obvious that what is required is the amount of carbonic anhydride at a particular time, and not the average amount during a considerable interval. Hence, in this connection the results obtained by a method like Pettenkofer's are of far more service than those of methods like Reiset's and Müntz and Aubin's, where air passes into the absorbent during several hours.

Petermann and Graftiau give the following figures concerning the effects of pressure in relation to the amount of atmospheric carbonic anhydride :—

Height of Barometer in mm.,	720–730	730–740	740–750	750–760	760–770
Vols. CO_2 in 10,000 of air, .	3·11	2·94	2·93	2·95	2·93

Whence they conclude that pressure is without influence, except with extraordinary depressions when the amount increases.

Spring and Roland give the following summary :—

Height of Barometre in mm.,	730	735	740	745	750	755	760	765	770
Vols. CO_2 in 10,000 of air,	3·476	3·116	3·492	3·198	3·330	3·356	3·460	3·638	3·821

from which it appears that the quantity increased steadily with increase of pressure from 745–770 mm.; but the effects at lower pressure are not so obvious.

We have examined the tables of Reiset's results, and find only two observations corresponding with a barometric height below 730 mm., and in both of these he found a low amount, viz. 2·943 and 2·955, and even taking into account the five occasions when he records "tempests," the mean is 2·944, which is below his general mean, *i. e.* 2·962.

It must be recollected that Reiset's observations were made practically at the seaside, whereas those of Petermann and Graftiau were made well inland, and it is possible that this difference of locality may account for the discrepancy in the above results.

We have also examined the (British) synoptic charts for 1879, on the dates of Reiset's maxima and minima (above 3·05 and below 2·875 respectively) to ascertain whether any distinct connection could be traced between the type of weather prevailing at Dieppe and the amount of atmospheric carbonic anhydride there, but without much success.

Of the sixteen minima, nine correspond with the cyclonic type of weather, and seven with the anti-cyclonic; while of the eighteen minima, ten correspond with the anti-cyclonic, and eight with the cyclonic type. Possibly this confirms Spring and Roland's view, that stagnation of the air leads to a *régime* of maxima, and agitation to one of minima, but the evidence is by no means conclusive.

This opportunity may be taken to mention v. Fodor's figures as regards the effects of a rising and a falling barometer.

According to him, in cold periods of the year, the carbonic anhydride increases when the barometer rises, and *vice versâ*. The reverse effects are produced in the warm periods. In support of these statements he gives the figures :—

	CO_2 in 10,000 vols. air.	
	Winter 1877–1879.	Summer 1877–1879.
Barometer rising, . .	4·10 . .	3·80
,, falling, . .	3·78 . .	3·95

As regards the influence of temperature as a solitary factor, we believe that Petermann and Graftiau are the only observers who have investigated it minutely. According to them it is one of the four natural causes affecting the amount of the carbonic anhydride of the atmosphere, and they give the following figures :

Temperature (C.), .	– 10 to – 5	– 5 to 0	0 to 5	5 to 10	10 – 15	15 – 20	20 – 25	25 – 30
CO_2 in 10,000 vols. air,	3·12	2·94	2·97	2·95	2·95	2·92	2·91	2·88

The explanation which they give is that cold abates the velocity of diffusion of the carbonic anhydride from the lower layers of the air to the upper ones. The inverse phenomenon is produced by elevated temperatures, and they recall the fact that Reiset obtained his minima during days of strong insolation. That frost augments the amount of atmospheric carbonic anhydride is also maintained by v. Fodor, who obtained the figures :—

	CO_2 in 10,000 vols. air.
Days before frost	3·54
,, introducing	3·71
,, during thaw	3·69

and explains them by assuming that frost drives the carbonic anhydride out of the ground; while, during a thaw the water, robbed of its gases by the act of congelation, will reabsorb carbonic anhydride, and hence reduce the amount in the air. According to the same observer, even when there is no frost, but the temperature falls considerably, a quantity of warm, and therefore light ground air containing carbonic anhydride, escapes—more, indeed, than when the temperature rises, and in this way he explains the excess of the gas found at night time in the air.

Influence of the Seasons.

Considering the well known and powerful effect of plants in decomposing carbonic anhydride under the influence of sunlight, it might be expected that a marked decrease in the amount of that gas in the atmosphere would occur during that period of the year when the days are long and plant-life is most active, that is to say, in spring and summer, or, for our latitudes say, from April to September; while, on the other hand, an increase might be anticipated when plant-activity ceases, and the days are short, commencing with the fall of the leaf in October and lasting until about the end of March. But it must be remembered that during spring and summer—and especially the latter—the conditions are most favourable for the production and evolution of carbonic anhydride from the soil; while in autumn, and especially in winter, with the fall in temperature, putrefactive and fermentative changes are arrested, and the production and evolution of carbonic anhydride from the soil cease to a more or less corresponding extent. The effect, then, of the seasons on the amount of atmospheric carbonic anhydride should be to induce two sets of actions which are opposed to each other, and tend to maintain a state of equilibrium: the absorbent action of plants in summer being compensated more or less by the additional evolution of carbonic anhydride from the soil; while in autumn and winter the want of activity on the part of plants is also compensated by the decreased evolution of the gas from the soil. But to what extent these opposing actions will affect each other it is impossible to foresee.

De Saussure was of opinion that there was a very decided *increase* in the amount of atmospheric carbonic anhydride in summer, and a *decrease* in winter. Hässelbarth and Fittbogen also found the lowest proportion of the gas in December, while Spring and Roland came to the opposite conclusion, namely, that there is a higher proportion in winter than in summer.

The experimental evidence available for the discussion of the effects of the seasons is also of a very conflicting nature, as will be seen from a comparison of the results obtained by the same observer in different years and of those obtained by different observers in the same year.

Thus, Marié-Davy found in the year 1877 the maximum amount in December, while two years later he recorded the minimum quantity for the year in the same month. In this latter year he noticed a very marked decrease in October, and especially on the 24th of the month.[1]

These differences he sought to account for by the oscillations of the great equatorial atmospheric currents, and was of opinion that they might be of service in predicting meteorological phenomena, such as seasons of rain and of drought, long beforehand. Without discussing the value of this hypothesis, Reiset pointed out that Marié-Davy's results were entirely different from those obtained by himself in the same year (1879). Thus, he did not find any abnormal diminution in the proportion of atmospheric carbonic anhydride between the 2nd of October and the 14th of November. "During this period," he says, "thirty analyses have given a mean of 3·01 for 10,000 of air: this number is slightly in excess of the general mean." On Plate XVI. we have plotted graphically all the results we have been able to collect of importance, in our judgment, which bear on the subject of seasonal variations. The amounts are the mean monthly quantities found by each observer, with the exception of those of Reiset which we have ourselves calculated from the observations made by him on certain days each month, but not daily. Thus, the quantity given as the monthly average for October, 1879, is the mean of thirteen analyses made by him in that month. The results, then, which we give as his are not strictly comparable with those of the other observers, but we did not like to omit them, as his work was so thoroughly trustworthy, and is of considerable importance.

It does not seem possible to draw any very definite conclusions from the chart; but, treating the curves statistically as regards

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[1] The figures were really obtained by Lévy and Allaire at the Montsouris Observatory, of which Marié-Davy was the Director.

the number whose trend for particular periods is either upward or downward, a seasonal effect may possibly be revealed. The results of such an analysis are as follows :—

Period.	Number of Curves trending—		Showing
	Upwards.	Downwards.	
January—February, . .	10	9	?
February—March, . . .	10	10	?
March—April, . . .	9	12	Increase.
April—May, ...	9	12	Increase.
May—June, ...	13	8	Decrease.
June—July, ...	14	9	Decrease.
July—August, . . .	12	9	Decrease.
August—September, . .	6	11	Increase.
September—October, . .	12	7	Decrease.
October—November, . .	10	11	Increase.
November—December, . .	9	12	Increase.
December—January, . .	6	14	Increase.

Viewing the matter broadly, we think that the indications (masked as they no doubt frequently are by the interference of other factors) are in favour of seasonal variations, and that the increase caused by production and evolution of carbonic anhydride from the soil during the early spring receives a well-marked check in the summer months, to be followed in the latter period of the year by an increase when vegetable activity has ceased.

The figures given by Petermann and Graftiau in their very careful work on the air at Gembloux in Belgium are in harmony with such variations, viz. :—

Spring.	Summer.	Autumn.	Winter.
2·958	2·919	2·927	2·958

although the variations from the mean figure for the whole series of their analyses, viz. 2·944, are very small.

If the results obtained by De Saussure and Boussingault, respectively, are added to the preceding, the following figures are obtained—

Period.	Number of Curves trending—		Showing.
	Upwards.	Downwards.	
June—July,	10	16	Decrease.
July—August,	9	16	Decrease.
August—September,	14	8	Increase.
September—October,	9	14	Decrease.
October—November,	14	11	Increase.
November—December,	15	10	Increase.

These additions therefore fortify the above conclusions.

A comparison of the trend of the curves of atmospheric carbonic anhydride, and of the carbonic anhydride in ground air is also of interest. For the latter we have taken v. Fodor's figures.

Period.	Atmospheric CO_2 Trend of Curves shows—	Ground Air CO_2 Trend of Curves shows—
January—February,	?	?
February—March,	?	?
March—April,	Increase.	Increase.
April—May,	Increase.	Increase.
May—June,	Decrease.	Increase.
June—July,	Decrease.	Increase.
July—August,	Decrease.	Decrease.
August—September,	Increase.	Decrease.
September—October,	Decrease.	Decrease.
October—November,	Increase.	Decrease.
November—December,	Increase.	Decrease.
December—January,	Increase.	Decrease.

Thus the movements in the variations of the carbonic anhydride in the atmosphere and in ground air follow each other very closely during the period January to May. From May to July the increase in the carbonic anhydride of the ground air continues while that of the atmosphere diminishes, and the most probable explanation is the great activity, during this period, of vegetation in decomposing the gas, and thus overcoming the increased amount streaming out of the ground. From October to January an increase occurs in the atmospheric carbonic anhydride and a decrease in that of the ground air. The latter is, no doubt, due to the gradual lowering of temperature and decrease in the activity of the micro-organisms of decay. The former is more difficult to account for, but the cessation of vegetable activity may possibly be the cause.

Influence of Cloud and Sun.

Intimately connected with the effects both of day and night, and of vegetation, are those which should be produced by cloud and sun respectively; and here, too, the factor of the seasons should come into play.

During bright, sunny weather in summer it might be anticipated that owing to the resulting activity induced in vegetation in decomposing carbonic anhydride, a diminution of that gas would occur in the atmosphere over a land surface. That this effect actually is produced has been maintained by some of the chief observers. Thus Reiset says—" The minima correspond with cloudless days and bright sun"; and Müntz and Aubin—" The proportion of carbonic anhydride is at its minimum when the sky is clear and the air agitated. It is at its maximum during cloudy and calm times. It is easy to put in evidence the variations which are produced by these influences on the same day. Example:—

April 1st, 1881, 9 a.m.	sky clear, air agitated,	2·73
,, ,, 1.30 p.m.,	,, covered, . .	2·90
,, ,, 4.0 p.m.	,, much covered, commencement of rain, .	2·99

Russell, speaking of London air, says — " On examining Table 7 it will also be seen that it very often happens that the amount of carbonic acid is very considerably below the average, and that when this is the case the weather is fine, with bright sun. The diminution of the amount of carbonic acid in bright weather in the country has been assumed to arise from the increased activity of the chlorophyl in vegetation. In the city the diminution probably arises from the production of an active circulation in the air."

Lastly, we may give the figures obtained by Petermann and Graftiau, which do not support the view that sunlight causes a diminution:—

General mean of 525 determinations, . .	2·94
"Temps beaux," mean of 217 determinations, .	2·95
"Temps couvert," mean of 103 determinations,	2·92

Influence of Height.

The influence of height *per se*, and apart from changes of pressure produced by other causes, has been discussed by several observers.

The elder De Saussure was, no doubt, the first of these:—"I was anxious," he says (in 1787), "to know if the gas, whose weight is nearly double that of ordinary air, can raise itself to the height of Mont Blanc"; and he satisfied himself that it could do so, both by the lime-water test and by the loss in alkalinity of caustic potash when exposed to the air at the summit. His son Théodore, in his memorable researches on the amount of atmospheric carbonic anhydride, and on the causes of its variation, came to the conclusion that the amount was actually greater on mountains than in valleys.

The brothers Schlagintweit, in 1849, were, however, the first to investigate the question of any possible effects produced by considerable heights. Their experiments were conducted on the Eastern Alps, and the conclusions at which they arrived were—(1) That the amount increased from 3·2 to 5·8 vols. in 10,000 up to a height of 3365·8 metres, when a constant maximum was reached; (2) at great heights the variations were less than in lower places; (3) the atmosphere over a glacier is poorer in carbonic anhydride than in its neighbourhood.

Frankland, in 1861, investigated the amount in the neighbourhood of Mount Blanc with the following results—

Chamounix (3445 ft.),	6·30
Grand Mulets (10,007 ft.),	11·10
Mount Blanc (summit 15,784),	6·10

Angus Smith, in 1863, made a number of determinations in the air of Scotch mountains giving the mean results—

Summits,	3·32
Bases,	3·41

He also gives the following figures—

Height below 1000 ft.,	3·37
„ of 1000–2000,	3·34
„ of 2000–3000,	3·32
„ over 3000,	3·36

In 1873 Truchot obtained the following results :—

	Altitude	CO_2 in 10000 vols. air.
Clermont Ferrand,	395 m.	3·13
Summit Puy de Dome,	1446 m.	2·03
„ Pic de Sancy,	1884 m.	1·72

Two years later Tissandier during ascents in the balloon "Le Zénith," found 2·4 at an altitude of 800 m., and 3·0 at 1000 m., but pointed out that no definite conclusions could be arrived at until more numerous observations had been made.

Müntz and Aubin in 1881 were unable to find any appreciable difference between the amount of carbonic anhydride in the air on the Pic du Midi (2877 m.), and in the neighbouring valleys. As a mean of fourteen determinations 2·86 were found on the first, and as a mean of three determinations 2·82 in the second. "All the figures we have obtained," they say, "approximate those found in the inferior part of the atmosphere both by ourselves as well as by Reiset and Schulze at very varied stations. In our experiments on the Pic du Midi the direction of the wind, and the state of the atmosphere experienced variations: we have then worked under diverse conditions, yet the proportion of carbonic anhydride has remained sensibly constant."

Ebermayer gives the following results of his own investigations in the Bavarian Highlands:—

1883		Altitude	CO_2 in 10,000 vols. air.
Nov.	1, Tölz,	688 m.	3·09
,,	2, ,, Zollhaus,	603 m.	3·27
1884			
Aug.	24, Fallek bei Hirschbichel,	1132 m.	3·26
,,	27, Funtensee,	1568 m.	2·93
Sept.	19, Wendelstein	1849 m.	3·35
,,	17, Chiemsee,	513 m.	2·80
Oct.	2, Hohenschwangau,		
	Marienbrücke,	905 m.	2·68
	Spiegel des Alpsees,	834 m.	3·79
	Auf einer Waldwiese,	886 m.	3·24
		General mean,	3·16

The mean obtained by him for the Bavarian plains (560 m.) being 3·20. In 1885 and 1886 Marcet and Landriset made simultaneous observations at Geneva, 90 to 100 feet above the lake (*i.e.* about 1300 feet above sea level), and on the summit of the Dole (5493 feet), thus giving a difference of altitude of nearly 4200 feet. Their results were as follows:—

	Malagny near Geneva.	Summit of the Dole.
Aug. 31st, 1885 mean	3·88	3·53
Sept. 1st, ,, ,,	4·06	3·38
Aug. 26th, 1886 ,,	3·50	3·62
,, 27th, ,, ,,	3·76	3.75
General mean	3·763	3·754

And their conclusions—

(1) In fine clear weather on a mountain chain of a moderate Alpine altitude, and in the neighbouring valley or plain, the atmosphere holds the same proportion of carbonic anhydride.

(2) When the summit of a mountain chain is in a cloud, the air in the cloud contains less carbonic anhydride than it would hold in clear weather—this result applying perhaps more fully when the mountain cloud is extensive in its area than when very low and circumscribed. A cloud on a mountain appears to interfere with diffusion from below—the main region the gas is derived from. This view is consistent with Russell's experiments on air.

The present explanation is still incomplete as it does not dispose of the carbonic anhydride which was on the mountain when the cloud arose, or when the moisture was condensed into cloud on the spot.

Two other observers have touched on the effects of altitude, namely, N. V. Lorenz, who found on the Sonnblick (3100 m.), on August 27 and 28, 1887, 2·05 and 2·36, respectively, which are certainly very low figures; and Andrée who collected air from balloons in 1894, and found that its content of carbonic anhydride at altitudes of 1000–3000 m. (3·23) was practically the same as at the surface (3·03–3·20). It would, therefore, appear that whereas the earlier observers found that attitude had a distinct influence on the amount of atmospheric carbonic anhydride—according to some, lowering it, and according to others, increasing it—their successors have been unable to detect any very distinct effect one way or the other.

The experimental evidence is, however, scarcely sufficient to warrant any very definite conclusions, and further observations would be of interest especially from balloons in calm weather.

For reasons mentioned elsewhere, atmospheric carbonic anhydride—at least over land surfaces—should decrease with altitude, and some observers have drawn attention to the fact that the determinations made by the later and more reliable methods favour this view.

(As regards the amount of atmospheric carbonic anhydride at ground level, and at moderate heights above it, see p. 216.)

APPENDIX I.

ON GROUND AIR AND ITS RELATIONS TO ATMOSPHERIC CARBONIC ANHYDRIDE.

As v. Fodor, Wollny, and others have expressed very decided opinions as regards the *rôle* which ground air plays in influencing the amount of atmospheric carbonic anhydride, it may not be out of place to give a short *resumé* of the facts which have been ascertained as to the nature of ground air and the changes which occur in its composition, much of which we have taken from v. Fodor's work on "Air, Soil, and Water."[1] The first observers to investigate ground air were, we believe, Boussingault and Levy, in 1852, who aspirated air from the soil at depths of 0·3 and 0·4 metres, and found that it was rich in carbonic anhydride, but, on the contrary, poor in oxygen. Pettenkofer made a series of experiments, in 1857, with air aspirated from different depths of the soil, with the object of tracing the processes of decay there occurring, at least as regards the nature of the resulting gaseous substances. For this purpose a hole was dug, in the courtyard of the Physiological Institute at Munich, and five narrow lead tubes were inserted at depths of 4, 3, 2½, 1½, and ⅔ metres respectively, and the soil then carefully replaced. The other ends of the tubes passed into the Laboratory, and the gases present in the soil were obtained by slow aspiration.

A similar method of investigation was pursued by Fleck, v. Fodor, and later observers.

The general conclusions arrived at regarding the nature of ground air appear to be somewhat as follows:—

(1) Ground air results from atmospheric air which has diffused into the soil and has there suffered change—chiefly loss of oxygen and considerable gain in carbonic anhydride. The sum, however, of these two is not very different from the original proportion of oxygen, but usually exceeds it by 2–3 per cent. by volume, showing that not only does a part of the oxygen become replaced by carbonic anhydride owing to oxidation of organic matter, but that there is also a definite evolution of carbonic anhydride from the soil, which is, no doubt, largely due to the operations of the micro-organisms concerned in

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[1] v. Fodor, "Luft, Boden, u. Wasser": Brunswick, 1881.

decay. Fleck obtained, among others, the following analyses of ground air :—

GROUND AIR FROM DEPTHS OF SIX, FOUR, AND TWO METRES.

	6 Metres.		4 Metres.		2 Metres.	
	Minm. CO_2.	Maxm. CO_2.	Minm. CO_2.	Maxm. CO_2.	Minm. CO_2.	Maxm. CO_2.
Oxygen, . . .	14·94	14·85	15·67	16·79	16·33	19·39
Carbonic anhydride, .	4·22	7·96	4·11	5·56	2·99	2·91
	19·16	22·81	19·78	22·35	19·32	22·30

(2) More carbonic anhydride is found in the ground air from lower than from higher levels.

(3) The amount of this gas at both levels has a definite connection with the seasons, increasing during spring and summer, reaching a maximum in July or August, then diminishing and remaining more or less stationary during the winter months. These effects are, as might be expected, due to temperature variations, the curve showing the temperature changes at the surface, corresponding on the whole, with those showing the variations of the carbonic anhydride of the ground air.

(4) The variations in the amount of the carbonic anhydride of the ground air at lower and higher levels correspond with each other, but the curve is steeper in the former than in the latter.

(5) The amount of carbonic anhydride in the ground air is related to the nature of the soil in two ways, depending (*a*) on its porosity, and (*b*) on its organic matter. The less porous a soil the greater the amount, and *vice versâ.* This is no doubt due to the obstacle the first imposes to diffusion of the gas, while with a porous soil it readily escapes, and does not accumulate. As regards the organic matter, the greater its amount in a given soil the higher the proportion of carbonic anhydride in the ground air.

(6) Rainfall has a marked influence on the amount of the carbonic anhydride of the ground air, and v. Fodor is of opinion that three distinct effects may be traced to it. First, the pores of the soil are sealed, thus offering an obstacle to the escape of ground air, and causing an accumulation of carbonic anhydride. This latter is then absorbed by the mineral constituents of the soil—(leading, we presume,

to the production of bicarbonates, which are washed downwards). Finally, there follows a period during which the micro-organisms of decay are in full activity, and carbonic anhydride is produced in abundance.

(7) Two other meteorological factors[1] intermittently affect ground air, leading either to its escape into the atmosphere or to its imprisonment in the soil, namely, changes of pressure and of temperature, and v. Fodor is of opinion that from these causes very considerable "streamings" of ground air occur. These streamings could, he thought, be best traced by a comparison of the amount of carbonic anhydride found in the atmosphere close to the ground with that at some distance above it, and accordingly he systematically determined these amounts simultaneously (at $\frac{1}{2}-1$ cm. and $2\frac{1}{2}$ m. above the ground, respectively) during three years (1877–1879).

The conclusions at which he arrived from these determinations were as follows:—The carbonic anhydride at ground level is, during the greater part of the year, considerably in excess of that above the surface, and the variations in the former are much more considerable than those in the latter. Both increase and decrease at ground level precede those occurring in the higher layers of the atmosphere, and, in general, the fluctuations in the amount of atmospheric carbonic anhydride are mainly due to the absorbing action of the soil on the one hand, and the evolution of ground air on the other.

Soil possesses the power of diminishing atmospheric carbonic anhydride at times, and then the air at its surface contains less than at higher levels. Rain causes this, especially in spring; and that thoroughly moistened ground is the factor leading to absorption of the gas is further shown by the circumstance that the carbonic anhydride in the air at ground-level is least at the end of winter and the commencement of spring—that being the period when the soil, and especially it upper layers, are wettest.

v. Fodor has plotted out graphically, in a series of curves, the diurnal variations in the amount of carbonic anhydride in ground air at two different levels, those of the atmosphere close to the ground and at some distance above it, as well as the variations of temperature, rainfall, &c., during his three years' investigation.

As his diagrams are somewhat complicated and unwieldy, we have taken the liberty of constructing from the data supplied by him two

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[1] In addition to wind, which according to v. Fodor displaces ground air by pure air, thus leading to an escape of carbonic anhydride from the soil.

diagrams showing the *average monthly variations* of the above factors, which bear out most of his general conclusions.

So far as ground air is concerned (Plate XVII.), it will be seen that the variations of its carbonic anhydride, both at higher and lower levels, correspond fairly closely with those of atmospheric temperature, and consequently with the seasons. It is also clearly seen that the amount at deeper level is always greatly in excess of that at higher level.

The second series of curves (Plate XVIII.) is more complex; but certain points are clearly brought out. Thus the air at ground-level is shown to contain more carbonic anhydride than that at some distance above the ground during the warmer part of the year, but sinks below it in winter and early spring; also, as v. Fodor insists, the variations in carbonic anhydride at ground-level are much more considerable than those in the air above it. The effects of rain are clearly shown—the maxima of rainfall corresponding, as a rule, with minima of carbonic anhydride at ground-level, and, broadly speaking, the converse is also true.

As to the effects of ground air on atmospheric carbonic anhydride, if we neglect the parts of the curves from November to April, when the soil appears to be acting as absorbent, we certainly find an increase both in the carbonic anhydride of the ground air as well as in that of the atmosphere from April to June; but from June to September the curves for these two slope in opposite directions. It is possible that the effects of rain, wind, and changes in pressure, may partly explain this, and also it is by no means inconceivable that outward streamings of ground air would lower the amount of its carbonic anhydride, while increasing that of the atmosphere close to the soil.

As regards the probability of ground air influencing to any considerable extent the amount of atmospheric carbonic anhydride, the following considerations have occurred to us:—

Imagine a tube, 100 square centimetres in sectional area, inserted through the soil and projecting into the air. Suppose that in the soil it became sealed by underground water, at a depth of 25 metres, and that it projected into the air to a height of 2 metres. It now contains 20 litres of ordinary air above and 250 litres of soil below. Further, suppose that the porosity of the soil amounted to 20 per cent. of its bulk, then the tube would contain 50 litres of ground air. Let us assume that this ground air contains 1 per cent. by volume of carbonic anhydride. [1]

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[1] From the monthly averages given by v. Fodor, the mean annual values for the carbonic anhydride in the soil, at depths of 1, 2, and 3 metres, are respectively 1·02, 1·61, and 2·81 per cent. by volume.

In order to increase the amount of carbonic anhydride in the air in the upper part of the tube to the extent of 1 in 10,000 volumes, 2 c.c. of that gas must be added to it, and therefore 200 c.c. of ground air.

Let us now see to what extent changes of temperature and pressure, both separately and together, will affect the amount of carbonic anhydride in the atmospheric air contained in the tube; and for this purpose let us assume that the changes occur suddenly, and that the ground air instantaneously diffuses into the two-metre layer of atmosphere. As to the effects of changes of temperature alone, each rise of 1° C. (supposing the initial temperature to be zero) will liberate 183 c.c. of ground air, or nearly sufficient to give the increase of 1 in 10,000, and, as to the effects of diminished pressure, a fall of the barometer from 760 to 757 mm., or 3 mm., would produce the same effect.

Finally, let us suppose a fall in the barometer of 25 mm. (1 inch), and at the same time a rise in temperature of 10° C.; the effect would then be an evolution of 3536 c.c. of ground air, which would be nearly equivalent to 18 of carbonic anhydride in 10,000 of air.

It thus seems clear that changes of temperature and pressure, either alone or combined, should have a very distinct influence on the evolution of ground air, which in its turn must distinctly affect the proportion of atmospheric carbonic anhydride, at all events in calm weather, and at heights not too remote from the surface of the ground.

APPENDIX II.

A COMPARISON[1] OF THE RESULTS OF DETERMINATIONS OF CARBONIC ANHYDRIDE BY PETTENKOFER'S ORIGINAL PROCESS, AND THE METHOD PROPOSED BY PROFESSOR LETTS AND MR. BLAKE, AND ON THE ERRORS INCIDENTAL TO PETTENKOFER'S PROCESS. By WM. CALDWELL, B.A., Hon. Demonstrator of Chemistry in the Queen's College, Belfast, and 1851 Exhibition Scholar.

PROFESSOR Letts and Mr. Blake have described a modification of Pettenkofer's process, whereby results of very great accuracy may be obtained; and at Professor Letts' suggestion, I have made a series of experiments in order to compare the results obtained by this method with Pettenkofer's original process.

It is difficult to decide as to what is really meant by Pettenkofer's process, for Pettenkofer himself describes, at least, three modifications of it, and many of those who have employed his process have introduced their own.

The question is further complicated by the fact that the principle involved did not originate with Pettenkofer at all, but with Dalton,[2] who had his own disciples, namely, Watson and Emmett.

Angus Smith says that the use of oxalic acid makes the process Pettenkofer's; but, against this, we have Pettenkofer's own statement that "any dilute acid which is not volatile at ordinary temperatures may be used."[3]

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[1] We thought it would be more satisfactory if the comparison were entrusted to an independent observer, and was not made by ourselves, as we had acquired a good deal of experience of the working of our method, but none of Pettenkofer's. There was therefore, we thought, a chance that the results we might obtain by the latter would not be so favourable by comparison as might be the case if we had equal experience of the two.

For this reason we entrusted the work to Mr. Wm. Caldwell, in whose care and accuracy as an analyst we knew we might have full confidence. The subject was perfectly new to him, and he had had no experience whatever of these determinations.

We requested him to carry out both processes exactly as described in the original memoirs and with all the precautions stated therein. He has pursued the work with zeal and ability, and the results he has obtained are very striking and of considerable importance.

[2] Phil. Trans., [1826]. Part 2, p. 174.

[3] Chem. Soc. Journ., 10 [1858], p. 292.

The first thing necessary, therefore, was to decide what Pettenkofer's process really is.

In the Chemical Society's Journal, there is an original paper,[1] in which Pettenkofer describes one modification of his process, and in the Journ. f. prakt. Chem.[2] another modification is described by him.

There is a third method, which is usually termed the "Aspiration" method, in contradistinction to the "Bottle" method, which Pettenkofer employed originally in his experiments on Respiration.[3]

In each of the two first processes, a standard solution of lime or baryta water is used as the absorbent, the excess of either of which is afterwards titrated with standard oxalic acid, turmeric paper being used as indicator. Similar absorbing vessels are employed in both of these methods, namely, glass bottles or flasks, closed by bungs or india-rubber capsules, the important point of difference between the two methods being that, whereas, in the first, the titration is performed within the absorbing vessel, in the second, it is made in a small bottle on an aliquot portion of the absorbent (after the latter has done its work) which has been pipetted off. As regards the third or "aspiration" method, it is not, I think (at least in Great Britain), closely associated with Pettenkofer's name. The main principle is that a certain volume of air is aspirated slowly through a tube filled with the absorbent (lime or baryta water) placed at a slight angle, and an aliquot portion of the liquid subsequently titrated with oxalic acid, and turmeric paper as indicator.

Of these three methods, I have adopted, in all the experiments I have performed, the second, for two reasons—first, because I believe it was the one which is chiefly associated with Pettenkofer's name, and with which he did most of his work; and secondly, because the first method (from the description of the process) would appear to be more difficult of execution, and more subject to errors of manipulation.

I may now describe, in as few words as possible, the precautions I observed in carrying out the process.

First of all, as regards the absorbing vessels, and the method of filling them with the air sample to be examined.

Several series of experiments were performed. In the first of these, flasks of nearly three litres capacity were used, and in the latter series, similar vessels of about twice that capacity.

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[1] *Loc. cit.*

[2] Journ. prakt. Chem. 85 [1862], p. 165.

[3] Liebig's Annalen, [1862–1863], Supplb. 2, p. 23.

The vessels before use were thoroughly washed—not with acid, for after cleansing a flask with acid, and subsequently using it for the absorption of carbonic anhydride, even though the acid had been completely washed out, the results were found to be higher than if the flask had been merely washed out with water. The flasks were, however, very thoroughly washed for the first experiments, and in all future experiments they were only rinsed out, and the slight skin of barium carbonate with which they were coated allowed to remain. As soon as the distilled water had drained from the flasks, they were dried by blowing warm air through them by the foot bellows.

To fill them with the air sample to be examined, the flasks were allowed to remain where the air was collected for some time, to come to the temperature of their surroundings, and a quantity of air was then pumped through them sufficient to displace the original volume five times, as Pettenkofer recommends.

Both flasks were filled as quickly as possible, each experiment being made in duplicate.

The absorbing solution was then added by means of a pipette, the flasks securely closed with india-rubber corks, and absorption allowed to proceed for two hours. In all the operations connected with the absorption and subsequent titration, I have followed Pettenkofer's description of the process as closely as possible.

After absorption, the solution was rapidly transferred to a very narrow beaker, the pipette rinsed out with a small portion of the solution, and then an aliquot part—30 cubic centimetres of the 45 cubic centimetres originally added—titrated with the standard oxalic acid, and the amount of carbonic anhydride deduced.

For the standard oxalic acid solution, the pure acid of commerce was taken, and recrystallized quite a number of times after the manner indicated by Fresenius.

About 20 per cent. was first crystallized from the solution. This contained the impurities, which in the first case were extremely minute. The remainder of the solution was then carefully evaporated and allowed to crystallize.

The resulting crystals were again taken, and they underwent similar re-crystallization, until acid was obtained, which, on ignition, just left the merest speck of impurity. Its strength was determined by standard permanganate solution, which had been factorized by pure ferrous ammonium sulphate. From this pure acid a solution was prepared, one cubic centimetre of which was equal to one milligram of carbonic anhydride.

I have not been able to find the process by which Pettenkofer himself prepared his turmeric paper. In the preparation of the turmeric paper I have followed Sutton. The turmeric powder was first digested several times with hot water, and then transferred to a flask and digested with alcohol. The yellow solution was filtered into a large porcelain dish, through which strips of filter paper were drawn, and after draining for a moment or so were dried in the dark-room, and kept there until required for the several daily titrations.

The whole process, therefore, consists of—(1) displacing the air in the flask by the air which is to be examined; (2) the addition of the absorbent, followed by (3) its titration, without the adoption of any extraordinary precautions to eliminate the errors arising from the transference of the absorbent, and the subsequent titration, during both of which operations the solution is exposed, not only to the air of the laboratory, but also, to a certain extent, to the breath of the operator, concerning which point Pettenkofer himself says:—"It is merely the upper layer of the liquid that is affected by the carbonic anhydride in the air of the laboratory." Hence, in transferring the solution to the titrating bottle, the pipette was allowed to reach almost to the bottom of the beaker and the lower layer of liquid only, used for titration.

Next, as regards the process adopted by Professor Letts and Mr. Blake. The details of the method are described in the first part of their Paper, and in my experiments these details were adhered to. Certain points, however, require mentioning. The preparation of neutral distilled water for use in making the standard acid solutions was very interesting, and at Professor Letts' suggestion the following experiment was tried:—

To ordinary distilled water more than sufficient potassium hydrate was added to make it alkaline. It was then distilled, and portions of the distillate examined from time to time. They were at first alkaline, no doubt from ammonia, but then became acid, and eventually of a constant degree of acidity. This degree of acidity was found to correspond with the amount of carbonic anhydride in the laboratory in which the water was distilled. Thus the water, distilling over, saturated itself with carbonic anhydride at the tension due to that amount of carbonic anhydride in the atmosphere of the laboratory. A number of experiments showed that the amount of carbonic anhydride varied between ·5 and ·6 cubic centimetres per litre of water, whereas the amount calculated on the basis of four parts in 10,000 of air, and solubility coefficient 1·187 at 10° C. (the mean temperature of the laboratory at the time these experiments were conducted), was—

$$\frac{\cdot 4}{1000} \times 1187 = \cdot 4748 \text{ cubic centimetres of carbonic anhydride.}$$

In preparing a supply of water for my experiments, this acidity was determined and exactly neutralized with baryta. For the standard solution, an exactly decinormal hydrochloric acid was first made. This was prepared by the use of the corresponding decinormal sodium carbonate solution, and then verified, after neutralization, by decinormal silver nitrate solution (which had been factorized by pure ammonium chloride), and potassium chromate as indicator. Neutralized distilled water was used both for the preparation of the sodium carbonate solution and also for the preparation of the decinormal hydrochloric acid solution, 89·6 cubic centimetres of which, when diluted with the same water to 1000 cubic centimetres, correspond with 100 cubic centimetres of carbonic anhydride at normal temperature and pressure. One cubic centimetre of this solution was therefore equivalent to 0·1 cubic centimetre of carbonic anhydride at normal temperature and pressure, the strength always employed in the determinations.

The absorbent baryta water was prepared from barium hydrate, which had been recrystallized three or four times, and the solution was made to correspond with the strength of the acid nearly. Its strength was, however, exactly determined in terms of the acid.

The absorbing vessels used were similar to those employed by Professor Letts and Mr. Blake in their determinations. In the first series of experiments, Winchester quart bottles, coated with paraffin wax inside, were used, and in the later series of experiments large flasks of about six litres capacity and similarly coated, were employed.

The flasks were filled with the sample of air after the manner adopted by Professor Letts and Mr. Blake, namely, by drawing the air through them by means of a suction pump, so that the air was renewed five times.

In performing the titrations, the vacuous vessel described in the original paper (fig. 4, p. 127) was employed, into which the absorbent was drawn from the receiver, together with the subsequent rinsings with neutralized distilled water, containing a little phenol-phthaleïn. The burettes were of the special construction, also described in the paper.

The following are the results of *all* the different series of experiments I have made with the two methods.

I may mention that all the air samples were collected in the grounds of the Queen's College, Belfast.

FIRST RESULTS.

The air samples for both processes were not collected simultaneously.

PETTENKOFER.				LETTS AND BLAKE.		
Number.	CO_2 in 10,000 parts of air.	Duplicate.	Difference.	CO_2 in 10,000 parts of air.	Duplicate.	Difference.
	I.	II.		I.	II.	
1	6·07	—	—	3·41 [1]	3·16	·25
2	4·40	4·73	·33	3·19	3·16	·03
3	4·04	4·27	·23	2·69	2·67	·02
4	3·35	3·46	·11	3·20	3·16	·04
5	4·46	4·79	·33	3·44	3·47	·03
6	3·28	3·44	·16	—	—	—
Mean, ..	3·90	4·14	·23	3·18	3·12	·07

The above determinations may be considered as merely preliminary trials to accustom me to the necessary manipulation.

SECOND SERIES—COMPARATIVE DETERMINATIONS.

(SMALL RECEIVERS.)

The air samples for both processes were collected simultaneously.

PETTENKOFER.				LETTS AND BLAKE.		
Date.	CO_2 in 10,000 parts of air.	Duplicate.	Difference.	CO_2 in 10,000 parts of air.	Duplicate.	Difference.
	I.	II.		I.	II.	
Feb. 8	4·70	5·13	·43	3·13	3·15	·02
,, 9	4·42	4·85	·43	2·96	—	—
,, 10	4·40	4·75	·35	2·81	2·86	·05
,, 13	4·23	4·31	·08	2·73	2·77	·04
,, 14	4·13	4·31	·18	2·68	2·68	·00
,, 15	4·02	4·15	·13	2·67	2·67	·01
Mean, ..	4·31	4·58	·27	2·83	2·82	·02

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[1] This determination was performed by Mr. Blake, to show me the method of manipulation.

In the above series, with the Pettenkofer process, it was impossible to obtain results which differed from one another by less than ·2. This was, however, overcome to a great extent in the third series of experiments by the use of very much larger flasks.

The results of the third series of experiments are:—

THIRD SERIES—COMPARATIVE DETERMINATIONS.

(LARGE RECEIVERS.)

The air samples for both processes were collected simultaneously.

	PETTENKOFER.			LETTS AND BLAKE.		
Date.	CO_2 in 10,000 parts of air.	Duplicate.	Difference.	CO_2 in 10,000 parts of air.	Duplicate.	Difference.
	I.	II.		I.	II.	
Feb. 28	4·03	3·98	·05	2·95	2·96	·01
Mar. 1	3·94	3·95	·01	2·90	2·90	·00
,, 2	3·96	3·92	·04	2·85	2·85	·00
,, 3	4·00	3·96	·04	2·86	2·86	·00
,, 6	3·86	3·82	·04	2·81	2·82	·01
Mean,..	3·95	3·92	·03	2·87	2·87	·004

As a result of these experiments, we are thus confronted with the fact that Pettenkofer's method of determination gives higher results—some 30 per cent.—than those obtained by the process devised by Professor Letts and Mr. Blake, and by other processes which are apparently reliable. Other investigators have also drawn attention to the high results obtained by Pettenkofer's process.

Ebermayer[1] obtained almost the same difference in comparative and simultaneous experiments with Pettenkofer's ordinary process ("Flaschen methode") and the "Aspiration methode."

It remained, therefore, to decide two important questions:—

Is the Pettenkofer process at fault? and, if so, what is the reason?

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[1] Ebermayer, "Die Beschaffenheit der Waldluft." Stuttgart, [1885], p. 16.

To decide the first of these questions, several series of experiments were performed. In the first of these accurately measured volumes of carbonic anhydride at a given temperature and pressure were carefully transferred to corked receivers containing only a small quantity of air, and nearly filled with a measured volume of absorbent. The apparatus employed for this purpose was similar to that figured on p. 130, and was used as there described—with the difference that the measured volume of carbonic anhydride was driven by pressure through a *long* tube which nearly touched the bottom of the receiver: the latter, however, being inverted.

After absorption, the excess of the latter was determined precisely as in the Pettenkofer process.

The results were as follows:—

CARBONIC ANHYDRIDE AT N. T. P.

Number.	Taken.	Found.	Difference.	
			Absolute.	Percentage.
1	·9185 c.cm.	1·210 c.cms.	+ ·3015 c.cm.	+ 32 per cent.
2	·9185 ,,	1·240 ,,	+ ·3215 ,,	+ 34 ,,
3	·9420 ,,	1·210 ,,	+ ·2680 ,,	+ 28 ,,
4	·9420 ,,	1·230 ,,	+ ·2880 ,,	+ 30 ,,
5	·9610 ,,	1·256 ,,	+ ·2950 ,,	+ 30 ,,
6	·9610 ,,	1·256 ,,	+ ·2950 ,,	+ 30 ,,
			Mean, . .	31 per cent.

These experiments indicate that the results obtained by Pettenkofer's process are some 30 per cent. too high, thus *agreeing with my previous experiments on air.*

In order to ascertain the true source of error, a similar series of experiments was performed, but the absorbent was drawn off into the vacuous vessels, and the titrations performed as in Letts' and Blake's process, using phenol-phthaleïn as indicator, as it is obvious that it was impossible to employ turmeric paper under these conditions.

The following are the results :—

CARBONIC ANHYDRIDE AT N. T. P.

Number.	Taken.	Found.	Difference.	
			Absolute.	Percentage.
1	1·900 c.cms.	1·89 c.cms.	– ·010 c.cm.	– 0·5 per cent.
2	1·900 „	1·91 „	+ ·010 „	+ 0·5 „
3	1·937 „	1·93 „	– ·007 „	– 0·3 „
4	1·937 „	1·92 „	– ·017 „	– 0·8 „

The results show that *the chief source of error lies in the absorption of Carbonic Anhydride from the atmosphere (and breath ?) during the transfer of the absorbent from the receiver, and its subsequent titration in open vessels.*

As regards the relative delicacy of phenol-phthaleïn and turmeric paper as an indicator, I have made the following experiments :—To separate portions of neutralized distilled water—50 cubic centimetres—I added, drop by drop, weak standard solution of baryta (one cubic centimetre of which = 0·1 cubic centimetre of carbonic anhydride), and tested the point at which incipient alkalinity was manifest (A) with turmeric paper, and (B) with phenol-phthaleïn.

RELATIVE DELICACY OF INDICATORS.

Number.	Turmeric.	Phenol-phthaleïn.
1	8 drops.	1 drop.
2	7 „	1 „
3	7 „	1 „
4	7 „	1 „
5	7 „	1 „
6	7 „	1 „
	Mean, 7 drops.	

These results show that phenol-phthaleïn is seven times more delicate than turmeric paper when used as an indicator.

In the modification of Pettenkofer's process, adopted by Professor

Letts and Mr. Blake, every precaution is taken to ensure absolute accuracy and elimination of all errors.

The absorbent is kept in a vessel coated inside with paraffin wax, and so arranged that, when a charge is withdrawn, its place is taken by air freed from its carbonic anhydride. The absorbent, therefore, retains its strength unchanged as I have verified for a period of forty days. (Fifty cubic centimetres of baryta water required 48·32 cubic centimetres of standard hydrochloric acid, one cubic centimetre of which was equal to 1 cubic centimetre of carbonic anhydride. After a lapse of forty days, 50 cubic centimetres of the same solution of baryta water required 48·14 cubic centimetres of the above standard hydrochloric acid, an almost inappreciable alteration.)

The charge of the absorbent is transferred to the receiver without coming in contact with the atmosphere. The titrations are performed *in vacuo*, with very delicate burettes, and, as has been shown, with a more delicate indicator than turmeric paper ; and, lastly, as Professor Letts and Mr. Blake have shown, the error arising from the action of the absorbent on the glass of the receiver is also eliminated.

In Pettenkofer's method of manipulation, there are no precautions taken to ensure the constancy of the strength of the absorbent, nor care taken to avoid errors due to absorption of carbonic anhydride from the air during the transfer of the absorbent to the vessel in which the titrations are made and during the titrations themselves. It is not to be wondered at, then, that errors arise ; but it is somewhat surprising to find that they may be so large.

It may, however, be remarked that, as I have already mentioned, various modifications of Pettenkofer's process have been employed in which these sources of error are to some extent avoided. Thus F. Schulze[1] employed turmeric tincture as indicator, and, when titrating, pierced the rubber sheet tied over the absorbing vessel with the end of the burette.

To confirm the foregoing results, known and definite volumes of carbonic anhydride, at definite temperature and pressure, were added to the large flasks of about six litres capacity, and titrations performed according to Pettenkofer's method, as far as possible, at least. The absorbent had to be added and withdrawn without coming in contact with the air ; but the subsequent manipulation was performed as in the Pettenkofer process. Thus only about half the process was really Pettenkofer's. Simultaneous experiments were performed according to the method of Professor Letts and Mr. Blake.

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[1] Landw. Vers. Stat., 9 [1867], p. 217.

The following are the results :—

EXPERIMENTS WITH KNOWN VOLUMES OF CARBONIC ANHYDRIDE.

No.	CO_2 added at N. T. P.	CO_2 found.	Absolute error.	Error per cent. of amount taken.	Capacity of receiver.	CO_2 added in parts per 10,000.	CO_2 found in parts per 10,000.	Error in parts per 10,000.
PETTENKOFER.								
	c.cms.	c.cms.			c.cms.			
1	1·88	2·17	+ ·29	+ 15	6541	2·87	3·31	+ ·44
2	1·88	2·10	+ ·22	+ 12	6760	2·78	3·40	+ ·32
3	1·90	2·17	+ ·27	+ 14	6541	2·90	3·31	+ ·41
4	1·90	2·10	+ ·20	+ 11	6760	2·81	3·10	+ ·29
5	1·94	2·14	+ ·20	+ 10	6541	2·96	3·27	+ ·31
6	1·94	2·12	+ ·18	+ 9·4	6760	2·87	3·13	+ ·26
LETTS AND BLAKE.								
1	1·90	1·89	– ·01	– ·5	5562	3·40	3·40	– ·00
2	1·90	1·91	+ ·01	+ ·5	5782	3·28	3·30	+ ·02
3	1·94	1·93	– ·01	– ·5	5562	3·48	3·47	– ·01
4	1·94	1·92	– ·02	– 1·0	5782	3·35	3·32	– ·03

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Amer. Assoc. Proc.,	Proceedings of the American Association for the Advancement of Science.
Amer. Chem. Journ.,	American Chemical Journal.
Amer. Journ. Science,	American Journal of Science and Arts.
Annales Agronom.,	Annales Agronomiques, Paris.
Annales de Chimie,	Annales de Chimie et de Physique.
Annales Sci. Nat.,	Annales des Sciences Naturelles.
Archiv f. Hyg.,	Archiv für Hygiene.
Archiv d. Pharm.,	Archiv der Pharmacie.
Berichte,	Berichte der deutschen chemischen Gesellschaft.
Bibl. Univ.,	Bibliothèque Universelle des Sciences, Belles-Lettres, et Arts, Genève, 1816–1845.
Biedermann's Centrbl.,	Biedermann's Centralblatt für Agrikulturchemie und rationellen Landwirthschafts-Betrieb.
Brit. Assoc. Rep.,	Reports of the British Association for the Advancement of Science.
Bruxelles Mém. Couronn.,	Mémoires Couronnés et autres Mémoires publ. par l'Acad. Roy. des Sciences, etc., de Belgique.
Bull. Soc. Chim.,	Bulletin de la Société Chimique de Paris.
Centrbl. f. med. Wiss.,	Centralblatt für die medicinischen Wissenschaften.
Chem. Centrbl.,	Chemisches Centralblatt.
Chem. News,	Chemical News.
Chem. Soc. Journ.,	Journal of the Chemical Society.
Compt. Rend.,	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingler's Polytec. Journ.,	Dingler's polytechnisches Journal.
Fresenius' Zeitschr.,	Fresenius' Zeitschrift für analytische Chemie.
Gilbert's Annalen,	Annalen der Physik und Chemie, 1799–1824.
Hofmann's Jahresber.,	Jahresbericht über die Fortschritte auf dem Gesammtgebiete der Agrikulturchemie.
Journ. f. Landw.,	Journal für Landwirthschaft.
Journ. de Pharm.,	Journal de Pharmacie et de Chimie.
Journ. prakt. Chem.,	Journal für praktische Chemie.
Landw. Vers. Stat.,	Landwirthschaftliche Versuchs-Stationen. Organ für naturwissenschaftliche Forschungen auf dem Gebiete der Landwirthschaft.
Liebig's Annalen,	Annalen der Chemie und Pharmacie, 1832–1874. ,, ,, Chemie, 1874–1900.

München, Akad. Sitzber.,	Sitzungsberichte der mathematisch-physikalischen Classe der k. b. Akademie der Wissenschaften zu München.
Neu. Repert. f. Pharm.,	Neues Repertorium für die Pharmacie.
Oester. Zeitschr. f. Meteorologie,	Zeitschrift der oesterreichischen Gesellschaft für Meteorologie, Wien.
Pharm. Centrbl.,	Pharmaceutisches Centralblatt.
Phil. Mag.,	The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science.
Pogg. Annalen,	Annalen der Physik und Chemie, 1824–1877.
Roy. Dublin Soc. Proc.,	The Scientific Proceedings of the Royal Dublin Society.
Roy. Soc. Proc.,	Proceedings of the Royal Society of London.
Wiedemann's Annalen,	Annalen der Physik und Chemie, 1877–1900.
Wien, Akad. Sitzber.,	Sitzungsberichte der mathematisch-naturwissenschaftlichen Classe der kaiserlichen Akademie der Wissenschaften.
Wollny's Forsch.,	Forschungen auf dem Gebiete der Agrikultur-Physik.
Zeitschr. f. anorgan. Chemie,	Zeitschrift für anorganische Chemie.
Zeitschr. f. Biol.,	Zeitschrift für Biologie.
Zeitschr. f. Hyg.,	Zeitschrift für Hygiene.

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XVI.

COLLEMBOLA FROM FRANZ-JOSEF LAND (collected by Mr. W. S. Bruce, 1896–97). By GEORGE H. CARPENTER, B.Sc. Lond., Assistant Naturalist in the Science and Art Museum, Dublin.

[Read November 22; Received for Publication December 2, 1899;
Published January 25, 1900.]

The Collembola or Springtails are a group of insects which seem to be abundant, both in species and individuals, in the Arctic regions. Since the first comprehensive memoir of Tullberg (7) on the Arctic Collembola appeared, our knowledge of these insects from northern Siberia has been greatly enlarged by the work of Schött (5), while springtails from Spitzbergen have been studied by Schäffer (4*c*), Lubbock (2), Stscherbakow (6), and Wahlgren (8), and from Greenland by Meinert (3). So far, however, no insects of this order seem to have been recorded from Franz-Josef Land. It was with much satisfaction, therefore, that I received from Mr. W. S. Bruce, of Edinburgh, the collection of Collembola which he made on that archipelago in 1896 and 1897, while attached to the Jackson-Harmsworth expedition. Seven species are represented, one of which proves to be new to science. By the generous action of Mr. Alfred Harmsworth and Mr. Bruce, the collection has been divided between the Science and Art Museums of Edinburgh and Dublin.

Family.—PODURIDÆ.

Anurida granaria (Nic.).

A few examples only of this species occurred at Cape Flora (27th June, 1896), and Cape Gertrude (14th July, 1897).

According to Schött (6) *A. granaria* has a wide range in Europe (it occurs throughout the British Islands); it has also been found in northern Siberia and in Spitzbergen (6).

Lipura grœnlandica, Tullb. (7).

Several specimens of this species were found at Cape Flora (19th August, 1896; 9th, 14th, and 19th July, 1897). Its presence in Franz-Josef Land might have been expected since it occurs both in Greenland (7) and in Spitzbergen (2, 7). Its structural features are clearly figured by Tullberg, and the presence of only a single prominence in each post-antennal organ makes its identification easy.

Achorutes dubius, Tullb., **var. concolor**, nov.

Numerous examples of this springtail were found at Cape Flora (19th August, 1896), at Cape Gertrude (27th June, 1896),

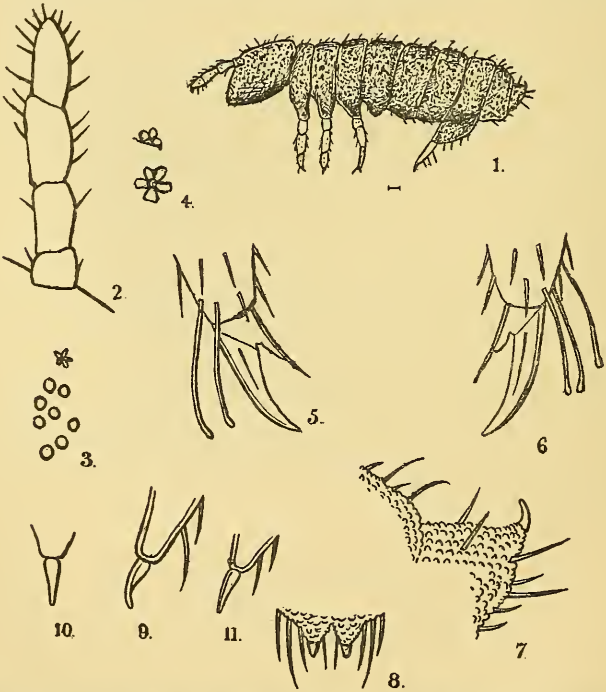

Fig. 1, *Achorutes dubius*, var. *concolor*, × 27; fig. 2, antenna, × 120; fig. 3, post-antennal organ and ocelli of right side, × 120; fig. 4, post-antennal organ in plan and elevation, × 300; fig. 5, foot of first pair, × 180; fig. 6, foot of third pair, × 180; fig. 7, tip of abdomen from side, × 180; fig. 8, same from above, × 180; fig. 9, tip of dens with mucro from side; fig. 10, from beneath fig. 11, same in half-grown individual from side; all × 180.

and on rocks between Capes Gertrude and Barentz (21st March, 1897). The species is recorded from Novaya Zemlya and northern Siberia (5, 7); specimens which Dr. C. Schäffer, of Hamburg, has most kindly sent me for comparison are from Spitzbergen.

The examples of this species from Franz-Josef Land are characterised by a somewhat larger size (1·5 mm.) than that of the typical form, and by the whole body, except the legs and spring, being of a uniformly blue-black colour. I therefore propose to distinguish them as var. *concolor*. In typical *A. dubius* the pigment is in scattered patches.

It seems advisable to give structural figures of this interesting and little-known form. The post-antennal organ (figs. 3, 4) is of an almost regular rosette-shape, consisting of five prominences surrounding a central circular one. The fore-foot (fig. 5) has two tenent hairs, the middle and hind-feet (fig. 6) three; the lamella of the small claw of the fore-foot is narrow. The mucro, seen from the side (fig. 9), has a narrow but distinct lamella, hardly noticeable in immature specimens (fig. 11). The hairs are of the type of *A. purpurascens*, Lubbock, a few long, curved bristles being mixed with the short ones (fig. 7); only on the last abdominal segment are the bristles straight. In the present variety (*concolor*) the curved bristles are less long and less numerous than in typical *A. dubius*.

This variety is, in some respects, intermediate between the typical form of *A. dubius*, Tullb., and *A. Theelii*, Tullb. (7). It agrees closely with the latter species in size and colour, but that insect has the anal papillæ separated, and the spines straight. In the Franz-Josef Land form, as in typical *A. dubius*, the papillæ arise close together (fig. 8), and the spines are curved (fig. 7).

Achorutes longispinus, Tullb.

This is evidently a common and widespread species; it occurred in numbers at Cape Flora (19th August, 1896, 1st July, 1897) and on Bruce Island (23rd May, 1897). First described from Novaya Zemlya (7), it has since been recorded from Spitzbergen (4*c*), Scotland (1), and Buenos Aires (4*b*).

FAMILY.—ENTOMOBRYIDÆ.

Isotoma fimetaria (Linn.).

A few examples of this delicate species occurred at Cape Flora (19th August, 1896, and 14th July, 1897) and Cape Gertrude (27th June, 1897). It is doubtless a widely distributed form, as it occurs in Greenland, Siberia (7), Finland (5), Sweden (7), Scotland (1), northern Germany (4*a*), and Bohemia (5).

Isotoma bidenticulata, Tullb.

Judging by the present collection, this seems by far the commonest and most dominant springtail of Franz-Josef Land. It occurred at Cape Flora (21st May, 30th June, 11th and 14th July, 1897), in Windy Gully, Miers Channel (25th August, 1896), and on pools by Carpenter's Rock (16th August, 1896). At the last-named locality, as also at Cape Flora (in June), an enormous number of specimens were collected. The species is already known from Greenland (7), Spitzbergen (4 *c*), Novaya Zemlya (7), northern Siberia (Cape Chelyuskin), and the mountains of Scandinavia (5).

Isotoma brevicauda, sp. nov.

Length 1·7 mm. Antennæ as long as head, the fourth segment twice as long as the third, and half as long again as the second (figs. 12, 13), post-antennal organ shortly ovate (fig. 13), fore-feet with two (fig. 14), middle and hind-feet with three (fig. 15) tenent hairs; both large and small claws toothed on inner margin; tip of abdomen with slender feathered bristles (fig. 16); spring short, manubrium not projecting beyond last abdominal segment; dens, one and a-quarter times length of third abdominal segment (fig. 12); mucro with four teeth (figs. 17, 18); colour, deep blue-violet, except legs, distal part of dens, and third and fourth antennal segments, which are pale yellow.

Six specimens of this springtail occurred at Cape Gertrude, 27th June, 1897.

This species is nearly allied to *Isotoma Reuteri*, Schött (5), and *I. sensibilis*, Tullb. (7), which have two or three tenent hairs on the feet—an exceptional character in the genus Isotoma. *I. brevicauda* is readily to be distinguished from these by its proportionally shorter spring and smaller size, as well as by its peculiarities of colour; the extension of the blue body-pigment into the proximal end of the dens, together with the pale terminal segments of the antennæ, gives it a very characteristic appearance.

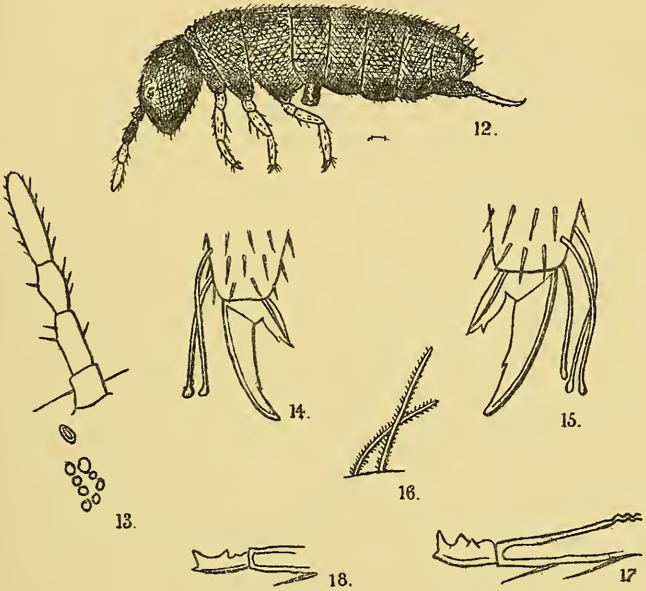

Fig. 12, *Isotoma brevicauda*, from side, × 27; fig. 13, antenna, post-antennal organ, and ocelli of left side, × 75; fig. 14, foot of first pair, × 180; fig. 15, foot of third pair, × 180; fig. 16, feathered bristles from tip of abdomen, × 200; figs. 17, 18, mucro from two specimens to show variation, × 180.

In one specimen, however, the whole antenna is dark. The foot-claws, more especially those of the second and third pairs, are distinctly toothed. This is a further character which, together with the four-toothed mucro, distinguishes the species from *I. Reuteri*; the latter, moreover, has the feathered bristles at the end of the abdomen longer, more robust, and clubbed. My best thanks are due to Dr. C. Schäffer for kindly sending me a specimen of *I. Reuteri* for comparison, and enabling me to make sure that the present insect is distinct from that species, which is recorded from the Tschuktschi peninsula of northern Asia. The other allied species, *I. sensibilis*, was, until recently, known only from high northern latitudes, but it has lately been obtained both in Scotland (1) and Ireland. The mucro of *I. brevicauda* exactly resembles that of *I. denticulata*, Schäffer (4*a*), a north German form which, after examination of specimens kindly sent me by the describer, I believe to be a variety of *I. sensibilis*.

The wide range of many species of Collembola is shown by the fact that three of the seven species mentioned in this Paper (*Anurida granaria*, *Achorutes longispinus*, and *Isotoma fimetaria*) are inhabitants of Great Britain, one of them being found also in the southern hemisphere. The remaining four species—*Lipura grœnlandica*, *Achorutes dubius*, *Isotoma bidenticulata*, and *I. brevicauda* must, for the present at least, be considered as characteristically northern species. No doubt, many more springtails remain to be discovered in the Franz-Josef archipelago, since seventeen species are already known from Spitzbergen, and sixteen from Greenland. In the accompanying table, I have indicated the distribution of the insects of the order as known from the principal Arctic islands. It is of interest to find that the presence of not a few species of these wingless insects in America, in Greenland, in the islands to the north of Europe and Asia, and on the Euro-Asiatic continent, lends support to our belief in a Pliocene or Pleistocene land connexion to the north of the Atlantic Ocean—a belief already upheld by so much evidence both geological and zoological.

[Table.

TABLE SHOWING DISTRIBUTION OF COLLEMBOLA FROM THE PRINCIPAL ARCTIC ISLANDS.

	GREENLAND.	SPITZBERGEN.[1]	FRANZ-JOSEF LAND.	NOVAYA ZEMLYA.
†_Anoura muscorum_ (Templ.)	Meinert.	—	—	—
Lipura ambulans (L.)	Meinert.	—	—	—
L. armata, Tullb.	Tullberg.	—	—	—
L. arctica, Tullb.	—	Tullberg.	—	Tullberg.
*_L. grœnlandica_, Tullb.	Tullberg.	Tullberg.	Carpenter.	—
Anurida granaria (Nic.)	—	Stscherbakow	Carpenter.	—
Tetracanthella pilosa, Schött.	—	Wahlgren.	—	—
Xenylla humicola (Fb.)	Tullberg.	—	—	Tullberg.
†_X. maritima_, Tullb.	Meinert.	—	—	—
Achorutes dubius, Tullb.	—	Schäffer.	Carpenter.	Tullberg.
*_A. Theelii_, Tullb.	—	—	—	Tullberg.
†_A. armatus_ (Nic.)	Tullberg.	—	—	—
†_A. longispinus_, Tullb.	—	Schäffer.	Carpenter.	Tullberg.
†_A. viaticus_ (L.) (= _humicola_, Mein.)	Tullberg.	Tullberg.	—	Tullberg.
Schötella uniunguiculata (Tullb.)	Meinert.	—	—	—
†_Podura aquatica_, L.	Fabricius.[2]	—	—	—
Isotoma Schöttii, D. Torre. (_litoralis_, Schött.)	—	Schött.	—	—
I. fimetaria (L.)	Tullberg.	Stscherbakow	Carpenter.	—
I. quadrioculata, Tullb.	Tullberg.	Lubbock.	—	Tullberg.
*_I. binoculata_, Wahlgr.	—	Wahlgren.	—	—
I. sensibilis, Tullb.	—	—	—	Tullberg.
I. brevicauda, Carp.	—	—	Carpenter.	—
I. bidenticulata, Tullb.	Tullberg.	Schäffer.	Carpenter.	Tullberg.
*_I. spitzbergenensis_, Lubb. (= _arctica_, Stsch.)	—	Lubbock.	—	—
†_I. palustris_ (Müll.) (= _Stuxbergii_, Tullb.)	—	Tullberg.	—	Tullberg.
†_I. viridis_, Bourl.	Meinert.	Stscherbakow	—	—
Corynothrix borealis, Tullb.	—	—	—	Tullberg.
*_Lepidocyrtus elegantulus_, Mein.	Meinert.	—	—	—
L. lanuginosus (L.)	—	Stscherbakow	—	—
Tomocerus minutus, Tullb.	—	—	—	Tullberg.
Sminthurus viridis (L.)	—	—	—	Tullberg.
S. Malmgrenii (Tullb.)	—	Tullberg.	—	Tullberg.
*_S. concolor_, Mein.	Meinert.	—	—	—

All the above species occur on the Euro-Asiatic continent except those marked with an asterisk, but *Isotoma spitzbergenensis* has been found in Scotland. The species marked with a dagger are known to inhabit also the American continent.

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[1] Including White Island and King Karl's Land. All the species in this column occur in Spitzbergen proper, except *Isotoma binoculata* which is peculiar to White Island. *I. bidenticulata*, *I. quadrioculata*, and *Achorutes viaticus* are recorded from King Karl's Land; while *Lipura armata*, *L. arctica*, *L. neglecta* (Schäff.), *Tetracanthella pilosa*, *Xenylla humicola*, *Achorutes viaticus*, and *Isotoma viridis* are known to inhabit Bear Island to the south of Spitzbergen (8).

[2] Doubted by Meinert.

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XVII.

PANTOPODA FROM THE ARCTIC SEAS. (Dredged by Mr. W. S. Bruce, 1897–98.)

By GEORGE H. CARPENTER, B.Sc.
Assistant Naturalist in the Science and Art Museum, Dublin.

[Read November 22; Received for Publication December 2, 1899;
Published January 25, 1900.]

Through the courtesy of Mr. W. S. Bruce, of Edinburgh, I have already had the privilege of examining and describing (1) the collection of Pantopoda from the seas around Franz-Josef Land, made by him while attached to the Jackson-Harmsworth expedition during 1896 and 1897. During the summer of 1898 Mr. Bruce was cruising in the S.S. "Blencathra," in the Arctic Ocean; and he has now committed to me the task of determining the pycnogons which were dredged on that expedition. Any addition to our knowledge of the distribution of these interesting creatures is to be welcomed, and I am glad therefore to be able to place on record the localities and depths at which Mr. Bruce's specimens were obtained. Two specimens from the neighbourhood of Franz-Josef Land, which were, by oversight, not forwarded to me last year, are inserted here; one of them belongs to a species, *Eurycyde hispida* (Kröyer), not included in my former Paper.

All the species here mentioned are fully described and figured in Sars' beautiful monograph (2). The specimens in this collection are, by Mr. Bruce's generosity, deposited in the Science and Art Museums of Edinburgh and Dublin.

Family.—PALLENIDÆ.

Pseudopallene circularis (Goodsir).

Lat. 68° 52′ N.; Long. 49° 23′ E. 20 fms. 1 male (6th June, 1898).

Lat. 70° 48′ N.; Long. 53° 9′ E. 20 fms. 1 male, with newly-hatched larvæ (16th June, 1898).

These occurrences of this species off the coast of Kolgouev, and at the entrance to Kara Straits, does not add materially to our knowledge of its range as given by Sars (2), who states that it is known from the coasts of North America, Greenland, Scotland, Norway, Lapland, and Novaya Zemlya.

Cordylochele malleolata (Sars).

Lat. 76° 54′ N.; Long. 36° 48′ E. 76 fms. 1 female (8th July, 1898).

This locality to the south-east of Spitzbergen extends the known range of this scarce Arctic species, which is recorded by Sars (2) only from the north-west coast of Spitzbergen, a station midway between Finmark and Beeren Island, and the Kara Sea. It occurs at depths varying from 40 to 459 fathoms.

Family.—NYMPHONIDÆ.

Nymphon grossipes (Fab.)

Lat. 70° 48′ N.; Long. 53° 9′ E. 20 fms. 1 male, with eggs (16th June, 1898).

Lat. 70° 2′ N.; Long. 49° 10′ E. 34 fms. 1 male (6th June, 1898).

The capture of only two examples of this widespread northern species on the present cruise contrasts strongly with the large number taken by Mr. Bruce in the neighbourhood of Franz-Josef Land in 1896-7 (1).

var. **mixtum**, Kröyer.

Off glacier between Cape Flora and Cape Gertrude, Franz-Josef Land. 1 male (21st July, 1897).

Nymphon gracilipes, Heller.

Lat. 76° 28′ N.; Long. 33° 6′. 100 fms. 3 males, with egg-masses. 3 females (13th July, 1899).

This, the largest species of the genus Nymphon, has a very wide range in the Arctic Seas. It is noted by Sars as occurring in the Varanger Fjord, off Jan Meyen, Spitzbergen, Grinnel's Land, and North America, as well as in the Barents and Kara Seas. Though the type-specimens were taken near Franz-Josef Land, the species was unrepresented in Mr. Bruce's collection from there, which I examined last year. The bathymetric range of this Nymphon varies from 10 to 459 fathoms. The specimens now recorded are clearly referable to *N. gracilipes*, as distinguished by Sars from *N. Strömii*, Kröyer; the latter form, as restricted by him, has a more southern range.

Chætonymphon macronyx (G. O. Sars).

Lat. 76° 28′ N.; Long. 33° 6′ E. 100 fms. 1 male, with eggs; 1 female; 1 immature (13th July, 1898).

This station to the south-east of Spitzbergen adds to our knowledge of the range of this beautiful species, which is recorded by Sars from various localities to the west and north of Norway, as well as from the Faröes, the south and north-west coasts of Spitzbergen, and the Kara Sea. It was obtained by Mr. Bruce to the south of Franz-Josef Land in some numbers (1).

Boreonymphon robustum (Bell).

Lat. 76° 28′ N.; Long. 33° 6′ E. 100 fms. 5 males with young in all stages (13th July, 1898).

Lat. 78° 21′ N.; Long. 27° 55′ E. 100 fms. 1 young specimen (15th July, 1898).

This is a widespread and well-known Arctic species.

Family.—COLLOSENDEIDÆ.

Collosendeis proboscidea (Sabine).

Lat. 76° 28′ N.; Long. 33° 6′ E. 100 fms. 1 male.

Another well-known species with a wide circumpolar range.

Eurycyde hispida (Kröyer).

Off Cape Mary Harmsworth, Franz-Josef Land, 53–93 fms. (7th July, 1897).

This appears to be a somewhat scarce species, though it has a wide distribution in the Arctic seas, having been dredged at different localities from the Norwegian coast to Greenland and the Kara Sea. It is of interest to know that it ranges northward to Franz-Josef Land.

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NOTE ADDED IN PRESS.

Mr. Bruce desires that special acknowledgment should be made to Mr. Andrew Coats, of the "Blencathra," for his courtesy, kindness, and generosity in enabling this collection to be made.

XVIII.

A FRACTIONATING RAIN-GAUGE.

By J. JOLY, D.Sc., F.R.S.,
Hon. Sec., Royal Dublin Society.

[Read January 17; Received for Publication, January 19;
Published March 8, 1900.]

In the course of a recent communication to this Society on the Geological Age of the Earth, I referred to the amount of sodium chloride carried in the atmosphere from the sea to the land as an important factor in the mode of estimating geological time, which I was then advocating.

But little appears to be known on the matter beyond the broad fact that, in inland regions, the amount of this constituent in rain-water becomes very small. There is also evidence, derived from observations made at different altitudes in Switzerland, that falling rain grows richer in this constituent as it descends through the atmosphere.

This latter observation also leads to the inference that samples of rain collected at the beginning and during the progress of a shower should reveal a diminution in the quantity of sodium chloride. Bunsen has shown that certain dissolved constituents in rain-water diminish in this manner.

The matter is well worthy of observation by those who live outside the impure atmosphere of a city. The chemical operation of determining the amount of chlorides present is a simple one. Continuous records should be made, and should include successive analyses of successive samples as referred to above, and simultaneous observations of wind direction.

In order to effect the subdivision of rain received in the gauge into fractional parts as the rainfall progresses, I have devised the apparatus described in this note. It may be inexpensively made, and includes no valves or machinery. It cannot deceive, and may be constructed throughout of material which will not contaminate the rain-water. It delivers its catchment into separate bottles for the most part (if the rainfall is at all considerable); and by simply varying the dimensions of these bottles, they may be arranged to receive the rain in various fractional parts. Thus the first one-tenth inch of rainfall may be automatically delivered into the first bottle, the second tenth into a second bottle, and so on. Or the second bottle may be of such dimensions as to receive the subsequent two-tenths of an inch or three-tenths, and, in short, any one of the receiving bottles arranged to take up any desired number of tenths of an inch rainfall. Again, the basis of the fractionation may be one-twentieth of an inch rainfall, and any number of successive twentieths arranged to collect in each bottle or in any one of the bottles.

How this is effected will be seen by reference to the accompanying diagram. The catchment basin or funnel of the rain-gauge is lettered *c*, and appears at the top of the gauge. This discharges through a narrow tubulure into the wider tube *t*, which, in turn, communicates with the receiving reservoir *a*. In the figure this reservoir is shown as provided with two siphons only. It will presently be seen that this suffices to effect, in general, a three-fold division of the rainfall received.

Two other vertical tubes, *t′*, *t′*, support the siphons, which are shown dipping to the bottom of the bottles 1 and 2 placed beneath. The bend or turn-over of the one siphon (that communicating with bottle 1) is at a lower level than that of the other. The only peculiarity in the construction of these siphons is the use of a wide-mouthed bell-shaped or thistle funnel suspended on a short length of rubber tubing, to form the shorter leg of the siphon. The rubber tubing hangs vertically within the tubes *t′*, and may be about five or six inches in length.

The action is as follows:—As the rain collects in the reservoir, it at length fills this, and rises in the siphons and in the central tube till the lower siphon comes into action and runs the whole contents of the reservoir in bottle 1. If the reservoir is of such dimensions as to fill when one-tenth of an inch rainfall has been received in the funnel above, evidently this first bottle receives the first tenth of an inch rainfall.

The reservoir being now empty, and assuming for the present that the siphon, which has just operated, is again completely filled with air (save for that part of its longer limb dipping beneath the water in bottle 1), it remains to consider what will ensue when the reservoir is again filled in the progress of the rainfall. This time, when the water begins rising in the siphons, the siphon leading to bottle 1 has evidently the hydrostatic pressure due to the depth of water covering its exit in bottle 1 opposing its operation. It thus

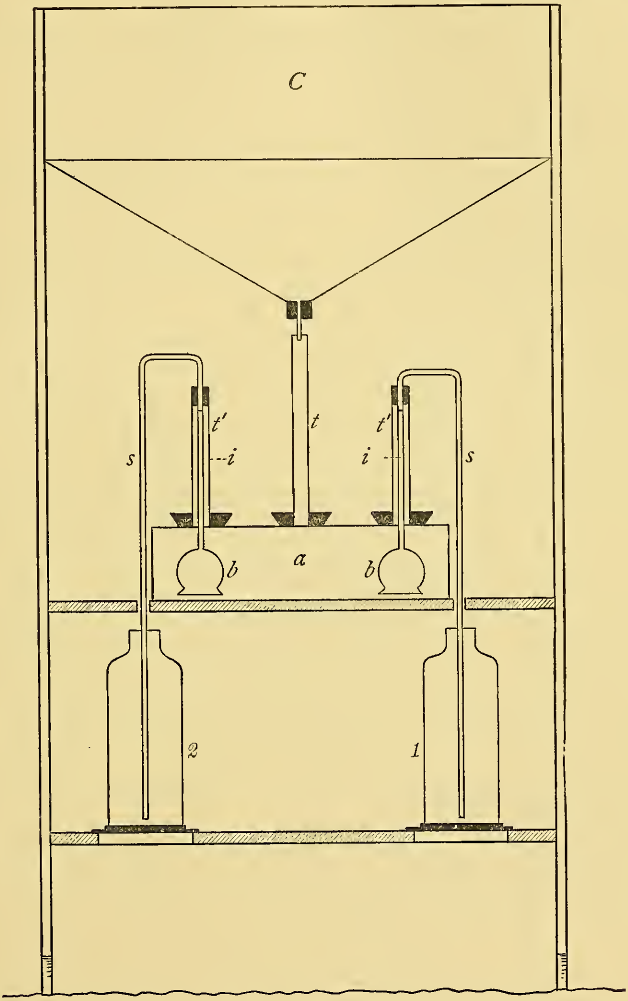

Diagram of Fractionating Rain-Gauge.

virtually becomes the higher of the two siphons, and *now* it is the siphon supplying bottle 2 which operates. The second tenth of an inch is thus stored in bottle 2. If the rain continues after this, it remains stored in the reservoir, which thus receives the third tenth. Finally this may overflow by a tubulure attached at the upper end of *t* into a large bottle placed on the shelf beneath (not shown in the figure).

It is apparent that the bottle 2 may be at once arranged to receive a second or a third charge by simply using one sufficiently capacious, and bringing its siphon but a little way downwards within its tubulure—just so much that the last charge received will throw the siphon out of action by opposing to its action a hydrostatic head greater than the difference in level between the bend of the siphon and the overflow tubulure on *t*. This sufficiently explains the manner in which this gauge may be made to deliver its catch into a succession of bottles in any aliquot parts of the content of the reservoir *a*. To suit the possibilities of this climate, a total storage capacity for about one inch rainfall is sufficient. This would, perhaps, be best received as follows—two bottles and siphons being used, the first bottle receiving one-tenth, the second three-tenths, the remainder being caught in the reservoir and overflow. A rainfall of from 0·1 to 0·2 in. is in this case subdivided between 1 and reservoir, from 0·2 to 0·4 in. between bottles 1 and 2 and reservoir; from 0·4 to 0·5 in. between 1, 2, and reservoir. There will but seldom be a rainfall exceeding this between daily periods of attendance on the apparatus; but when this does occur the subdivision is between 1 and 2 and reservoir + overflow. A threefold subdivision will be sufficient. If no more than a twofold one is sought, bottle 2 may be made so capacious as to receive any quantity over the first tenth. Again, if it is desired to bottle off the first twentieth, the reservoir must be made of the suitable dimensions. Obviously any desired number of siphons may be used.

Returning now to the construction of the siphons, it is requisite to say a word explanatory of the use of the indiarubber continuations of the shorter limb. Those who have used cup-of-Tantalus arrangements will be familiar with the difficulty of effecting the sudden and complete cessation of the siphon when the liquid in the cup sinks sufficiently to uncover the mouth of the siphon within. The siphon leaves off by sucking in a mixture of air and water, and if a continuous trickle is entering the cup, one of two things will then happen—the siphon will start prematurely into action owing to the downward pull of the short beads of water in the longer limb, or it will fall into continuous action, such a quantity of water passing over mingled with air as will just equal the inflow. This difficulty recently presented itself to me in the construction of an apparatus involving the use of an intermittent siphon, and I then found that the method adopted in this gauge completely surmounted the difficulty. A moment's consideration will, in fact, show that the bell-glass, being full of water till the last moment, will stretch by a little the thin rubber tube supporting it. When, therefore, the mouth of the bell-glass is finally uncovered, and its contents thereby discharged, the rubber contracts, effecting the complete disengagement of the siphon for an interval which, even with a fairly rapid inflow, is sufficient to put the siphon entirely out of action, and leave it filled with air. Any form of spring suspension will evidently effect this end, provided it permit of some appreciable lengthening of the shorter limb of the siphon due to the weight of water within it.

As regards the dimensions which I have adopted in the case of the apparatus which is before you, and which is intended for trial only, I have made the catchment funnel 16 inches in diameter. The area of this is just 201 square inches. A rainfall of $\frac{1}{10}$ in. gives, in this case, a volume of 20·1 cubic inches. The first bottle just possesses this volume when filled to a depth of about 6 inches. The second bottle possesses an equal capacity, but, of course, may be interchanged for one of greater capacity, so as to effect a different subdivision of the rainfall. The reservoir is an oblong tinned-iron box about 5 by 2 inches in plan, and 2 inches deep. This permits of sufficient room for the thistle-shaped bells which are cut from thistle-funnels, and each about 1 inch in diameter. The reservoir would be better made in glass.

Finally, I may point out that, while preserving two siphons only in the reservoir, any sub-division may be effected by arranging that the bottles first receiving a charge from the reservoir shall be also fitted with siphons on the foregoing principles, so that, when just filled, they transfer their contents to yet other bottles placed beneath. The latter siphons, being thrown out of action by the hydrostatic pressure of the water in the lowest bottles, will not again act. Thus bottle 1 in the figure transfers the first tenth to a bottle 1′ placed beneath it; bottle 1 then receives the second tenth. After this bottle 2′ takes up the third tenth, etc. Obviously, too, *one* siphon in the reservoir may supply quantities which are multiples of the contents of the reservoir to two or more bottles placed at different levels.

XIX.

ON THE OCCURRENCE OF CYANOGEN COMPOUNDS IN COAL-GAS, AND OF THE SPECTRUM OF CYANOGEN IN THAT OF THE OXY-COAL-GAS FLAME. BY W. N. HARTLEY, F.R.S., Royal College of Science, Dublin.

[Read FEBRUARY 21; Received for Publication FEBRUARY 23;
Published APRIL 6, 1900.]

In a memoir[1] giving an account of an elaborate investigation, by Messrs. Eder and Valenta, of the spectrum of the flame afforded by coal-gas when supplied with oxygen, the authors remark that one of them had discovered the ultra-violet spectrum of the inner blue cone of the flame of a Bunsen burner in 1886, and in 1890 had published photographs of the visible and ultra-violet emission spectrum of feebly illuminating hydro-carbon flames with wave-length measurements of the principal lines and bands. They state that the spectrum of the oxy-coal-gas flame, described by me in "Flame Spectra at High Temperatures," Part I., "Oxyhydrogen Blow-pipe Spectra" (Phil. Trans., vol. 185, p. 16, 1894), contains a list of measurements of lines and markings on the bands, which are erroneous to the extent in some cases of five-tenth metres in wave-length, and that no regard was paid to the work mentioned above. It may here be explained that I was quite unaware of this work at the time, and, moreover, the spectrum of the oxy-coal-gas flame was photographed and described by me in 1888–89, and therefore anterior to its date of publication. The account of it formed a small part of a long communication made to the Royal Society in 1893, and was intended as a study preliminary to the fuller examination of the flame spectra of metals and metallic oxides; also of flames arising from metallurgical operations, such as the Bessemer and open-hearth steel processes. The lines and bands to the number of 111 observed in the oxy-coal-gas flame when using a single quartz prism, and a "somewhat wide slit"[2] (see p. 170,

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[1] Denkschr. K. Akad. Wiss. Wien. Vol. 67, Sept., 1898. Also Beiblätter, Wiedemann's Annalen, vol. 23, p. 557, Sept., 1899.

[2] On p. 2 of Eder and Valenta's paper, these words are wrongly translated—"Mit *sehr weitem Spalte*," which is a departure from the true meaning and from the actual fact.

loc. cit.), were mostly of a very feeble character; "the exposure was one hour." "No attempt was made to purify the coal-gas, as the object of examining this spectrum was to determine the origin of any lines which might be caused by hydrocarbons in the oxy-hydrogen flame."

The oxyhydrogen blow-pipe was used in subsequent experiments for obtaining metallic spectra. It was not intended that the lines observed in the oxy-coal-gas flame should be considered as having been accurately measured, it is quite obvious indeed that the conditions necessary for their observation rendered the usual degree of accuracy impossible, on account of—first, the small dispersion, particularly of the less refrangible rays; secondly, the "somewhat wide slit"; and thirdly, the feeble spectrum.[1]

The wave-lengths assigned to the lines and edges of bands are expressly stated to be merely approximations, which were to serve for the recognition of the same lines and bands, in case they were observed in photographs taken subsequently under other conditions. It could hardly have been anticipated that this would be misunderstood if the original publication was consulted, seeing that at the head of the description it is so prominently stated that the measurements were approximations.

Messrs. Eder and Valenta, in the following words, state what is decidedly, though no doubt quite unintentionally, misleading:—"Hartley glaubte die Kayser und Runge'schen Cyanbanden $\lambda = 4215$, 4208, &c., des elektrischen Kohlenbogenlichtes in der Oxygen-Leuchtgasflamme zu finden. Dagegen ergeben unsere Messungen zweifellos, dass die mit $\lambda = 4216$ beginnende violette Cyanbande mit der violetten Leuchtgasflammen-Spectralbande (ζ) gar nichts gemein hat, und nur ungenaue Messungen können zu solchen irrigen Schlüssen führen."

Now, between wave-lengths 3893 and 3487·8 there are eighteen bands, and opposite to each is the wave-length of a band measured by Kayser and Runge placed under the head of "Remarks." There are also three other measurements, each described as a

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[1] The following quotations give some idea of the definition of lines and bands on the photographs, p. 170:—"The edges of the bands are as sharp as they are generally seen in the spectrum of a Bunsen flame, and the lines of which the bands are composed are somewhat wide," p. 173. "Then appears a series of beautiful, very fine, and closely-adjacent lines."

"marking in the continuous spectrum, or band," 4215, 4208, and 4196: opposite to these are the wave-lengths of three bands measured by Kayser and Runge, 4215·26, 4208·24, 4196·05.

There is no statement to the effect that these are cyanogen bands or that they were believed to be such; moreover, in the general description of the spectrum on p. 170, it is expressly stated, "All the principal bands observed are probably due partly to carbon and partly to what generally is considered to be the cyanogen spectrum."

It will be noticed that the word *probably* is used, and the bands named are designated as those *generally considered* as the cyanogen spectrum. Moreover, it is to the principal bands that this remark is applied. This clearly indicates what was actually the case, namely, that I had not concluded they were carbon bands, and had not believed them to be cyanogen bands. In point of fact, as two subsequent publications prove,[1] there were facts known to me at that time which rendered it difficult to believe in the existence of a distinct and individual cyanogen spectrum. Photographs of a number of flame spectra, including that of cyanogen-gas and of ordinary coal-gas had been obtained some years previously, namely, in 1882; but in view of the facts that some of the cyanogen bands could be obtained by passing sparks between graphite electrodes in air, when moistened with strong solutions of such chlorides as those of zinc and calcium, and could not be obtained when the graphite was moistened with cyanides, such as those of potassium and of mercury, it appeared to be not improbable that these were in reality a modification of the carbon spectrum. At the same time it was known that imperfectly purified coal-gas might contain cyanogen compounds, and the combustion of these would give the banded spectrum or a portion of it, peculiar to the cyanogen flame. Even the combustion of carbon at a high temperature in the presence of nitrogen in air might be expected to do so.

It will thus, I think, appear evident that my views at the time were clearly stated, but they have been imperfectly understood, and to some extent misinterpreted. Had I been aware of the

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[1] "On Variations observed in the Spectra of Carbon Electrodes," Proc. Roy. Soc., vol. 55, p. 344, 1894, and "On the Spectrum of Cyanogen as produced and modified by Spark Discharges," Proc. Roy. Soc., vol. 40, p. 216, 1896.

work done by Dr. Eder in 1890, it would have been a pleasure to have recognised it with that of other investigators whose works were mentioned.

In justice to the paper criticised, however, it may be mentioned, first, that with the same dispersive power the method of operating adopted by me made it evident that there were more lines and bands than occur in Eder and Valenta's spectrum. Thus in Lecocq de Boisbaudran's δ group I observed 12 lines or bands: they measured but 3.

The respective measurements are here given:—

	Hartley.	Eder and Valenta. (Small dispersion.)	
Yellow, . .	5473	5471	*Yellow.*
	5446	5442	
	5422	5423	

They designated this the β band.

Between the δ and the γ group I have given ten measurements: they give four.

I quote their numbers and mine, with those of others, for comparison:—

	Hartley.	Eder and Valenta. (Small dispersion.)	—	—
Green, .	5193	—	—	—
	5170	5765	5165·50 Watts.	—
	5138	5129	5138·40 Fievez.	5138·56 5138·34 5138·13 K. & R.
	5098	5096	5097·90 Fievez.	5100 Watts. 5098·34 5098·19 K. & R.
	5086	5084	5086·90 Fievez.	5086·31 5086·43 K. & R.
	4952	—	4951·5 Kayser and Runge.	—
	4899	—	4899·98	
	4816	—	4815·66	
	4774	—	4775·32	
	4765	—	4763·86	

THE γ GROUP.

	Hartley.	Eder and Valenta. (Small dispersion.)	—	—
Blue, . .	4735·5	—	4739·80 Watts.	—
	4732	4737	4731·90 Fievez.	4732·33 4731·93 } K. & R.
	4720	—	4719·87 K. & R.	4720·1 F.
	4702	4697	4702·30 K. & R.	4702 F.
	4688	4684	4688·20 K. & R.	4688·9 F.
	4679	4679	4678·90 F.	—
	4672	—	4672·20 F.	—
	4462	—	—	—

THE ε GROUP.

	Hartley.	Eder and Valenta. (Small dispersion.)	—
Violet, . .	4405	—	—
	4395	—	—
	4378	4380	4381 L. & D.
	4364	4364	4365 L. & D.
	4350	4348·4	—
	4342	4344	—

The β Group.

	Hartley.	Eder and Valenta, (Small dispersion.)	Remarks.
Violet, . .	4332	4335	—
	4312	4314·3	—
	4302	4306	—
	4288	4286	—
	4282	4282	—
	4273	4276	—
	4268	4268	—
	4260	4262	—
	4255	4256	—
	4248	4250	—
	4240	4237	—
	4230	4231	—
	4215	4218	4215·26 $(CN)_2$, K. & R.
	4208	4206	4208·4 $(CN)_2$, K. & R.
	4196	4195	4196·05 $(CN)_2$, K. & R.
Ultra-Violet,	4003	4007	—
	3998	—	—
	3992	3994	—
	3984	3983	—
	3973	3972	—
	3963	3962	—
	3954	3953	—
	3946	3944	—
	3938	3936	—
	3932	—	—
	3926	3928	—
	3920	3922	3920·6 D.
	3913	3915	—
	3908	3910	—
	3904	3906	—
	3898	3898	—
	3893	3896	3893·1 D.
	3882	3884	3883·1 $(CN)_2$, D.

From this point onwards to wave-length 3487·8, there are nineteen lines or edges of bands, only one of which is recorded by Eder and Valenta. They all agree fairly well with the bands in the spectrum of cyanogen, whether they really belong to this substance or not, and they agreed with no other spectrum which was known to me at that time:—

	Hartley.	Eder and Valenta. (Small dispersion.)	Remarks.
Ultra-Violet,	3868	3871·4 $(CN)_2$, D.	—
	8356	3855·06 $(CN)_2$, K. & R.	—
	3846	—	—
	3840	3839·98 $(CN)_2$, K. & R.	—
	3831	3831·15 $(CN)_2$, K. & R.	—
	3825·5	3825·4 $(CN)_2$, K. & R.	—
	3823	3823·9 $(CN)_2$, K. & R.	—
	3818·3	3819·36 $(CN)_2$, K. & R.	—
	3815	3816·24 $(CN)_2$, K. & R.	—
	3790	—	—
	3642·5	3642·63 $(CN)_2$, K. & R.	Eder and Valenta give a line 3642·5.
	3579·5	3579·22 $(CN)_2$, K. & R.	—
	3568·5	3568·4 $(CN)_2$, K. & R.	—
	3563	3563·92 $(CN)_2$, K. & R.	—
	3544·5	3545·07 $(CN)_2$, K. & R.	—
	3528	3528·71 $(CN)_2$.	—
	3522	3522·49 $(CN)_2$.	—
	3498·5	3497·7 $(CN)_2$.	—
	3487·8	3487·61 $(CN)_2$.	—

In conclusion, it may be admitted that a spectrum obtained with a prism of small dispersion is not the same as that photographed with a grating of very great dispersion, though both may have their origin in the same flame. The greatest differences between the two will appear at the less refrangible end, where the bands shown by the prism are resolved into groups of lines by the grating. It is therefore better to compare the numbers obtained by Eder and Valenta with small dispersion with my quartz prism photographs obtained in a similar manner; and it will be noticed that the difference between them is not very remarkable, particularly in the violet and ultra-violet.

That these photographs contain a greater number of lines than those of Eder and Valenta may be accounted for—first, by the difference in the flame employed and the part of it examined; secondly, by the composition of the gas not being exactly the same. It has been observed by Lecocq de Boisbaudran (and this has been mentioned in my original paper) that even a Bunsen burner may offer, under slightly different conditions, spectra which materially differ. With compressed oxygen used in a blow-pipe with a large flame such differences may be greatly increased, and this is believed to have been the case in consideration of the fact that a whole group of lines, not recorded by Eder and Valenta, are in close agreement with a group peculiar to the spectrum, which I have since recognised as belonging to cyanogen.

Eder and Valenta examined the inner cone of a Bunsen burner, fed with oxygen at ½ to ¾ of an atmosphere pressure, with an instrument of small dispersion, and also with a grating of 15 feet radius. I studied the upper half of a gas blow-pipe flame supplied with oxygen under a pressure of as much as 22 atmospheres, using merely a quartz prism, and by such means only could the purpose of the investigation have been satisfactorily fulfilled.

There is, however, one further remark to be made, namely, not only was the method of burning the gas different to that employed by Eder and Valenta, but the composition of the gas itself may have been very different.

If, for instance, the gas contained cyanogen or cyanides it would certainly yield the cyanogen lines or bands upon combustion, for very minute traces suffice to produce some part of that spectrum. I entertained no doubt whatever that the cyanogen bands entered into the spectrum of the oxy-coal-gas flame examined by me. Moreover I have proved the existence of cyanogen compounds in the gas in quite sufficient quantity to account for it in the flame.

The supply pipe of an ordinary Bunsen burner was made to deliver gas at the rate of five cubic feet per hour, and for a period of one hour, into a series of bulbs containing a solution of ferrous sulphate, made strongly alkaline with caustic potash solution.

On examining the liquid it was found to possess a strongly ammoniacal odour. On the addition of a few drops of ferric chloride and acidifying the mixture with dilute hydrochloric acid, there was a voluminous precipitate of Prussian blue, sufficient to make some 15 c.c. of liquid thick with the solid substance.

This completely sets at rest the question of the possibility of the lines being due to cyanogen. Irrespective of this evidence it should be mentioned that a very peculiar yellow and yellowish-green colour tinged the oxy-coal-gas flame in a manner similar to the coloration which may be observed like a halo on the edges of the mantle of the peach-blossom coloured flame of cyanogen. This at the time seemed to be probably due to the synthesis of cyanogen or of hydrocyanic acid by the action of intensely heated hydrocarbons in contact with nitrogen.

It should be stated that, in testing the coal-gas, an alkaline solution without the addition of ferrous sulphate did not absorb so much of the cyanogen compound, and that plain water gave merely a very distinct Prussian blue colour. From this it would appear that the substance is either ammonium cyanide or some other cyanogen compound that splits up into ammonia and hydrocyanic acid.

It is of no little interest that the presence of cyanogen compounds in the gas supply of a large city like Dublin should first have been indicated by the bands and lines observed in the spectrum photographed from the flame of the burning gas.

XX.

THEORY OF THE ORDER OF FORMATION OF SILICATES IN IGNEOUS ROCKS.

By J. JOLY, D.Sc., F.R.S., Hon. Sec. R.D.S., Professor of Geology and Mineralogy, Trinity College, Dublin.

[Read March 21; Received for Publication March 23;
Published May 12, 1900.]

It is well known to petrologists that the order of solidification of the silicates of igneous rocks is not that of their melting points; and the fact has been stated generally by Prof. H. Rosenbusch that this order is that of decreasing basicity. That is to say, the minerals successively formed contain ever increasing quantities of the acidic constituent, silica. Thus (1) ores, (2) ferro-magnesian minerals, (3) felspathic minerals, (4) quartz, is the order of solidification. Within these groups the rule is also followed: thus, in the second group, olivine precedes biotite, and biotite precedes pyroxene. In the third group, the less acidic triclinic felspars precede the monoclinic.

Again, in porphyritic rocks, in which interruption due to physical causes in the slow process of segregation has occurred, the minerals of the second consolidation obey the same general rule.

To the general rule there are exceptions—or apparent exceptions. Thus, some of the minerals of the second and third groups may appear in inverted order in the dolerites and gabbros. Again, in pegmatitic and ophitic structures, simultaneous crystallization of quartz and felspar, or of pyroxene and felspar, may occur.

When it is remembered that rock formation was often carried on under conditions sufficient to magnify the importance of the volume relations of the constituents, and under conditions of quiescence favouring super-cooling, the fact that other than the intrinsic chemical and physical properties did not always govern the result, is not to be wondered at. The object of this note has, however, reference to the rule, not to the exceptions.

I have lately found that the softening point of quartz is far below what is currently thought. My experiments on this point were carried out in the following manner:—

A quartz fibre was stretched horizontally, fixed at one end, and at the other a tensile force was applied. This was produced by causing the fibre to displace from the vertical a pendulum carrying a small mass as its bob.

For 10 cms. of its length, this fibre traversed an open trough of platinum foil—square in section and 0·15 × 0·15 cms. in dimensions. This trough, being arranged so that it replaced the ribbon of a meldometer, could be heated to any required degree by a current, and its temperature determined by its thermal expansion. The fibre was so placed in the trough as to be depressed somewhat below the axis or central line of the latter.

Two micrometer microscopes observed points on the fibre (obtained by wetting a short length of it with varnish and dusting charcoal powder upon it) placed well to right and left of the heated portion. The displacement of the point on the cross wires of the right-hand micrometer measured the extension; the micrometer to the left of the trough served merely to safeguard against unnoticed displacement occurring at the fixed extremity of the fibre.

The data are:—

Force, . . .	0·425 grams.
Length heated, .	10 cms.
Diameter of fibre, .	0·00136 cms.
Cross-section of fibre,	$0{\cdot}145 \times 10^{-5}$ cms.
Stress, . . .	293×10^3 kilogrames per sqr. cm.
Temp. of trough, .	850° C.

Under these conditions one set of observations gave—

In 55 minutes extension = 0·076 cms.
In next 35 ,, ,, = 0·039 ,,

Many other observations were made at this temperature. The extension continually progressed: finally the fibre broke when cooling the trough. I may observe here that the stress applied is about $\frac{1}{30}$th the minimum carrying power of quartz fibre.

The quartz here is obviously at a temperature considerably below that of the walls of the trough, seeing that this latter is open freely to radiation and convective cooling.

Further experiments, using a platinum tube and stronger fibres, appeared to reveal slow extension at still lower temperatures, but the completion of these I have had to defer.

Previous results have always placed the softening point of quartz at a much higher temperature ; the apparent melting point *is*, in fact, higher. Not till temperatures of between 1400° and 1500° C. are reached does fine quartz dust show any change appreciable in the time we ordinarily assign to observations of the kind. Mr. Ralph Cusack, working with a meldometer, gives its softening point at 1406° C. ("On the Melting Points of Minerals," Proc. Royal Irish Academy, 3rd ser., vol. iv., p. 399), and in my own previous observations I had fixed its softening point as only a little over 1400° C. (see Plate VI., "On the Determination of the Melting Points of Minerals," Proc. Royal Irish Academy, 3rd ser., vol. ii., p. 38). Previously to these observations, it had been fixed as very much higher—above the melting point of platinum by some—that is, over 1750° C.

Evidently the observations indicate that silica is a body possessing an extraordinary range of viscosity. It is a thick—a very thick—liquid at about 1500° C. At a temperature of about 800° C. it is plastic, and yields with considerable rapidity to distorting forces. We may, perhaps, infer from the complete absence of cleavage that it is a substance which never crystallizes very vigorously.

Let us now see if the oxides, entering as bases into the constitution of the silicate, possess similar properties. These are chiefly—alumina, lime, magnesia, soda, potash, and iron-oxides.

Alumina.—According to M. Moissan ("Le Four Electrique," Paris, 1897), when melted and again cooled, this substance rapidly crystallizes. The crystallization of small rubies (coloured with a little sesqui-oxide of chromium) is so rapid that 10 to 15 minutes suffices for their formation. Crystals may also be obtained by sublimation. This, then, is evidently a body of very different properties from silica. It is a rapid and vigorous crystallizer from the state of fusion.

Calcium Oxide.—This can be crystallized by sublimation in the oxy-hydrogen flame, covering the lime cylinders with a thin transparent film and brilliant crystals (Proc. Royal Dublin Society, vol. vi., p. 225). M. Moissan reports that it cools from liquidity to a crystallized solid. It possesses a very high melting point, which is lowered by addition of Al_2O_3.

Magnesium Oxide.—Much like calcium oxide, but with a higher melting point: gives in the electric furnace large, transparent crystals out of the liquid, often several millimetres in length.

Sesqui-oxide of Iron.—Fuses rapidly, losing some oxygen, and pasing into the ferroso-ferric oxide, Fe_3O_4, which remains partly crystallized. It combines vigorously with the material of the furnace.

Potassium Oxide and Sodium Oxide.—These are known to become liquids at a full-red heat. Further information I have not obtained.

Now, if we assume that the properties of the first three of these bodies are in any marked degree additive, there is evidently a full explanation of the *apparent* abnormality in the order of crystallization of many silicates. The silica enters as an influence retarding crystallization and prolonging the viscous properties downwards in the scale of temperature. CaO, MgO, Al_2O_3, on the other hand, are crystallizers at high temperature, and influence the molecule accordingly.

That some such additive result is to be expected follows, perhaps, from the nature of the silicates, which, as Prof. Mendelieff observes, partake greatly of the nature of alloys.[1] He adduces the fact in support of this, that their specific volumes are additive. Thus, the volume of the silicate orthoclase can be closely calculated from the volumes of the constituents—Al_2O_3, K_2O, $6SiO_2$; and also the fact that the chemical union of these oxides is feeble, water, H_2CO_3, and such weak agencies, being able to gradually break them up.[2] The properties of glasses, too, are in many

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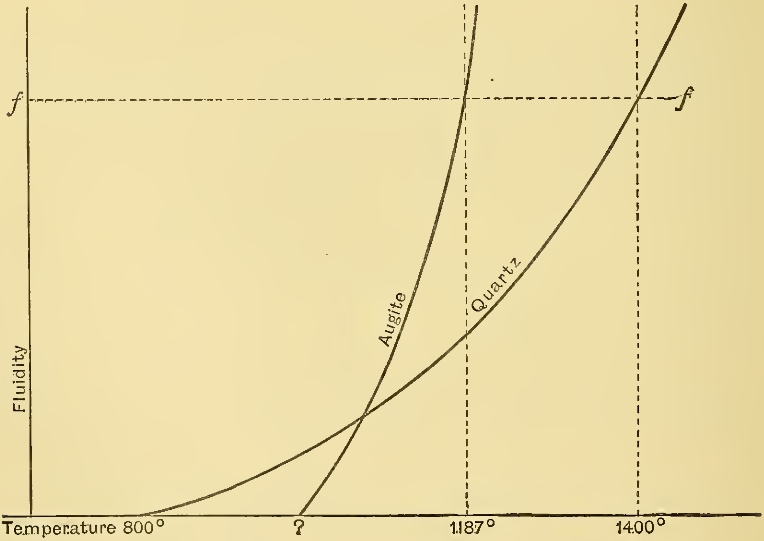
[1] It is noteworthy, in this connexion, that the solidifying points of alloys are only exceptionally below or above those of the constituents. These exceptions are well-known. Such curves as Gautier's, while showing that rarely is the solidifying point influenced directly proportionately to the percentages of ingredients, reveal that the introduction and increase of a constituent of high melting point involves, in general, a rise in solidifying point.

[2] "Principles of Chemistry." *London & New York*, vol. ii., p. 118.

particulars additive. In solutions of electrolytes, which may, perhaps, be looked upon as chemically similar to glasses, viscous properties, and many others, are additive.[1]

According to the theory I advocate here, the silicate, *A*, containing a small quantity of silica, crystallizes out at a higher temperature than the silicate, *B*, containing a larger percentage of silica, because the crystallizing point of *A* is less affected by the silica than in the case of *B*. A test of the melting point under ordinary conditions may not reveal this, for the rigidity of *B*, due to its greater amount of silica, may confer apparent solidity upon it at a temperature at which *A* has yielded to gravitational and surface tension forces. This will be understood from the diagram below.



Here, at the level, *f*, *f*, the fluidity has attained to such a degree as to cause yielding to gravitational distortion. This occurs at a lower temperature for the augite than for the quartz. According to the hypothesis now put forward, approaching the

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[1] The elaborate work "On the Relations between the Viscosity (Internal Friction) of Liquids and their Chemical Nature," by Messrs. Thorpe and Rodger (Phil. Trans., vol. 185 A, p. 397, and vol. 189, p. 71), applies to very definite chemical compounds, but even in these cases many interesting regularities are described by the authors. See Whetham's "Solution and Electrolysis" (Cambridge, 1895), chap. XI.

base-line, we should find that the quartz has retained some fluidity *below* the temperature at which the augite is solid.

In so far as this diagram is hypothetical, it derives support from the *observed* more rapid liquefaction of the more basic silicates at high temperatures. The steeper rise of the fluidity curve for augite at high temperatures (that is the part prolonged above f, f) is, in fact, matter of observation. This fact is very probably also shown in the volume-change at these temperatures.[1]

The true melting point, from the present point of view, is only to be obtained by observations on the behaviour of bodies under distorting forces. These observations I am now making, but they will be tedious, and delayed by other work. Unfortunately, while the observations of viscous yield will undoubtedly afford valuable data, the possibility of obtaining estimations of the molecular forces concerned in bringing about crystallization, and so completing the test of the theory, is not so apparent, unless we may consider that the resistance to distortional force offered by the crystallized substance involves this quantity. But even should direct observation fail to completely elucidate the question at issue the knowledge of the viscous curves must enter any complete theory of the order of solidification of the silicates. It appears, too, that the experimental means affording these data may be extended to reveal how far hysteresis attending the solidifying points may exist, and, if so, whether this is related to the percentage of silica present in the silicate: a line of inquiry at once suggested by the views expressed in this note.

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[1] "On the Volume-Change of Rocks and Minerals attending Fusion." By J. Joly. Trans. Royal Dublin Society, New Series, vol. vi., p. 283.

XXI.

RECENT ANALYSES OF THE DUBLIN GAS SUPPLY AND OBSERVATIONS THEREON.

By J. EMERSON REYNOLDS, M.D., Sc.D., F.R.S., Professor of Chemistry, Trinity College.

[Read April 25; Received for Publication April 27;
Published May 12, 1900.]

Large quantities of the city gas are used for various purposes in Trinity College, and it is the practice to analyse it occasionally in the Chemical Laboratory in order to ascertain whether its quality is maintained. In the course of the series of analyses made during the last five months, in conjunction with my excellent Assistant Mr. E. A. Werner, F.I.C., I detected a marked change in composition which began in February and continues to the present time. This change indicated that plain coal-gas was no longer supplied, but that a mixture which includes a considerable proportion of "water-gas" has since been delivered. On the 12th of last March I drew attention to this change in the course of a lecture delivered in College on that date. Extracts from that lecture appeared in the daily papers and led to considerable discussion, in the course of which opinions were attributed to me as to the probable effects of the change which I did not express and cannot be in any way responsible for.

I therefore desire in this paper to place on record the analyses made, and to shortly state the related considerations which should influence opinion as to possible danger attending the public use of mixtures of coal and water-gas.

Twelve analyses of the Dublin gas supply performed between the 25th of November, 1899, and the 16th of February, 1900, gave the following mean results, which agree with those of average coal-gas, and supply a fair standard of composition by means of which any variations can be recognised:—

Constituents in 100 volumes.	Mean results of twelve Analyses made between November 25th, 1899, and February 16th, 1900.
Carbon dioxide, ...	2·5
Carbon monoxide, . . .	6·2
Oxygen, ...	0·7
Illuminating hydrocarbons, . .	4·3
Non-illuminating hydrocarbons, .	86·3
	100·0

The results of a series of analyses of the Dublin supply performed *since* the 16th of February, 1900, are given in the table at end of this Paper (see p. 313).

Apart from minor variations, to which I shall not further refer, the significant difference in this series is the increase in the percentage of carbon monoxide found in the specimens examined.

The first series of analyses proves that the ordinary coal-gas supply to Dublin during nearly three months contained on the average 6·2 per cent. of carbon monoxide. The second series shows that there has been a gradual rise in the proportion of carbon monoxide until it had doubled on the 7th of March, and, two days later, the percentage had nearly trebled at 17·9: it then fell away, and subsequently rose again to 13·9 per cent. on the 20th March, and reached 15·6 per cent. on the 24th of April.[1] So great a change could, practically, only be due to the addition of water-gas. As soon as the trend of the results became clear, I communicated with the Gas Company (on March 6th), and they admitted that a proportion of carburetted water-gas had been mixed with the coal-gas.

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[1] No analyses were made between March 21st and April 24th.

Members of the Society are well aware that what is technically known as "water-gas" is produced by passing steam over red-hot coke when the following change is realised:—

$$H_2O + C = CO + H_2.$$

That is to say, the carbon in the form of coke, when sufficiently heated, removes the oxygen from water vapour, and produces therewith carbon monoxide gas, while hydrogen is also set free. The mixture of combustible gases so obtained gives a very slightly luminous flame and has little odour. When petroleum or other oils are vaporised at a sufficiently high temperature in this gas, their products render the flame much more luminous and communicate a strong odour. The product is "carburetted water-gas," and contains about 30 per cent. of carbon monoxide, the rest consisting of hydrogen and small proportions of its carbides.

This gas is much cheaper than coal-gas; it is more readily and quickly manufactured, and its production enables a gas company to use up a considerable proportion of its coke to advantage. Moreover, it can be easily made of almost any desired illuminating power, and is not more explosive with air than plain coal-gas. It is therefore much to the interest of a gas company to mix a considerable proportion of this water-gas in their supply, and such mixtures have been used in the United States since 1878, and to a much smaller extent in these countries since 1891. Some American cities such as Boston, New York, and Chicago now use almost unmixed water-gas; but in the United Kingdom comparatively few towns as yet use a mixture, and in those which do, 50 per cent. of water-gas is seldom added. In London very little has hitherto been used, and several companies are said not to have distributed any. There does not seem to be any statutory difficulty in the way of the companies substituting water-gas for coal-gas, and there would not be any general objection to their doing so wholly, provided there was no greater risk to health and life than with ordinary coal-gas. But that such danger does exist is beyond question, as carbon monoxide gas is a powerful and direct poison. A gaseous mixture which contains much of it, as Dublin gas now does, is necessarily more poisonous than the ordinary coal-gas which seldom included more than 6 per cent. Therefore, in the lecture already referred to, I said just so much by way of warning, but was careful to add:—"I do not want you to suppose that there is any ground for undue alarm, or that the addition of water-gas to coal-gas is not legitimate; I think, however, that the fact of so material a change in the nature of the supply should have been notified to all consumers, in order that they might be on their guard against escape of the new gas from any causes."

I do not think it would be possible to draw attention to a serious matter of the kind in milder terms than these, and no other statement was made by me. Nevertheless, at a recent general meeting of the Dublin Alliance Gas Company, the Managing Director is reported in the newspapers to have said that the question was brought forward in order to create a "scare," although I had specially deprecated anything of the kind. It is therefore desirable to support the reasonable warning I gave, as to the risk which attends the use of the mixed gas, by references which I did not consider necessary in the first instance.

In doing this, I shall set aside, as far as possible, any merely personal opinions, and only state fairly those of a tribunal of undoubted authority, expressed in a public document, after careful examination of all the points which could be brought forward by all interested persons.

The document I refer to is an important Report of a strong Departmental Committee appointed by the Home Office, which was issued last year, on the "Manufacture and use of Water-Gas and other gases containing large proportions of Carbonic Oxide."[1] This Committee examined a large number of gas managers as well as medical and other experts, and after taking evidence, which was obtained from America as well as the United Kingdom, requested a distinguished member of the Committee, J. S. Haldane, M.D., F.R.S., to draw up a digest of the evidence affecting the poisonous action of carbon monoxide mixtures, and to make independent experiments in order to clear up some doubtful points. This important digest forms the chief of the several Appendices to the Report of the Committee, and they state that "The results arrived at represent the grounds upon which much of this Report has been

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[1] Carbonic oxide is the name commonly given to carbon monoxide; but the latter is generally preferable in order to distinguish this gas from the familiar carbon dioxide, or "carbonic acid" gas.

based" (see page 8 of Report of the Committee). Anyone desiring to correctly estimate the value of the conclusions expressed in the general Report should therefore refer to Dr. Haldane's excellent digest, but it is sufficient for my purpose to cite the statements of the Committee which affect the main question.

The Report states (page 8) that "The poisonous action of coal-gas and water-gas is due *solely* to the carbonic oxide which they contain, that the higher the proportion of carbonic oxide the greater is the poisonous property of the gas, and that given equal conditions as to size of room, flow of gas, length of exposure, &c., the danger to life from an escape of carburetted water-gas or of coal-gas mixed with any considerable proportion of water-gas is far greater than that from an escape of ordinary coal-gas. The danger, in fact, increases at a much greater ratio than the proportion of carbonic oxide." This deliberate statement of conclusions drawn from facts well ascertained by the Committee, disposes once for all of the assertions made by interested persons that the water-gas mixture is not more poisonous than ordinary coal-gas.

Carbon monoxide is well known to act as a poison by forming a strong compound with the hæmoglobin of the blood, and so preventing that absorption of oxygen from the air which is necessary for the maintenance of life. So strongly is the carbonic oxide held by the blood that it is desirable to resort to inhalation of pure oxygen in cases of partial poisoning by it.

According to Dr. Haldane's report, air containing anything more than 0·2 per cent. or 2 parts per 1000 ought to be regarded as entailing risk to life. Half a part per 1000 is still capable of causing, even in healthy persons, giddiness and headache. Dr. Haldane adds (see page 71):—"The after-symptoms of carbonic oxide poisoning are often of a very serious nature," and then details the various symptoms which I do not think desirable for quotation here.

It is only fair to say that there is no real evidence that carbon monoxide is a cumulative poison in the strict sense of the term; but the statement just mentioned indicates considerable interference with nerve power, and consequent lowering of vitality even long after the poison has disappeared from the organism. It is probable that repeated inhalation of minute quantities—without any real storing in the system—would ultimately lead to similar results.

Gas managers and others, interested in the supply companies, have strongly urged that the water-gas mixtures have not caused more accidental or other deaths than plain coal-gas. They laid their case fully before the Committee, but the latter do not adopt their views. On the contrary, the Committee point to the American statistics, and quote the case of Boston where there were 29,554 consumers using plain coal-gas in 1886, but *no accidents* were recorded. In 1890 there were 46,848 consumers of a gas supply of which only 8 per cent. was water-gas, and there were six deaths from gas poisoning. In 1895 the number of consumers reached 68,214, while 90 per cent. of the supply was water-gas, and 24 deaths occurred. In 1897 the consumers numbered 79,893, the gas contained 93 per cent. of water-gas, and there were 45 deaths. After discussing the cases of other towns, the Report goes on to say:—"After making every other due allowance, we feel that the state of affairs disclosed in Boston, New York, San Francisco, and other towns is decidedly serious.[1] As regards Boston this is the opinion of the Gas and Electric Light Commissioners also." Dr. Haldane points out that the number of accidents by the use of mixed gas increased approximately as the cube of the gain in percentage of carbon monoxide. Thus, if the percentage of monoxide be increased from 6 to 12, the chances of poisoning were not merely doubled, but were 8 times greater. Similarly, if the percentage rose to 18 per cent. the number of accidents was 27 times greater than at 6 per cent. "This rule," he adds, "would seem to be borne out in the case of Toronto[2], and, so far as it is possible to judge from the very partial information available in the case of towns in the United Kingdom distributing any water-gas, experience in this country also points in the same direction."

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[1] "The total death-rate for poisoning of every kind in this country, whether accidental or suicidal, and whether by solids, liquids, or gases, is only about half the average death-rate from water-gas poisoning alone in Boston, New York, San Francisco, and Washington" (Digest, page 73). It is, however, desirable to point out that there are high percentages of water-gas in these towns; thus, following the above order, they are 90, 80, 70, and 100 per cents.

[2] Where 50 per cent. of water-gas is used, *i.e.* equal volumes of the two gases. It is well to point out that the Dublin gas analysed on March 9th contained nearly as much water-gas, and that on April 24th nearly 40 per cent. It is right to add that on two other occasions only, when analyses were made, did the Dublin gas contain more than 20 per cent. of added water-gas.

As to the way in which accidents may occur, it is to be noted that the Committee consider that very slight escapes due to doubtful fittings, even at night, do not appear to be rendered more formidable by the introduction of carburetted water-gas; but, when—

"These escapes occur owing to various accidents, such as the unnoticed turning on again of a tap which has been turned off; the blowing out of the gas-light; the extinguishing of the light by stoppage of the pipes or turning off at the meter, and the renewed flow of the gas without the taps having been turned off. Fatal results have also been traced to breakages or leaks in mains or service pipes, whereby gas has percolated—sometimes being deodorised—through the earth into a house; and to leaks through a wall or through a ceiling or floor from a gas pendant in the room below. In these ways accidents have been caused in houses and rooms to which gas was not laid on" (page 7).

Although the Committee do not consider that "very slight" escapes from imperfect fittings are likely to do material harm, they go on to say (page 9)—

"Our attention was called by several witnesses to the very imperfect and unsatisfactory gas-fittings often used in the poorer class of houses in large towns, and the constant leakages which exist without any attempt to discover or rectify them; and it has been suggested that powers might be given to Local Authorities to enable them to enforce a standard of fittings when newly put up in such houses (as is done in the case of water fittings), and also to inspect such fittings when required. We think that such powers might with advantage be given, to be used at the discretion of the Local Authority."

This is an important opinion in view of the general *malaise* which is known to follow the continued inhalation of air containing small proportions even of ordinary coal gas.

In concluding their Report, the Committee place on record their matured opinions in the following words:—

"To sum up, we have come to the conclusion that, if the accidents attributable to water-gas are not yet very numerous in Great Britain, the reason is, that the proportion in which this gas (carburetted water-gas) has been used has not hitherto, except in a few instances, been high. A large increase in the use of the gas is, however, to be expected in several localities, and in some places the use of pure carburetted water-gas is contemplated in the absence of legislative restriction."

"We therefore think the present time opportune for dealing with the matter before the manufacture of water-gas is established on a larger scale; and we beg to submit the following recommendations, to which, if approved, effect should be given by a Public Bill."

Among these "recommendations" are the two following, with which we are directly concerned:—

"That before any kind of water-gas is distributed in any place, due public notice of the proposal should be required to be given: and that, as long as there is any water-gas in a gas supply, that fact should be stated on every demand note."

This was precisely the view I took as to the duty of the Alliance Company to consumers, and I rather expected that the Company—especially after I had early notified them of the detection of the water-gas mixture—would have been glad to render any public warning from me unnecessary by stating their view of the matter to their customers, and they had ample time to do so in the interval before my lecture was delivered. It is clear, from the reference to the "demand note," that every quarterly gas bill should be a renewed notification, as a reminder to consumers that there was need for continued and special caution.

The other "recommendation" referred to is:—

"That power should be conferred upon a Central Department to make regulations, enforceable by adequate penalties, limiting the proportion of carbonic oxide in the public gas supply at night to 12 per cent., or such greater amount as the Department may consider desirable," *i.e.*, as I understand, such greater amount being permissible in order to meet special emergencies.

I have now laid before the Society the chief conclusions arrived at by the Commission which the Home Office charged to inquire and report as to the safety or otherwise of introducing any large proportion of water-gas into city gas supplies. It will be seen from the quotations that my warning of the 12th of March rather *understated* the case against water-gas mixtures. Nevertheless, I desire to repeat that, so far as the Dublin supply was concerned in March,[1] when I made the chief analyses, there was no need for undue alarm or for exaggerated fears, but rather for much increased caution in dealing with the new gas. On the other hand, monopolies of dwindling value, as gas companies undoubtedly are, cannot afford to disregard the deliberate opinion of so competent a body as the Home Office Commission. I therefore trust that the 12 per cent. limit recommended for carbon monoxide may not be exceeded in Dublin gas, as it seems an equitable compromise, and that adequate public supervision of the supply shall be secured and regularly maintained.

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[1] It is unfortunate that the only analysis made in April (on 24th) gave 15·6 per cent. of carbon monoxide, which represents a mixture including about 40 per cent. of carburetted water-gas.

CONSTITUENTS IN 100 VOLUMES.	FEBRUARY.		MARCH.											APRIL.
	22	27	1	3	6	7	8	9	10	13	15	20	21	24
Carbon Dioxide, . . .	2·1	4·5	3·0	2·4	3·0	2·5	2·6	1·8	1·8	2·0	2·1	2·1	2·4	1·4
Carbon Monoxide, . . .	7·2	8·6	8·7	8·5	10·8	12·6	11·2	17·9	10·6	10·5	11·2	13·9	12·3	15·6
Oxygen, ...	0·4	0·2	0·1	0·4	0·2	0·2	0·3	0·3	0·1	0·3	0·2	0·6	0·3	0·4
Illuminating Hydrocarbons, .	4·5	5·1	4·7	4·6	5·4	6·1	5·7	7·8	5·8	5·9	5·8	6·9	6·7	7·4
Non-illuminating Hydrocarbons, &c., ...	85·8	81·6	83·5	84·1	80·6	78·6	80·2	72·2	81·7	81·3	80·7	76·5	78·3	75·2
	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0

XXII.

ON CERTAIN ROCKS STYLED "FELSTONES," OCCURRING AS DYKES IN THE COUNTY OF DONEGAL. By GRENVILLE A. J. COLE, M.R.I.A., F.G.S., AND J. A. CUNNINGHAM, A.R.C.Sc.I., B.A. (PLATES XIX. AND XX.)

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AMONG the schists and quartzites of the north-west of Ireland, which are grouped together provisionally as Dalradian, a number of igneous dykes occur, which are divisible into three main series. First, there are the basic rocks that were intruded into the sediments prior to the period of their disturbance and metamorphism. These occur mostly as sheets and sills, but occasionally cross the bedding-planes, or swell out as larger intrusive masses. Their relation to the metamorphic rocks, and the contortion they have undergone, are excellently shown on sheet 11 of the 1-inch map of the Geological Survey of Ireland, in the region west of Rathmullan. These rocks are now mostly in the condition of epidiorites and hornblende-schists, and have probably supplied many of the dark inclusions of amphibolite that are found in the intrusive gneiss of Donegal.[1]

The second series of dykes is described in the publications of the Survey by the convenient field-term of "felstone." The mapping of this system of dykes shows that they belong to some period later than the general folding. One of them, for instance, in sheet 11, cuts right across the contorted epidiorites. Dr. Hyland has noted,[2] moreover, that these later intrusive masses do not show signs of mechanical deformation. At some points, as in the south-west of sheet 24, the "felstones" have been faulted; but

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[1] See G. Cole, "Metamorphic Rocks in Tyrone and Donegal," Trans. Roy. Irish Acad., vol. xxxi. (1900), (in the press).

[2] Geol. Survey of Ireland, Mem. Sheets, 3, 4, 5, 9, &c., p. 143.

the same faults cut the Carboniferous sandstone, and may even be of Cainozoic Age. The Carboniferous beds overlie both the first and second series of dykes, without being penetrated by them.

The third series of dykes includes the intrusive basalts and dolerites that follow so persistent a north-west and south-east trend throughout our islands. These are now generally admitted to belong to the Cainozoic epoch of activity. Associated with them are one or two veins of rhyolite-pitchstone, the characters of which are thoroughly in harmony with those of undoubted products of our Cainozoic volcanoes.[1] The dolerite dykes of this series cut through the felstones, and are clearly of later date.

It has been recognised in recent years that the "felstone" series of the north-west of Ireland contains rocks of somewhat dissimilar character. In 1888, Messrs. Mitchell and Kilroe[2] described several masses in the area of Barnesmore as mica-trap, porphyrite with hornblende, syenite with quartz, &c. A general northerly direction is noted for the dykes of this series which lie to the east and south-east of Lough Eask. Dr. J. S. Hyland,[3] in 1890, gave an admirable description of some of the dykes east of Lough Swilly, classing them, for the first time, with the lamprophyres of Rosenbusch, and placing them in the camptonite division. In 1891 the same author[4] described two other lamprophyres from the county of Donegal, regarding them as amphibole-vogesites, or as basic allies of the compact syenites rather than of the compact diorites. He pointed out at the same time that the felstones and felstone-porphyries of the area presented a wide range of structure and constitution; some are even "allied to micro-granites."

Messrs. M'Henry and Watts[5] mention a number of occurrences of lamprophyre in northern Ireland, including a vogesite

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[1] Mem. Sheets 3, 5, 9, &c., p. 147. Also W. J. Sollas, "On Pitchstone and Andesite from Tertiary Dykes in Donegal," Scien. Proc. Roy. Dublin Soc., vol. viii. (1893), p. 87; and Sir A. Geikie, "Ancient Volcanoes of Great Britain," vol. ii. (1897), p. 118.

[2] Mem. Sheet 24, pp. 32 and 33.

[3] Mem. Sheets 1, 2, 5, 6, and 11, p. 44.

[4] Mem. Sheets 3, 4, 5, 9, &c., pp. 141–143.

[5] "Guide to Coll. of Rocks and Fossils," Geol. Surv. Ireland (1895), pp. 71–75.

at Clondermot, and a considerable group of minettes and kersantites on the coast of the county of Down. The latter are compared with similar rocks cutting the Ordovician strata in the Southern Uplands of Scotland.

Our own observations on certain of the felstone dykes may be worth putting on record, if only to confirm the excellent diagnoses drawn up by the late Dr. Hyland. We were led to look into the matter during an examination of southern Donegal, since we were anxious to discriminate between rocks that have shared in the folding and deformation of the Dalradian series, and those of later date. Certain dykes, also described as "felstone," are represented on the Survey map, sheet 32,[1] as cutting Carboniferous strata. These cannot be included in the second series mentioned above, and it seemed probable that they might be classed, with the glassy rhyolites of Lough Eask, as of Cainozoic Age. We regret that a search along the Waterfoot River, south-west of Pettigo, where the banks are greatly overgrown, failed to reveal the "dyke of compact bluish black felstone" recorded by Mr. Symes in 1891. A careful examination of the actual bed of the stream is probably required. North of Laghy, however, we were more fortunate. On wading for some distance down the stream, we found a thin vein of grey-green igneous rock, its joints richly coated with pyrite. Lower down, at a little waterfall, a dark grey, compact, and more massive dyke occurs, which has baked the surrounding Carboniferous limestone for more than a metre from its visible margins. This rock has a remarkably phonolitic aspect. It also has films of pyrite on some of its joint-surfaces. Its specific gravity is 2·90.

Both these dykes seem to have suffered in their turn from contact-metamorphism, the source of which is not apparent in the field. A glance at them shows that they are very unlike any Cainozoic highly siliceous rocks in Ireland. Their flinty mode of fracture, due, as we believe, to secondary causes, probably led to their inclusion under the general name of "felstone." In microscopic section, the smaller dyke proves to be a tachylytic basalt, very rich in altered porphyritic crystals of olivine (Plate XIX., fig. 1). These crystals have been corroded by the brown glass of

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[1] See also Mem. Sheets 31 and 32, pp. 20 and 21.

the magma, as is often the case in modern rocks of the same kind.[1] Numerous steam-vesicles occur, partly filled up by intrusion of the glassy groundmass during cooling, and partly by secondary calcite. Pyrite has developed abundantly in these cavities, and, in smaller cubes, reddened by alteration, even within the serpentinised olivines.

The groundmass of the rock contains spherulitic sheaves of felspar microlites; many of these minute crystals are repeatedly twinned, though retaining the residual glassy band up the centre of the prism, which is so characteristic of the imperfectly developed plagioclase in tachylytes. Their optical characters place them between andesine and labradorite.

The brown glass becomes more prominent, and at the same time more vesicular, near the selvage, and is here crowded with little cumulitic patches. The ferro-magnesian constituent has not developed; but the alliance of the rock with the olivine-basalts is manifest. It is the kind of material that might have developed good variolitic selvages, had it occurred on a more massive scale.

The larger of the two dykes near Laghy has a more ordinary groundmass of minute crystals of plagioclase and very pale brown monoclinic pyroxene. The prisms of pyroxene are, however, very abundant, and it is improbable that the two dykes are direct offshoots of the same mass. Olivine is represented in this case by green and black pseudomorphs, and is by no means so prominent as in the smaller dyke. In one instance, the olivine crystal has formed about a pre-existing needle of felspar, which runs through its length, and projects at either end.

This compact basalt contains inclusions of a greyer olivine-basalt, of a somewhat unusual trachytic aspect. These have undergone partial absorption at their surfaces. Both the types of rock thus associated contain many small crystals of magnetite and pyrite.

The two dykes north of Laghy must, then, be removed from the field-class of "felstones"; but they cannot with certainty be correlated with the products of the Cainozoic eruptions. They are post-Carboniferous, and may perhaps represent some early

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[1] Compare G. Cole, "The Variolite of Ceryg Gwladys, Anglesey," Sci. Proc. Roy. Dubl. Soc., vol. vii. (1891), p. 117.

Eocene intrusion; their secondary characters, in so far as they indicate contact-metamorphism, may be due to the arrival of some later igneous mass, which still lies concealed beneath the surface.

The "felstones" that are so common in the area of the Dalradian schists fall, as Dr. Hyland first pointed out, very largely in the vogesite and camptonite series of Rosenbusch. The officers of the Geological Survey have allowed us to examine their section of the rock of Aughagault,[1] which they have properly re-named camptonite, rather than vogesite, owing to the prevalence of plagioclastic felspar. It contains dull brown hornblende similar to that occurring in the porphyritic dyke at Convoy, which is about to be described.

The Convoy "felstone" is mapped in sheet 17[2] as a band some six miles long, running N.N.W., and broken up by faults. From the description in the memoir, its characters appear to vary considerably, and the detached strips are possibly not all portions of the same mass. The band from which our specimens were collected cuts the Dalradian limestone about a mile north-east of Convoy. The rock is rich in hornblende, and has in its fresh condition, a compact grey phonolitic groundmass. This weathers to a browner colour; but the specimens gathered in the wood north of the main road from Convoy to Raphoe indicate that the brown earthy type is far from being an adequate representative of the rock. The same is true, no doubt, of the brown and reddish types so familiar among the lamprophyres as a group, whether in the Vosges, the Lake District, or the south of Scotland.

The specific gravity of a fresh example of the Convoy dyke is 2·73. The compact grey groundmass gives a fair potassium reaction (about 3 per cent. of potash) in a bead of sodium carbonate, but shows nothing definite even with a high power of the microscope. It is anisotropic, and trachytic in aspect; when the rock is weathered, the ferro-magnesian constituent becomes picked out in the ground, giving rise to chloritic specks. Minute amphibole and a felspar probably constitute the mass of the ground, which retains also abundant crystallites, belonging to its earliest phase

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[1] Mem. Sheets 3, 4, 5, 9, &c., p. 141. The dyke occurs in sheet 16.

[2] See also Mem. Sheet 17 (1889), p. 27.

of consolidation. In a specimen in which the felspar microlites are better developed in the groundmass, the species proves, by its optical characters, to be andesine.

The zoned and twinned porphyritic amphibole reminds one of that in the camptonite of Roda in Tyrol,[1] and the colour is somewhat similar. The ground of the Roda rock is, however, more completely differentiated, and is crowded with small brown idiomorphic crystals of amphibole. As we have already stated, the amphibole in the rock described by Dr. Hyland from Aughagault seems to agree with ours in all respects; and, in the decomposed parts of the Convoy dyke, the alteration-products of the larger groups of brown amphibole go far towards reproducing the complex pseudomorphic patches which are a feature of the camptonite of Aughagault.

The grouping of the amphibole crystals in the Convoy dyke here and there suggests that they may have been derived from the absorption of inclusions of foreign material. The arrangement appears, however, to be truly "glomeroporphyritic," and detached crystals have often been corroded by the groundmass, which has finally crystallised within them. The groundmass has similarly intruded itself between the components of the groups, and is easily recognised by its characters between crossed nicols. At the same time, a colourless substance, with very striking phenomena of absorption when tested with a single nicol, is seen to unite many of the amphibole crystals in the groups. Microchemical examination proves this to be calcite; but its mode of occurrence makes it clear that it occupies the place of some pre-existing mineral in the groups. Possibly it represents a felspar; possibly it results from the alteration of a felspathoid. In any case, it offers a puzzle similar to those presented by the colourless constituent of the monchiquites, a family of rocks now so much under discussion. A certain amount of anisotropic material, with weak double refraction, remains in the interspaces between the hornblende after the calcite has been dissolved away. (Pl. XIX., fig. 2.)

Apatite occurs in the groundmass of the dyke, and is also included in the porphyritic amphibole. Though lighter in colour,

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[1] This rock is described by Rosenbusch, "Mikroskop. Physiographie der mass. Gesteine," 3te Auflage (1896), p. 546.

the Convoy dyke has many characters in common with the well-known augite-hornblende-andesites that occur near Wernstadt and Tichlowitz in the Tetschen district of northern Bohemia, where some of them are extensively quarried for road-metal. These rocks, which occasionally pass into olivine-basalts, none the less contain sufficient potassium in their groundmass for the production of a fair flame-reaction. Rosenbusch[1] has allied them with his leucite-monchiquites, owing to the presence of leucite in the groundmass of some members of the group. The rarity of porphyritic felspar, and the abundance of brown hornblende prisms in the groundmass, certainly connect them with the lamprophyres; but a slight decrease of magnesium and iron in the groundmass, and a substitution of porphyritic hornblende for augite, would give us a type closely allied to the dyke of Convoy in Donegal. This latter rock may well be placed with the camptonites; but its possible modifications at points to the south-east of Convoy have yet to be studied microscopically. Olivine has not been observed in it; but this mineral is not regarded by Rosenbusch as essential in his comprehensive camptonite division.[2]

A second dyke that we have examined is of interest, inasmuch as it has not been previously mapped, although it has been quarried for some time by the local road-contractor, to whom it furnishes excellent road-metal. The rock is traversed by numerous irregular joints, which render it very easily broken down to the size required for road-mending, while very difficult to reduce to a smaller size. It occurs on the promontory of Drumboy on the southern shore of Lough Swilly, two miles north-west of the village of Newtown Cunningham. The locality lies near the south-west corner of Sheet 11 of the one-inch map of the Geological Survey of Ireland. The dyke cuts across the conspicuously exposed rocky summit to the south-east of the road, and can be

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[1] "Mikrokoskop. Physiographie," 3te Auflage, p. 545. The more recent views as to the character of the isotropic matter, analcim or glass, in the monchiquites are expressed by Loewinson-Lessing, "Studien über die Eruptivgesteine," Congrès géol. internat., Compte rendu, session 1897 (pub. 1899), p. 289, and by J. S. Flett, "Trap Dykes of the Orkneys," Trans. Roy. Soc. Edinburgh, vol. xxxix. (1900), p. 889.

[2] *Op. cit.*, p. 536; also "Elemente der Gesteinslehre" (1898), p. 233.

traced at short intervals through several fields on the other side of the road. The lower slopes of the promontory are covered by deep glacial drift, but apparently the same dyke reappears upon the shore. Through the kindness of the officers of the Geological Survey of Ireland, we have been enabled to consult the manuscript six-inch map, on which the surveyor of the district has marked a "rotten dyke ? Gabbro" to the south of this point. This may possibly refer to the mass that we are now describing. The whole length of the Drumboy dyke is a little over half a mile. At the highest point, where the rock is well exposed, the structural planes of the coarse micaceous grit dip at an angle of 23° towards a point 10° west of north. The dyke cuts through these, dipping at about 30° in a direction 40° south of east, and is thus clearly posterior and intrusive (Pl. XX.).

The rock is vesicular throughout, the hollows being lined with red soda-orthoclase; subsequently, calcite has often been deposited in the central part of the cavities. The mass is pinkish or greyish brown, and is a good deal decomposed. In microscopic section, the felspathic constituent is seen to be too greatly altered for determination by specific gravity; but the large number of untwinned or simply twinned crystals indicates the presence of orthoclase or anorthoclase. The repeatedly twinned felspar is a basic andesine; but the groundmass as a whole gives a flame-reaction indicating some five per cent. of potash. The same association of felspars is recorded by Mr. Flett in the camptonite of Rennibuster near Kirkwall.[1] The other mineral uniformly scattered through the groundmass is green hornblende, yellowish in cross-section, and occurring in small elongated prisms. Magnetite is present in octahedra, altering to hæmatite, and giving rise to "martite" pseudomorphs. Crystals of titanic iron oxide, probably titaniferous magnetite, now altered for the most part into leucoxene and translucent sphene, play the part of a porphyritic constituent, but do not measure more than ·2 of a millimetre in diameter. They are clustered together in little groups, especially in the outer regions of the dyke.

Near the margin, the constituents diminish in size, and the rock becomes more and more compact. A few felspar crystals stand

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[1] *Op. cit.*, Trans. R. Soc. Edin., vol. xxxix., pp. 876 and 887.

out porphyritically. At the actual contact with the schists, the groundmass becomes trachytic when viewed in section; but the proportionate abundance of the hornblende prisms and the felspar appears to be the same as in the central mass. The rock, which would be styled a porphyrite by many in the field, may be placed with Rosenbusch's vogesites, rather than with the compact syenites, on account of its richness in amphibole. It is, moreover, in all probability, near the basic end of the vogesite series, and must be regarded as indicating a passage from that series to the camptonites.

It would be of considerable interest if we could trace these lamprophyric dykes down to the caldron from which they have arisen. The view at present favoured is that such rocks have come up as products of differentiation from a magma of more basic character, and their poverty in silica, as compared with their richness in alkalies, is one of the main points that distinguish them from the contents of ordinary igneous caldrons in the crust. Prof. W. C. Brögger's admirable work on the basic eruptive rocks of Gran[1] met with a somewhat natural criticism from Prof. Johnston-Lavis,[2] who pointed out that the rock-types alleged to have been produced by differentiation might have arisen from the intermingling of a normal magma with matter derived from the sedimentary or other masses with which it came in contact. The camptonitic zones formed round inclusions of sedimentary rocks immersed in a "bostonite" magma[3] certainly appeared to lend themselves to such an explanation; but Prof. Brögger has more than once[4] reaffirmed and strengthened his position, refusing, at the same time, any assistance from the theories as to the potency of contact-absorption, which have been developed by the observations of M. Michel Lévy and other writers. When Messrs. M'Henry and Watts[5] suggested that the "micaceous felsites" of the Barnesmore area in southern Donegal

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[1] Quart. Journ. Geol. Soc. London, vol. L., (1894), p. 15.

[2] Geol. Mag., 1894, p. 252.

[3] Quart. Journ. Geol. Soc., vol. L., p. 25.

[4] "Die Gesteine der Grorudit-Tinguait-Serie" (1894), p. 158; and, in some detail, "Das Ganggefolge des Laurdalits" (1898), p. 347, also, in general, pp. 334–351.

[5] "Guide to Collection of Rocks and Fossils," Geol. Surv. Ireland (1895), p. 72.

are probably offshoots from the adjacent mass of granite, we may presume that they had in their minds the large body of evidence in favour of magmatic differentiation. It is noteworthy, however, that the Barnesmore granite becomes highly charged with biotite, and is obviously darkened at its junction with the Dalradian schists. Any magma thus modified by contact-absorption will naturally occur as a superficial shell, so to speak, about the underlying large intrusive mass; and the impure material will often be the first to find its way into the fissures opened in the surrounding rock. Its junction with the walls of the fissures may be clean and clear, seeing that the material which has rendered the magma of the dykes more basic has been derived, not from the walls of the dykes, but from blocks absorbed in the caldron far below. If, at a later date, the fissure opens again, along the centre of the consolidated dyke, the purer magma from below will have a chance of rising, and a "composite dyke" will result, its centre being far more rich in silica than its margins. These remarks are not put forward as a theory to account for all similar phenomena, especially in regions with which we have no personal acquaintance; but it is obvious that in the county of Donegal, where the modification of granitic magmas by absorption is so clearly demonstrable in the field, the possibility of such interaction must be borne steadily in mind.

The final chemical composition, and the final products of crystallisation, of any dyke, or sheet, or "batholite," may thus be related, not only to events taking place within a subterranean caldron, but to the whole previous geological history of the district.

In conclusion, it will be clear that there is a wide field for further study among the "felstone" dykes of the county of Donegal. The question of their age naturally arises, and cannot, we fear, be satisfactorily settled. If the final shearing and foliation of the schists of Donegal is, as is very likely the case, post-Silurian, the "felstones" are at the earliest of Devonian age. At the same time, dykes of this type have not been seen to cut Carboniferous strata in Donegal; they are, moreover, as we have already stated, traversed by the Cainozoic dolerites. In the south of the county of Tyrone, there are a number of "porphyrite" lavas among the Lower Devonian sandstones, presenting the characters of the andesitic series of the same age in southern Scotland.

The groundmass of one of these, from the quarry east of Six-Mile-Cross, crowded as it is with minute dark needles of amphibole, must possess a composition not far removed from that of the camptonites. The magma from which the lamprophyres arose may, whatever theory we adopt, have produced andesitic rocks when it reached the surface. We are inclined, then, to connect the series of lamprophyric and allied dykes in northern Ireland with the concealed caldrons that played so considerable a part in the British Isles in Lower Devonian times. Northern Ireland in the Old Red Sandstone period can hardly have escaped the disturbing influences that worked their will in southern Scotland. We are strengthened in this view by the fact that Sir Archibald Geikie[1] states that the "dykes of felsite, minette, lamprophyre, vogesite, and other varieties," which cut the Silurian and Ordovician rocks of the Southern Uplands, "may also be connected with the volcanic phenomena of the Lower Old Red Sandstone."

EXPLANATION OF PLATES.

Plate XIX.

Fig.

1. Microscopic section of glassy olivine-basalt from small dyke in stream north of Laghy, showing corroded crystals of olivine, and a few infilled steam-vesicles. × 37.

2. Microscopic section of camptonite of Convoy, showing porphyritic brown amphibole in a compact grey ground. A "glomero-porphyritic" group is included, with colourless interstitial matter between the crystals of amphibole. × 12.

Plate XX.

View of Quarry opened near Drumboy. The vogesite dyke forms a dark mass crossing the foreground, and cutting the structural planes of the paler schists, which appear above.

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[1] "Ancient Volcanoes of Great Britain," vol. i., p. 293.

XXIII.

ON THE INNER MECHANISM OF SEDIMENTATION—(PRELIMINARY NOTE).

By J. JOLY, Sc. D., F. R. S., Hon. Sec. Royal Dublin Society, Professor of Geology and Mineralogy, Trinity College, Dublin.

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It has long been known that the presence of dissolved salts accelerates the precipitation of finely divided matter, such as clay, &c., suspended in water. The phenomenon has not, however, met the consideration which its extreme importance as a factor in geological physics claims for it. The entire distribution of marine sediment had been widely different from that which exists, and sediments transported from continent to continent and carried from the land into all parts of the ocean, but for the intervention of this effect.[1] I propose in this brief note to summarise the results of an inquiry as to the nature of this phenomenon, upon which I have been engaged.

I find that a large part of the work which has been done within recent years on the coagulation of colloids applies to the precipitating powers of salts. It will be found that some contradictory statements of previous observers (as to the ineffectiveness of sodium chloride to effect precipitation) find explanation in the facts forthcoming.

It appears that the cessation of the phenomena of pedesis or Brownian movement is not concerned directly in producing precipitation, contrary to the idea of Jevons, but that the flocculation of the suspended particles attending precipitation and responsible for it, stops this motion, which, however, even then may continue to exist for free particles of sufficiently minute dimensions. The cessation of pedesis, therefore, does not primarily

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[1] Thus the Gulf-stream crossing the Atlantic in about 100 days would have been competent to transport the finer suspensions from the American rivers to Europe.

produce flocculation, but flocculation stops the pedetic motion of the majority of the particles.

On the basis that in order to produce the aggregation of colloidal particles a certain minimum electric charge has to be brought within reach of the colloidal groups, and that the conjunction of ions necessary to supply this charge must occur with a certain minimum frequency throughout the solution; and, further, that the electric charge on the ion is proportional to its valency, Whetham[1] arrives at the expression for the relative coagulative powers of equivalent solutions of monovalent, divalent, and trivalent solutions

$$p_1 : p_2 : p_3 = 1 : x : x^2.$$

From this it follows that the coagulative powers rise rapidly with the valency. If, for instance, in order to compare the formula with the experiments of Linder and Picton,[2] x is put equal 32, then the rise with the valency is given by the series 1 : 32 : 1023. This series involves the principle that the probability of an ion being within effective reach of a fixed point is expressed by a fraction having the volume of "the ionic sphere of influence" as nominator, and the entire volume of the liquid as denominator, certainty being expressed in this case by unity. Then for n ions, the probability of conjunction is the product of the separate chances n times, or is given by $(AC)^n$ where A is a constant and C the concentration.

This theoretical consideration appears, judging from the numerical agreement with experiments, to afford legitimate grounds for believing that its physical postulates are approximations to the truth; that, in short, such a minimum electric charge is required to bring about coagulation, and also that this charge is only attained in the case of the very small colloidal particles by the haphazard conjunction of ions in themselves not competent to effect the coagulative change. What this charge may be, we cannot now do more than guess. If the double-electric layer of Helmholtz and Quincke, the existence of which appears involved in the explanation of electric endosmose and the electric phenomena

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[1] Phil. Mag., v. 48, 1899, p. 74.

[2] Chemical Soc. Journ., vol. 67, 1895, p. 63.

attending the passage of water through capillary tubes, is ordinarily productive of mutual repulsion between the particles, then the free charge on the ion may serve to discharge or so reduce this, that conjunction of the particles becomes possible. Once this occurs, the tendency to minimum surface energy will effect the retention of the particles in close union. Hardy's recent experiments[1] confirm the idea that some such phenomena actually occur; for he finds that the ions which effect the discharge are those of opposite sign to that revealed in electric endosmose by the particles of the colloid. Thus a colloidal particle moving with the current may be assumed to be electro-positive. Now such particles are coagulated by the electro-negative ions: those moving against the current by the electro-positive ions. This is established by the fact of the valency law, working out, in the first case, for the valency of the acid radicle in solution; in the second, for the valency of the metal in solution. A further and very beautiful confirmation is contained in Linder and Picton's observation that the metallic ion may be carried down with the colloid. I find that the view that the action consists in each case principally of the neutralisation of the inner electric layer harmonises well with the experiments of Hardy and others.

We have so far reviewed the theory as it stands for the case of the very minute colloidal particles. The phenomena of the deposition of sediments involve particles rising to dimensions much greater than those which are considered in the foregoing theory. But, as will be seen, these larger particles, even of the most insoluble substances, reveal precipitating effects due to salts in solutions which are undoubtedly connected with the valency of the ions and also with the electric sign of these. It therefore becomes of interest to seek in the first place for some clue as to how the valency may affect the rate of precipitation of large particles. By large particles I mean particles which are large compared with the ionic grain of the liquid.

In this case, if U be the component of the mean ionic diffusive velocity perpendicular to unit area in the liquid, and $\frac{N}{3}$ be the number of ions of the proper sign having a component directed

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[1] Proc. Roy. Soc., vol. 66, p. 110.

towards the area, then the number of impacts, in unit time, is $U \times \frac{N}{6}$, where N is the total number of ions of the proper sign in unit volume. Or taking U constant, $= KN$.[1]

Now, equal effects are produced by $2N$ triads, $3N$ diads, $6N$ monads, owing to the charge on each being proportional to the valency. Hence if the solutions are of the same concentration (*i.e.* there are the same number of ions in unit volumes of triad, diad, and monad solutions), then the electrical effects produced in equal times in each solution (*i.e.* the quantity of free electricity brought to unit area) will be in the ratio

$$\frac{KN'''}{2} : \frac{KN''}{3} : \frac{KN'}{6}.$$

If N be above a certain value in these ratios, the "instantaneous" value of $\frac{KN'}{6}$ may represent a quantity sufficient to "discharge" adjacent suspended particles as effectively as the greater quantities $\frac{KN''}{3}$ or $\frac{KN'''}{2}$. In this case no valency effects will be revealed, and the salts will produce sedimentation indifferently as regards their chemical nature.

If the value KN is sufficiently small, the above phenomena will not be brought about, and an effect directly proportional to the valency will appear; finally, if there exist in the liquid effects of a restorative character, *i.e.* which continually tend to restore to the particles their electric layers, then there will be no effect on the sedimentation unless in each case KN is above a certain value. It is to be expected that intervening conditions between equal flocculation by like concentrations of monads, diads, or triads, and those producing no effect on the sedimentation will exist for varying strengths of solutions. Again, with increasing fineness of the suspension, the flocculative effects of the lower valencies will be delayed for the reasons given by Whetham. The finest

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[1] In comparing the effects of acids and alkalies, the higher velocities of H and HO cannot be left out of account. Similarly, "the ionic sphere of influence" must be considered greater for H and HO in comparative experiments whether on colloid or other particles.

sediments will conform to the square and cube law, the element of probability fully entering, even at considerable concentrations.[1]

The actual results as observed in the rates of clearing of suspensions in more concentrated solutions will be complicated by the influence of viscosity and specific gravity; and experiments will be further exposed to the disturbing effects of thermal convective currents, which are difficult to eliminate entirely.

The method of experiment is to produce fine suspensions by allowing the settlement of various finely powdered substances, such as carbon, kaolin, quartz, obsidian, basalt, &c., to proceed in distilled water for a few hours or days, and finally to pour off the upper portion for use. This is now diluted to a strongly opalescent liquid and exposed to the action of the salts, under conditions of perfect stillness and as nearly uniform temperature as possible. About 100 c.cs., contained in a wide test-tube, is sufficient liquid to deal with. The tubes are placed side by side, immersed in a tank of water having glass sides, and viewed against a black background by light which enters from behind and from above, and which should be uniformly intense for all tubes being compared. The tubes are supported by attachment in a board covering the tank, in which holes to receive the tubes are made closely adjoining.

The following are the principal experimental results dealing

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[1] The obscure phenomena of pedesis may find an explanation in the facts attending flocculation. There are, in all cases, along with the visible pedetic particles, necessarily large numbers of sub-microscopical particles present. The larger particles which are not discharged are unstable in the presence of these smaller particles; for any movement of the larger particles is attended with disturbance in the symmetry of its electrical layer, the forward side becoming more discharged than the rear side owing to the larger number of ionic encounters on the side of advance. Repulsions, due to mutual electrification, may now exist on the rear side, while attractions between the discharged surface and small electrified particles may operate on the forward side. Thus, the pedetic motion is the result of the diffusion throughout the liquid of electrified particles and ions, and derives its energy from the electric potential consequent on this distribution. In pedesis we *see* the process of flocculation in progress. In "pure" water the motion may persist for an indefinite time, for after a certain degree of growth the aggregates may become detached from the larger particle and break up by mutual repulsion. If ions are abundantly present, this break-up does not happen, discharge being complete, and sedimentation ensues.

with pure carbon [prepared from sugar], kaolin, quartz, obsidian, basalt, silica, or alumina:—

1. Settlement is effected much more rapidly in solutions of diads such as $MgCl_2$, $BaCl_2$, $CaCl_2$, than in equimolecular solutions of monads, as NaCl or KCl.

2. Between diads and monads the effects appear about equal when the molecular equivalent concentrations are as 1 : 32.

3. In the experiments the concentrations ranged from 1 gram molecule in 6 litres to 1 in 100 litres. Concentrations of 1 gram molecule in 2 litres showed little or no difference between equimolecular solutions of monad and diad salts.[1]

4. When Al_2Cl_6 was used as the triad salt, and compared with solutions of monads and diads, all made up to the concentrations of Linder and Picton's experiments, the triad was apparently of insufficient concentration, showing a marked lag in precipitation. $Al_2(SO_4)_3$ did not reveal this insufficiency.

5. The suspension generally reveals the valency effects only after 12 to 24 hours standing, the earlier settlement being effected without notable differences.

6. Suspensions in distilled water lag in precipitation behind those containing even small quantities of salts; but concentrations less than 0·04 gram-equivalents per litre of monads or diads produce very little effect.

7. Suspensions in acidified water clear much more rapidly than those in alkaline water. The latter may remain up indefinitely. The acidity of certain salts hence enters as a complication in the experiments.

8. Flocculation is earlier and more markedly visible to the eye or lens in the case of diads and triads than in the case of monads.

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[1] Later experiments have elucidated more fully the cause of this. There is an optimum concentration, for example, in the case of $MgCl_2$; less or greater concentrations precipitate more slowly. Compared with NaCl it is found that the curve of precipitating power of the latter crosses that of the former salt at a concentration of about 0·75 gram-equivalent molecules per litre. At about this concentration, therefore, both salts act alike. At further concentrations the monad salt has even the advantage. These curves cannot be explained as merely due to viscosity, but involve, apparently, the theoretical views given above as to the swamping of the valency effects at high concentrations. This is effected at lower concentrations for diads than for monads, as might be expected. Hence the curves cross.

9. Solutions of bodies which are not ionised, such as sugar, produce little or no effect.

10. In acidified K_2SO_4 solution settlement is much faster than in alkaline K_2SO_4, and in alkaline $MgCl_2$ or $BaCl_2$ settlement is faster than in acid $MgCl_2$ or $BaCl_2$. It would appear from this that a change of sign of the suspended particles is brought about in these cases. The acidifying of the solution probably renders the particles electro-positive; addition of alkali renders them electro-negative. In the first case they are acted on by the radicle of the salt (in the experiment SO_4''); in the second by the metal (in the experiments Mg'' or Ba''). In each case, therefore, the experiment is in accord with Hardy's results on colloids.

11. Picton and Linder found that the coagulative effects of salts of the same group as regards valency were additive, while with successive additions of quantities of salts of different valencies they were not additive. I find that among equi-coagulative quantities, the addition of $MgCl_2$ to $BaCl_2$ produces a greater effect than the addition of $MgCl_2$ to NaCl. The "inhibitory" effect noticed by Linder and Picton, p. 67 (*loc. cit.*), would therefore appear to be present in some degree.

12. In sea-water there are in approximate gram-molecules and gram-equivalents per kilo. the following principal salts:—

	Gram-molecules.	Gram-equivalents.
NaCl,	0·472	0·472
$MgCl_2$,	0·040	0·080
$MgSO_4$,	0·014	0·028
$CaSO_4$,	0·009	0·018
K_2SO_4,	0·005	0·010

It will be found on comparing these figures that, on the square and cube law, the $MgCl_2$ is present in distinctly greater coagulative strength than the NaCl; that the $MgSO_4$ is only a little greater in strength, taking its inferior ionisation into account; and, on the assumption of a coefficient of ionisation for $CaSO_4$ not much inferior to that of the NaCl present, it also is of superior coagulative strength.

We find in comparative experiments on separate solutions of salts made up to the above strengths that $MgCl_2$ and $CaSO_4$ are the most active in precipitating suspension; next follows $MgSO_4$, and a little behind NaCl. The viscosity of the NaCl solution will be about 1·0435; that of the $MgSO_4$ about 1·0042; and that of the $MgCl_2$ about 1·01.

Many phenomena find explanation in the effects which appear involved in the foregoing experiments. Thus the well-known greater compactness of marine sediments is probably referable to the coagulative or flocculative effects arising in the electric activity of the ions in discharging or neutralising the repulsive electric layers. It is probable, too, that minute traces of metallic ions are carried down with the sediments (Linder and Picton). Of such those of the higher valencies would form the chief part. The absence of the ions of higher valency—manganese and aluminium—from the sea, and their precipitation in the sediments, may wholly or in part be due to the processes we have here briefly considered. This must not be forgotten in considering the inner mechanism of sedimentation.

Again, this abstraction of the active ions must influence the alkalinity of the sea, reducing this somewhat where it receives the sediments of the rivers.

XXIV.

ON THE NATURE AND SPEED OF THE CHEMICAL CHANGES WHICH OCCUR IN MIXTURES OF SEWAGE AND SEA-WATER.

By PROF. E. A. LETTS, D.Sc., Ph.D.; R. F. BLAKE, F.I.C., F.C.S.; W. CALDWELL, B.A.; and J. HAWTHORNE B.A.

[COMMUNICATED BY DR. W. E. ADENEY, F.I.C., F.C.S.]

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It need scarcely be said that one of the commonest methods adopted by towns situated on the coast, for the disposal of their sewage, is to run it without treatment of any kind directly into the sea.

Mr. Richard Hassard has given us the following list of the chief towns in Great Britain which adopt this plan:—

Aberdeen.
Dundee.
Berwick-on-Tweed.
Newcastle.
Sunderland.
Scarborough.
Blackpool.
Liverpool.
Birkenhead.
Hull.
Great Grimsby.
Yarmouth.
Margate.
Dover.
Folkestone.
Hastings.
Brighton.
Portsmouth.
Sidmouth.
Teignmouth.
Devonport.
Swansea.
Bristol.

And to them may be added the following Irish towns:—

Belfast.
Dublin.
Londonderry.
Wexford.
Waterford.
Cork.
Limerick.
Galway.

The nature of the chemical changes which occur when sewage is thus treated, the speed at which they take place, the conditions which modify either the changes themselves, or the rate at which they occur, and the circumstances under which a nuisance may arise, are questions all of which are not only of scientific interest, but also of practical importance.

In order to decide these questions, and especially the effects of varying dilution and temperature on the speed, and possibly, on the nature of the chemical changes occurring, a very large amount of experimental work would be necessary, and for this reason the results which we now bring forward must be considered as chiefly of a preliminary nature.

In order to trace the nature of the chemical changes which occur when mixtures of sewage and sea-water are left to themselves, and the speed with which they take place, we have experimented under both fully aerobic and partially aerobic conditions. Indeed, in the second series of experiments, the conditions were, in one sense anaerobic, as no air, as such, was admitted to the mixture, which, however, contained the gases its constituents had dissolved from the atmosphere.

The method of investigation adopted in the second series of experiments was that originally employed by Dr. Adeney in his very important researches on "The Course and Nature of Fermentative Changes in Natural and Polluted Waters and in Artificial Solutions." Briefly stated, this method consists in analyzing, from time to time, the gases boiled out *in vacuo* from the polluted water or artificial solution, and thus ascertaining the amount of dissolved oxygen which disappears, and that of the carbonic anhydride which is produced.

In our experiments with mixtures of sewage and sea-water, we have adopted Adeney's method; and for boiling out and analyzing the dissolved gases, we have used an apparatus similar to his own, and, thanks to his kindness, largely constructed under his own supervision. Simultaneously with the gas analyses, determinations were made in the same sample of the mixture of—

(1) The "free" and "albuminoid" ammonia.

(2) The "oxygen absorbed" from acid permanganate during four hours at 80° F.

(3) The nitrites by the phenylene diamine process.

(4) The nitrates by the zinc-copper couple method.

In commencing a series of experiments, a stock of the mixture of sewage and sea-water was made, and a series of bottles filled to the brim with it and tightly stoppered.

These were then completely immersed in water contained in a zinc bath, the temperature of which was regulated by a sensitive thermostat and an automatic (water-driven) stirrer.

In analysing the dissolved gases, a given quantity (200 c.c.) of the mixture was withdrawn from one of the bottles through a tube plunged to the bottom, and rapidly transferred to the boiling-out apparatus. In this way, only the lower layers of liquid were removed for analysis, and contact of the sample with air avoided. As in Adeney's experiments, a small quantity of sulphuric acid was added before boiling out the gases, to decompose any bicarbonates present.

In the aerobic experiments, a large confectioner's jar was used to contain the mixture, and this was heated in a water-bath. Inside the jar a thermostat was placed, as well as a stirrer, both being made of glass. For obvious reasons no analyses of dissolved gases were made in this series of experiments.

The sea-water used in all the experiments was collected from a spot (near Black Head) just outside Belfast Lough, and at a time of the tide when there was a strong current from the Irish Channel, so that the water was uncontaminated. Three samples of sea-water (collected on different occasions) were employed, which we shall call 1, 2, and 3. The following determinations were made in them :—

SEA-WATER.

No. of Sample.	Temperature when collected in ° C.	(In cubic centimetres per litre at N. T. P.) Dissolved Gases.				(In parts per 100,000.)				
						Unoxidized Nitrogen as			Oxidized Nitrogen as Nitrates.	"Oxygen absorbed" in 4 hours at 80° F.
		CO_2.	O_2.	N_2.	Total.	Free NH_3.	Albd. NH_3.	Total.		
1	8·8	45·20	6·95	12·16	64·31	·0013	·0058	·0071	—	0·1328
2	9·9	—	—	—	—	·0013	·0066	·0079	·0033	0·0952
3	11·0	—	—	—	—	—	—	—	—	—

The sewage was obtained from the Belfast Main Drainage system, close to the Outfall Works, either from the sewer itself or from the tank into which the sewage is pumped previous to its discharge into the Lough on the ebb tide. Three samples were employed, each of which was filtered previous to its employment. The following determinations were made :—

FILTERED SEWAGE.

Number of Sample.	In parts per 100,000.			
	Total Solids.	Nitrogen as—		
		Free NH_3.	Albd. NH_3.	Total.
1	469·8	1·82	1·15	2·97
2	243·7	1·25	0·59	1·84
3	93·5	0·33	1·32	1·65

Experiments in Closed Vessels.

Three series of experiments were made, all at the same temperature, viz. 21° C., and with the same proportions of sewage and sea-water, viz. 1 part by volume of the former, and 99 parts of the latter.

In the first series, No. 1 sample of sewage and No. 1 sample of sea-water were employed. In the second series, No. 2 sample of sewage and No. 2 sample of sea-water; and in the third series No. 3 sample of sewage and No. 3 sample of sea-water.

In the following table we give the results of the different determinations.

SEA-WATER AND 1 PER CENT. SEWAGE IN STOPPERED BOTTLES AT 21° C.

Experiment.	Time.	(In cubic centimetres per litre at N. T. P.)				(In parts per 100,000.)					
		Dissolved Gases.				Unoxidized Nitrogen as—			Oxidized Nitrogen as		"Oxygen Absorbed" in 4 hours at 80° F.
		CO_2.	O_2.	N_2,	Total.	Free NH_3.	Albd. NH_3.	Total.	Nitrates.	Nitrites.	
1	When mixed, . .	45·81	5·23	10·13	61·17	·0171	·0165	·0336	·0066	None.	·144
,,	After 6 hours, . .	46·05	5·20	9·98	61·23	·0171	·0165	·0336	·0062	,,	·126
,,	,, 24 ,, . .	47·78	3·14	10·03	60·95	·0046	·0263	·0309	·0062	,,	·108
,,	,, 48 ,, . .	48·91	2·02	10·04	60·97	·0079	·0165	·0244	·0095	,,	·081
2	When mixed, . .	46·74	5·37	10·29	62·40	·0092	·0072	·0164	·0033	,,	·091
,,	After 12 hours, . .	47·18	5·20	10·14	62·52	·0066	·0046	·0112	·0119	,,	·052
,,	,, 18 ,, . .	46·95	5·08	10·08	62·11	·0079	·0072	·0151	·0058	,,	·059
,,	,, 38 ,, . .	47·04	4·97	10·11	62·12	·0066	·0059	·0125	·0078	,,	·087
,,	,, 90 ,, . .	47·18	4·60	9·87	61·65	·0099	·0066	·0165	·0041	,,	·062
,,	,, 528 ,, . .	47·56	4·42	10·01	61·99	·0138	traces.	·0138	·0062	,,	·069
3	When mixed, . .	46·23	5·30?	11·49?	63·02	—	—	—	—	—	—
,,	After 7 days, . .	47·31	4·41	11·11	62·83	—	—	—	—	—	—
,,	,, 14 ,, . .	47·33	3·81	10·60	61·74	—	—	—	—	—	—
,,	,, 21 ,, . .	47·13	3·87	11·06	62·06	—	—	—	—	—	—

The most striking feature of this table is the evidence afforded of the great rapidity of the changes which occurred in the first series of experiments compared with those which took place in the second and third series. In the former about 40 per cent. of the dissolved oxygen disappeared in 24 hours, and 60 per cent. in 48 hours, whereas in the second series only about 7 per cent. had isappeared in 38 hours, 14 per cent. in 90 hours, and only 18 per cent. in 528 hours (22 days).

Owing to an accident to the gas analysis apparatus when commencing the third series of experiments, the dissolved oxygen and nitrogen in the original mixture of sewage and sea-water could not be determined; but if it be assumed that the oxygen was about the same as in the preceding series (as was no doubt the case), then, in 7 days (168 hours), only 15 per cent. was lost, and at the end of 21 days, 26 per cent.

The composition of the sewage employed is, no doubt, mainly responsible for this remarkable difference in the behaviour of the mixtures, No. 1 sample being evidently far more concentrated than the other two.

Want of uniformity in the composition of sewage is one of the difficulties which must attend experiments of the kind described, and it is not easy to see how it should be overcome.

It is evident that what is really required is a stock of standard sewage—say, London sewage, but how could this be preserved? If evaporated to dryness, a stock of putrescible substances of uniform composition would, no doubt, be obtained; but they would, of course, have suffered considerable changes during evaporation, and would scarcely be of the same nature as sewage, especially as the characteristic bacteria would have been destroyed.

Another plan would be to experiment, as Dr. Adeney has done, with definite substances, such as urea, asparagine, albumen, &c., and, no doubt, much light would thus be thrown on the subject; but this method would involve an enormous amount of work, as each substance would require separate investigation, both at different temperatures and in different concentrations, and it might after all be urged that such substances do not represent sewage.

Turning, again, to the Table of Results, the evolution of carbonic anhydride—or rather its production—in relation to the oxygen absorbed, presents interesting features. For the sake of convenience we have tabulated them separately—

Series.	Time.	In cubic centimetres per litre.	
		Oxygen Disappearing.	Carbonic Anhydride Evolved.
1	After 6 hours.	0·03	0·24
,,	,, 24 ,,	2·09	1·97
,,	,, 48 ,,	3·21	3·10
2	,, 12 ,,	0·17	0·44
,,	,, 18 ,,	0·29	0·21
,,	,, 38 ,,	0·40	0·30
,,	,, 90 ,,	0·77	0·44
,,	,, 528 ,,	0·95	0·82
3	,, 7 days.	0·89 ?	1·08
,,	,, 14 ,,	1·49	1·10
,,	,, 21 ,,	1·43	0·90

It is evident that there is a fairly close agreement between the two sets of figures which is most striking in the case of the first series; and the conclusion seems warranted that, *when sewage decomposes in sea-water, the first chemical change which occurs is chiefly the absorption of oxygen and production of almost the equivalent quantity of carbonic anhydride.*

The question naturally arises as to the significance of this reaction. Does it mean that substances of the nature of carbohydrates are first attacked, for example, glucose as the simplest type, according to the equation:—

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O,$$

or are the nitrogenous bodies attacked with evolution of carbonic anhydride and the formation of more highly oxidized substances? This question can only be decided by experiments on mixtures of substances of definite composition and sea-water; but the first explanation appears the more probable one.[1]

A very instructive result of our determinations is the comparison of the "oxygen absorbed" by the permanganate test with the oxygen actually absorbed as shown by the analyses of the dissolved gases, which clearly show how fallacious the indications of the first-named test are.

This is shown in two ways, and to illustrate the point it will be sufficient to take the figures obtained in Series 1. First, if we take the results obtained from the "oxygen absorbed" test in the original mixture, and contrast it with the oxygen actually absorbed in 48 hours, the figures are, respectively, 0·144 parts by weight per 100,000, and 3·21 c.c. per litre. The latter is equivalent to 4·6 milligrammes per litre, or 0·46 parts by weight per 100,000. In other words, the oxygen actually absorbed was about *three times* as much as the amount shown by the permanganate test.

Next, if we contrast the differences in different periods of the two tests, and translate them into the same units, we obtain the following figures—

	Dissolved Oxygen actually disappearing after :—	Differences between "Oxygen absorbed" originally, and after :—
6 hours, . .	0·0043	0·018
24 ,, . .	0·2996	0·036
48 ,, . .	0·4602	0·063

The figures represent parts per 100,000, and should, of course, correspond if the oxygen of the permanganate acted in the same manner as the dissolved oxygen. This, of course, was not to be expected, but it is surely a remarkable fact that a more energetic oxidation is induced by micro-organisms and free oxygen than by the nascent oxygen of the permanganate solution.

Turning next to the determinations of nitrogen both "unoxidized" and "oxidized," we have, in the Table, expressed their amounts in the orthodox manner of parts per 100,000, but owing to the smallness of the quantities involved, and the magnitude of

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[1] It has been suggested to us that possibly both the absorption of oxygen and evolution of carbonic anhydride may be due to an act on the part of the micro-organisms analogous to ordinary respiration.

the unavoidable experimental errors, the result may be misleading. In all the determinations (with the exception of the nitrites), the nitrogen was eventually obtained as ammonia, and the latter estimated by Nesslerizing.

In determining both the free and albuminoid ammonia, a modification of the usual process was employed. 500 c.c. of the mixture of sewage and sea-water was distilled until 200 c.c. had passed over into a graduated flask. The contents of the latter were then well shaken, and 50 c.c. Nesslerized for the free ammonia. In a similar manner, after adding the alkaline permanganate, a further 200 c.c. were distilled off, and 50 c.c. Nesslerized as before. It is clear that the results in each case had to be multiplied by 4 to give the free or albuminoid ammonia in the original 500, and by 8 to obtain parts per 100,000.

It is obvious that a small error in the amount of ammonia found in the 50 c.c. of distillate becomes greatly magnified in the expression for the final result. Thus, an error of ½ c.c. of the weak ammonia solution used for the determination corresponds with ·004 parts per 100,000 or ·0033 of nitrogen, and such an error is quite probable.

In the case of the nitrates, the error becomes magnified five times, as 200 c.c. of the original fluid were treated with the zinc-copper couple, and the resulting ammonia determined in the whole of the distillate.

In view of these facts, a more accurate—or, perhaps, we should say a less misleading—method of expressing the results would be to give the actual number of cubic centimetres of the weak ammonia solution used in the different determinations, and this we have done in the following Table.

[TABLE.

SEA-WATER AND 1 PER CENT. SEWAGE IN STOPPERED BOTTLES AT 21° C.

The number of cubic centimetres of Standard Ammonia solution (1 *c.c.* = ·01 *mg.* NH_3) *actually required in the different determinations for :—*

Experiment.	Time.	$\frac{500}{4}$ = 125 c.c. of mixture.			200 c.c. of mixture.	125 c.c. of mixture (calculated).	
		Unoxidized Nitrogen as—			Oxidized Nitrogen as Nitrates.	Oxidized Nitrogen as Nitrates.	Total Nitrogen
		Free NH_3.	Albd. NH_3.	Total.			
1	When mixed,	2·6	2·5	5·1	1·0	0·62	5·71
,,	After 6 hours,	2·6	2·5	5·1	1·5	0·94	6·04
,,	,, 24 ,,	0·7	4·0	4·7	1·5	0·94	5·64
,,	,, 48 ,,	1·2	2·5	3·7	2·3	1·44	5·14
2	When mixed,	1·4	1·1	2·5	0·8	0·50	3·00
,,	After 12 hours,	1·0	0·7	1·7	2·9	1·81	3·51
,,	,, 18 ,,	1·2	1·1	2·3	1·4	0·88	3·18
,,	,, 38 ,,	1·0	0·9	1·9	1·9	1·19	3·09
,,	,, 90 ,,	1·5	1·0	2·5	1·0	0·62	3·12
,,	,, 528 ,,	2·1	Traces.	2·1	1·5	0·94	3·04

The Table brings out some curious features, which we scarcely like to discuss, as the body of evidence is not sufficient, we think, to warrant us in expressing any very definite conclusions. As a provisional criticism, we may offer the following remarks. The figures corresponding with the total nitrogen are sufficiently uniform to give us some confidence in the others.

As regards these, it would appear that, in the earlier stages of the fermentative process, interchanges occurred between the free and albuminoid ammonia. Thus, in both series of experiments, free ammonia disappeared at the commencement, and afterwards increased. Very possibly the mixture here functioned at first as a Pasteur's solution, the micro-organisms absorbing free ammonia for tissue formation.

In the first series of experiments, there is a fairly steady decrease in unoxidized nitrogen, and a decided, though not so steady, increase in nitrates.

In the second series, the quantities involved are much smaller, and the changes apparently much slower and more difficult to trace in any definite direction.

Experiments in Open Vessels.

The time at our disposal has only been sufficient to perform one series of experiments under fully aerobic conditions, the results of which are given below.

For reasons already mentioned a Table is appended of the number of c.c. of weak ammonia solution actually employed in Nesslerizing during the determinations of nitrogen as ammonia, albuminoid ammonia, and nitrates.

The sewage used was (as its examination showed) very dilute, and this possibly accounts for the slow rate of change which its nitrogenous constituents experienced when mixed with sea-water.

As in the case of the experiments in closed vessels, some free ammonia would seem to have disappeared during the first stages of the fermentation, but afterwards the amount increased. Nitrification seems to have set in after about a fortnight.

SEA-WATER AND 1 PER CENT. SEWAGE IN OPEN VESSELS AT 21° C.

(*Quantities in parts per* 100,000.)

Time.	Unoxidized Nitrogen as—			Oxidized Nitrogen as—		Total Nitrogen.	Oxygen absorbed. ($KMnO_4$ test at 80° F.)
	Free NH_3.	Albd. NH_3.	Total.	Nitrites	Nitrates		
Original Mixture, . .	·0112	·0146	·0258	None.	—	—	·0780
After 24 hours (1 day),	·0072	·0132	·0204	,,	·005	·0254	·0823
,, 92 ,, (4 days),	·0144	·0132	·0276	,,	·005	·0326	·0812
,, 164 ,, (7 ,,),	·0199	·0082	·0281	,,	·006	·0341	—
,, 260 ,, (11 ,,),	·0164	·0132	·0296	,,	·006	·0356	·0799
,, 428 ,, (18 ,,),	·0168	·0176	·0344	,,	·010	·0444	·0762
,, 644 ,, (27 ,,),	·0160	·0160	·0322	,,	·012	·0442	·1137
,, 3 months, . .	·0224	—	—	Some.	·064	—	—
,, 7 ,, . .	·0329	·0164	·0493	,,	·070	·1193	—
,, 11 ,, . .	·0288	—	—	·0028	·080	—	—

The number of cubic centimetres of Standard Ammonia solution (1 c.c. = 0·01 mg. NH_3*) actually required in the different determinations for* :—

Time.	$\frac{500}{4}$ = 125 c.c. of Mixture.			200 c.c. of Mixture.	125 c.c. of Mixture. (Calculated.)	
	Unoxidized Nitrogen as—			Oxidized Nitrogen as Nitrates.	Oxidized Nitrogen as Nitrates.	Total Nitrogen.
	Free NH_3.	Albd. NH_3.	Total.			
Original Mixture, , .	1·7	2·2	3·9	—	—	—
After 24 hours (1 day),	1·1	2·0	3·1	1·2	0·75	3·85
,, 92 ,, (4 days),	2·1	2·0	4·1	1·2	0·75	4·85
,, 164 ,, (7 ,,),	3·0	1·2	4·2	1·5	0·94	5·14
,, 260 ,, (11 ,,),	2·5	2·0	4·5	1·5	0·94	5·44
,, 428 ,, (18 ,,),	2·5	2·7	5·2	2·4	1·50	6·70
,, 644 ,, (27 ,,),	2·4	2·4	4·8	3·0	1·88	6·68
,, 3 months, . .	3·4	—	—	15·5	9·70	—
,, 7 ,, . .	5·0	2·5	7·5	17·0	10·62	18·12
,, 11 ,, . .	4·4	—	—	20·0	12·50	—

At the end of twenty-seven days, the jar containing the mixture was left at ordinary atmospheric temperatures, and no longer maintained at 21° C. The mixture then contained no nitrites, but the nitrates had increased in amount.

It was not again examined until an interval of about two months had elapsed (*i.e.* three months since the commencement of the experiment), when the nitrates were found to have increased very considerably, and a small quantity of nitrite had also been produced. The mixture was once more examined at the end of seven months, and finally at the end of eleven months.

The results of this series of experiments are, in one way, very puzzling, as the amount of total nitrogen was found to increase as the experiment progressed to an extent which cannot be accounted for by mere errors of experiment.

At first we thought that this increase might be accounted for by the following two causes : first, the room in which the mixture of sewage and sea-water was kept, adjoined a laboratory in which students were at work, and where at times a good deal of ammonia was present in the air; and, secondly, during the long period over which the experiment extended, some evaporation of the mixture of sewage and sea-water must have occurred (although the jar containing it was covered).

But, on the other hand, the increase in nitrogen continued after the vessel containing the mixture had been removed to a room specially reserved for water analysis where no free ammonia could be present in the air (beyond the amount normally found in it), to such an extent as cannot be accounted for by the second cause mentioned. As this investigation is of a preliminary character, further discussion of the matter may be deferred until more experimental data are available. Meanwhile it seems obvious from our experiments that the nitrifying organism can grow in sea-water, and that the changes which occur when putrescible substances are in contact with the latter are probably of the same nature as with fresh water.

The fact, however, that such a large proportion of free ammonia remained unnitrified after so long a period as eleven months is remarkable.

XXV.

STUDIES IN THE CHEMICAL ANALYSIS OF FRESH AND SALT WATERS. Part I. APPLICATIONS OF THE AËRATION METHOD OF ANALYSIS TO THE STUDY OF RIVER WATERS. By W. E. ADENEY, D. Sc., A. R. C. Sc. I., F. I. C., Curator, and Examiner in Chemistry, in the Royal University of Ireland, Dublin.

[Read May 16; Received for Publication July 30; Published September 3, 1900.]

I have recently had occasion to make some careful studies of non-tidal and tidal river waters, and it has occurred to me that a brief record of some of my results may prove of value at the present time, when the best methods of analysis of polluted waters is still a subject of inquiry and discussion.

Recent work upon this class of waters has all gone to emphasize the importance of distinguishing the unfermented organic matters from the fermented, and to estimate the proportion in which they exist, when present in a water.

I communicated a paper[1] to this Society some five years ago, in which I described a method of analysis, and the experimental investigation on which it was based, capable of effecting both these objects. Dr. George M'Gowan has very appropriately termed it the "Aëration Method," and I propose to adopt this term.

The Aëration Method of Analysis.

Although I have published a detailed description of the method, it will, perhaps, prove convenient, if I give a brief outline of it here. The bottle in which the sample of water for analysis is collected is completely filled and carefully stoppered, so as to exclude every trace of air. The bottle is then conveyed to the laboratory without delay, and the sample is divided into two portions; the dissolved gases, and inorganic nitrogen compounds, are determined in one portion; the other portion is carefully preserved out of contact with air in the bottle into which it has been transferred, and which it com-

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[1] Trans. R.D.S., N.S., vol. v., pt. xi., 1895.

pletely fills. This is easily done by keeping the bottle immersed in water, neck downwards.

After keeping for a sufficient time, the dissolved gases and inorganic nitrogen compounds are determined as with the first portion, and the two sets of results give the means of determining quantitatively the changes in composition of the dissolved gases, and of the nitrogen compounds, brought about by the fermentative processes which the sample has undergone during the time it has been kept.

ADVANTAGE OF THE AËRATION METHOD.

The advantage of the method was shown to be that it gave absolute results and not comparative, and determined with very great accuracy the amount of fermentable organic matter present in the water, in terms of the carbon dioxide, and of the ammoniacal, and (possibly) nitrous and nitric, nitrogen formed, and of the dissolved oxygen consumed by their complete aërobic fermentation, and that also it enabled a distinction to be drawn between the oxygen consumed in the fermentation of the organic matter, and that consumed in the fermentation, or nitrification, of the ammonia. The value of the method has been recognised by chemists having a special knowledge of the subject. It, however, necessitates the determination of the dissolved gases in a polluted water, both when fresh and after fermentation. This involves, of course, gasometric analysis; and gasometric methods have apparently been avoided where possible by analysts in water analysis as being too laborious.

Attempts have been made to obtain sufficiently definite results without the aid of gasometric methods of analysis, but I do not know that any of them have been followed with even partial success.

It was hoped that some definite relationship would be found to exist between the actual quantities of organic matters in polluted waters, and the "oxygen absorbed" by them from acid permanganate, and possibly also the "albuminoid ammonia" yielded by them with alkaline permanganate. Practical attempts, however, to establish such relationships have failed to realise this hope. The important paper[1] recently communicated to this Society by Professor Letts, D.Sc., and his pupils, gives some interesting

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[1] Scien. Proc. R.D.S., vol. ix. (N.S.), pt. III., p. 337.

experimental data, showing, amongst other results, that no relation exists between the oxygen actually consumed by the fermentation of the organic matters in a polluted water, and the "oxygen absorbed" from acid permanganate; and that albuminoid ammonia determinations likewise afford no definite information as to the character, or quantity, of the organic matters in a polluted water.

ALL THE DISSOLVED GASES IN A WATER SHOULD BE DETERMINED, AND NOT THE DISSOLVED OXYGEN ONLY.

Some hope has also been entertained that simple determination of the dissolved oxygen in the water at the time of collection by one of the well established volumetric methods might yield important information as to the condition of the water when collected, more especially in the examination of river waters for pollution.

It becomes obvious, however, upon reflection that such determinations, although capable of being made with great accuracy, can be of very limited value, since at best they must be liable to very serious errors when calculated into percentages of saturation in order to reduce them to a standard and comparable form, owing to the uncertainty as to the standard quantity of dissolved oxygen the water should contain, if unpolluted, when the only datum known in connexion with the water at the time of collection is that of its temperature. I may here note that this difficulty does not arise in the aëration method, since the dissolved nitrogen is determined in addition to the dissolved oxygen, and this gives us the means of calculating the maximum quantity of oxygen which should be dissolved in the water at the time of collection.

EXPERIMENTAL DETAILS OF THE AËRATION METHOD NOT LABORIOUS.

The failure so far to discover a reliable method of analysis without the use of gasometric methods, induces me to again draw attention to the aëration method, and to illustrate its value by some practical applications, more especially as extended experience with the method has convinced me that it can be carried out with greater ease and more quickly than would be anticipated by chemists not practically acquainted with it. With the special apparatus described in my original paper (see also Chemical News, vol. 62, pp. 196–199, and 204–206) for extracting, measuring, and analysing the gases dissolved in the water, and employing an extraction flask of not less than 1600 c.cs. capacity, and working with 100 c.cs. of a sample of water, I find that the dissolved gases may be extracted, measured, and analysed in six samples, one after another, easily within six hours, including the washing out of the Eudiometer and Laboratory vessel necessary between each analysis.

I am also induced to again draw attention to the aëration method, in that I am now prepared to describe a modification of it, whereby the "oxygen absorbed" by fermentation in a polluted water may be determined by a single gas measurement. A detailed description of this modification will shortly follow in Part II. of this paper.

APPLICATION OF THE AËRATION METHOD TO THE STUDY OF A SLIGHTLY POLLUTED NON-TIDAL RIVER WATER.

The value of the aëration method is well illustrated by the results of analyses, recorded in Table I., on next page, of samples of a slightly polluted non-tidal river water, viz., the river Liffey, from immediately above Chapelizod to the weir at Island Bridge.

The purpose of the examination of this water was to ascertain whether it was a safe water for out-door and strictly non-dietetic use.

The water is pumped up from a point just above the weir, and is stored in a large tank for the purpose of distribution.

Samples 1 and 2, Table I., were collected on the same day, September 21st, 1899, during dry weather. The first from immediately above the weir, and the second from the bottom of the distributing tank into which the water was being pumped at the time.

The ordinary analytical determinations recorded in Table I cannot be regarded as indicating the existence of any fresh polluting matters in the water; the only conclusion that can in fact be drawn from them, is that the water is an excellent river water.

TABLE I.—*Analyses of Samples of Water collected from the River Liffey above the Weir at Island Bridge, Co. Dublin.*

No.	Samples.		Dissolved Gases expressed as volumes at N.T.P. per 1000 volumes of water.			Other Constituents expressed as parts per 100,000 of the water.					
	Where Collected.	Description.	Carbon Dioxide.	Oxygen.	Nitrogen.	Nitrogen as		Organic Nitrogen in		Chlorine.	Total Solids.
						Ammonia.	Nitrates.	Suspension.	Solution.		
1	Just above the Weir, near the right bank, Sept. 21, 1899.	Slightly turbid, yellowish green tint; traces of suspended matter, . .	58·78	5·25	14·34	·0040	·0340	·008	·052	1·26	—
	Ditto after keeping 37 days, ...		62·13	0·88	14·25	·0015	·0385	—	—	—	—
2	From the bottom of the distributing tank, Sept. 21.	Very slightly turbid, yellowish brown tint; traces of suspended matter, .	60·54	5·48	14·11	·0045	·0375	·008	·0517	1·295	—
	Ditto after keeping 38 days, ...		62·84	3·98	14·11	·0015	·0405	—	—	—	—
3	Just above Chapelizod, Oct. 16.	Slightly turbid, brown colour; traces of suspended matter, . . .	41·38	7·49	15·55	·004	·027	·023	·029	1·205	18·0
	Ditto after keeping 15 days, ...		42·12	6·54	15·45	·004	·035	—	—	—	—
4	Just below Chapelizod, Oct. 16.	Similar to No. 3, but a little more turbid, . .	41·01	7·63	15·52	·004	·028	·013	·045	1·26	18·0
	Ditto after keeping 17 days, ...		42·68	5·20	15·59	·004	·037	—	—	—	—
5	Just above the Weir, near the right bank.	Distinctly turbid, olive green tint; small quantity of vegetable *debris* in suspension, . . .	43·47	5·98	15·52	·002	·026	·02	·081	1·26	18·4
	Ditto after keeping 15 days, ...		48·61	1·06	15·38	·035	·011	—	—	—	—
6	From bottom of distributing tank, Oct. 24.	Slightly turbid, yellowish green tint; traces of suspended matter, . .	63·30	5·46	15·27	·0032	·040	·02	·055	1·295	—
	Ditto after keeping 9 days, ...		64·78	2·97	15·19	·0010	·044	—	—	—	—
7	Just above the Weir, near the right bank.	Slightly turbid, yellowish green tint; traces of suspended matter, . .	72·64	3·23	14·93	·0028	·051	·02	·079	1·4	0·0
	Ditto after keeping 8 days, ...		75·62	0·44	14·99	·0230	·035	—	—	—	—

The weather was dry both on September 21st and on October 16th; it had just commenced to break when sample 6 was being collected, and heavy rain had fallen before sample 7 was collected on the following day.

The composition of the dissolved gases, however, before and after fermentation, show a marked difference, and indicate, when taken into consideration with the inorganic nitrogen compounds, the presence of very decided quantities of fresh organic matter in sample 1, and show also that the quality of sample 2, is much better than that of sample 1.

The difference in composition of the dissolved gases also affords the means of estimating exactly the quantity and character of the polluting matters in each sample. No. 1, for instance, is shown to have undergone a very decided fermentation on keeping, during which nearly the whole of the dissolved oxygen had been consumed; and the fermentative process is shown also to have consisted of both a carbon fermentation and a nitrogen fermentation.

We may also conclude from the relative proportions of carbon and nitrogen fermented that the unfermented organic matters, originally present in the water, were of vegetable origin.

The analysis of sample 2 shows that the fermentative process which went on in the sample, when kept, was almost entirely confined to a nitrogen fermentation, and that consequently but little, if any, unfermented organic matter was originally present in the sample.

The carbon fermentation in this sample had, no doubt, taken place during the time of storage in the distributing tank.

I ought, perhaps, to explain the particular meaning I attach to the terms 'carbon fermentation' and 'nitrogen fermentation' before proceeding further.

I have used these two terms to indicate the two progressive steps in which the bacterial fermentation under complete aërobic conditions of organic substance and of ammonia takes place.

The organic substances are first completely broken down, and oxidized almost entirely into carbon dioxide, water, and ammonia. Traces of oxidized organic matters are also formed, and these undergo a more or less complete further oxidation into carbon dioxide and nitric acid during the subsequent fermentative process of the oxidation of the ammonia into nitric acid. Thus during the first step of the fermentative process, the oxidation of the unfermented organic carbon is the main factor of the process; while the oxidation of the ammoniacal nitrogen into nitric acid is the main factor of the second step of the fermentative process;

hence the terms ‘carbon fermentation’ and ‘nitrogen fermentation’ which I have employed. When the ascertained consumption of oxygen covers both fermentative processes, the loss due to each process may be calculated with sufficient accuracy for practical purposes on the assumption that the loss due to the nitrogen fermentation is equal to the volume of oxygen theoretically required for the direct oxidation of the quantity of ammonia found to have been oxidized by fermentation. (I have fully treated this question in my original paper.[1])

The samples 3, 4, and 5 in Table I. were all collected on October 16th, and in dry weather. Their analyses again illustrate the very great value of dissolved gas determinations before and after fermentation. They indicate a very great difference in quality between samples 3 and 4 on the one hand, and sample 5 on the other.

In sample 3, a slight fermentation took place on keeping, but it was practically confined to a nitrogen fermentation. In sample 4 the fermentation was more decided, and it consisted of a slight carbon as well as a slight nitrogen fermentation.

The analysis for sample 5 shows not only a very decided fermentation, but also that it was entirely confined to a carbon fermentation. As a matter of fact, 0·28 part of carbon per 100,000 parts of the water underwent fermentation, and ·033 part of nitrogen were converted into ammonia during the process, but it is to be noted that about one-third of this nitrogen was derived from nitrates originally present, and only two-thirds from unfermented organic matter.

The analyses therefore show that the ratio of carbon to nitrogen in the unfermented organic matters originally present in the water was 1 : 10, a ratio which, taken together with the fact that the organic matters were unaccompanied by ammonia, proves them of vegetable origin, and that they were not derived from sewage. As a matter of fact I may explain that they were due to decaying vegetable matter of the autumn season.

The analytical details for samples 6 and 7 further illustrate the valuable and definite results obtainable by the aëration method. I need only refer to one point in connexion with them. Sample 6 was collected on October 25th, when rain was commencing to

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[1] Trans. R.D.S., vol. v., pp. 593–604.

fall after a somewhat lengthened period of fine dry weather, and at a time when rain had commenced to affect the water in the upper reaches of the river.

Sample 7 was collected on the following day, after heavy rain had been falling for some hours previously. I mention these points to draw attention to the marked influence of the rain upon the quantity of carbon dioxide in the water at the commencement of the autumn season.

Application to the Study of a Potable Water-supply.

The next subject of examination which I wish to notice is that of the Rathmines water-supply, and I notice it in order to illustrate the value of a knowledge of the composition of the dissolved gases in certain cases of doubt in connexion with potable waters.

The Rathmines water-supply is an upland surface-water of excellent quality, the catchment area being most carefully guarded against contamination of sewage matter of any kind.

In June and the early parts of July of last year, serious complaints were made by the residents of the Rathmines district, that the water as supplied to them was turbid and decidedly coloured, and often emitted unpleasant fish-oil odours, and even at times developed oily scums on its surface when drawn in large quantities for bath purposes, &c.

On investigation, the bad appearance and odour complained of were found to be due to unusually luxuriant growths of microscopic organisms of various kinds, but chiefly of Algæ and Diatoms. The water at the time was unfiltered, and consequently the consumers experienced to the full the effect of these luxurious growths immediately they began to die down and decay. The Waterworks comprise two reservoirs: the upper reservoir situated at Glan-na-Smol, Co. Dublin, and forming the storage tank, is 50 feet deep in the deepest part, and possesses a storage capacity of 350,000,000 gallons; and the lower or service reservoir, situated nearer Dublin, at Ballyboden, which has a storage capacity of 11,000,000 gallons.

The microscopic growths were particularly luxuriant in this latter reservoir, so much so, indeed, that the stones all round it, from the surface to a depth of 18 inches, were completely covered with a most luxuriant growth of filamentous Algæ.

TABLE II.—*Analyses of Samples of Water collected from the Rathmines Water Works at Glan-na-Smol, Co. Dublin.*

	SAMPLES.[1]		Dissolved Gases expressed as volumes at N.T.P. per 1000 vols. of water.				Other Constituents expressed as parts per 100,000 of the water.				
							Nitrogen as		Organic Nitrogen in		
	Where Collected.	Description.	Carbon Dioxide.	Oxygen.	Oxygen[2] in per cent. of saturation.	Nitrogen.	Ammonia.	Nitrates.	Suspension.	Solution.	Total Solids.
1	From the Lower Reservoir at Ballyboden, July 4, 1899, where supply enters.	Slightly turbid, yellowish green, faint indefinable odour, ...	20·50	4·79	69·0	13·76	·0015	·025	·028	·01	9·2
2	From the Screen Chamber, just below Lower Reservoir, July 4.	Slightly turbid, peat brown tint, faint fish-oil odour, ...	21·28	4·71	68·5	13·71	·0023	·032	·031	·011	8·4
3	From the tap in Town Hall, July 4.	Decidedly turbid, peat brown tint, slight indefinable odour, . . .	21·27	3·96	59·2	13·37	·0005	·033	·021	·014	9·6
4	Ditto, July 5, supply drawn direct from Upper Reservoir.	Very faintly turbid, yellowish green tint, odourless, ...	20·73	5·24	72·3	14·30	0·0	·028	·024	·015	9·2
5	From the Upper Reservoir, at Glan-na-Smol, 5 ft. below the surface, at the tower, July 24.	Very faintly turbid, yellowish green tint, odourless, ...	16·67	5·71	87·7	13·03	·007	·010	·012	·010	10·4
6	Ditto, about 20 ft. below the surface, July 24.	Faintly turbid, brown tint, slight indefinable odour, ...	19·54	2·00	30·23	13·23	·0035	·025	·026	·016	10·1
7	Ditto, July 24.	Ditto, ...	19·34	2·28	34·48	13·29	·0030	·026	·026	·016	10·0

[1] The bottles in which the samples were collected were completely filled and carefully stoppered, so as to leave no air in them, and their contents were preserved from contact with air until they were analysed. Samples 1, 2, 3, and 4 were kept for 29 days before the above analyses were made. The nitrogen as ammonia, and as organic (total), in proportions of the samples, when fresh, was ·01, ·012, ·007, ·008, and ·045, ·043, ·045, ·045, respectively.

Samples 5, 6, and 7 were kept 10 days before analysis.

[2] The figures in this column have been calculated upon the assumption that the volumes of oxygen required for saturation were equal to one-half those of the dissolved nitrogen.

NOTE.—None of the samples contained nitrites.

The effect of the *débris* from the luxuriant vegetation is shown by the analyses recorded in Table II. Samples 2 and 3 were drawn from the lower service reservoir. The other samples represent the condition of the upper storage reservoir. On comparing the analyses recorded in the table, it is at once seen that the water from the upper reservoir, during its passage through the lower reservoir, received a marked addition of polluting matters; but I am more concerned at the present to draw attention to the value of a knowledge of the composition of the dissolved gases in the samples 5, 6, and 7 from the upper reservoir. These were all collected on the same day, namely July 24th, and represent the condition of the water in the reservoir at two different levels below its surface—sample 5 at about 5 feet below the surface, and samples 6 and 7 at about 20 feet below the surface. Sample 5 may be fairly taken to represent the average condition of the water as it entered the reservoir through the catch-water channels. Its analysis shows it to be slightly different in quality from the samples 6 and 7 from the 20-foot level. The analyses of the two latter samples indicate the existence of slight quantities of polluting matter at the lower depths of the reservoir; but with a knowledge of the composition of the dissolved gases in addition to the ordinary analytical data, we find that an active state of both carbon and nitrogen fermentation was taking place in the lower levels of the reservoir, and that the carbon fermentation was practically wholly due to vegetable *débris*.

The dissolved gases determinations also afford the necessary data for distinguishing the proportion of the dissolved oxygen consumed by the carbon fermentation from that consumed by the nitrogen fermentation in the manner I have described above.

APPLICATION TO THE STUDY OF THE WATERS OF A TIDAL RIVER.

The third subject of study which I have to notice is the tidal portion of the river Liffey, or rather its estuary. Analyses of samples collected from both the surface and bottom waters of the estuary are recorded in Tables III. and IV. in the following pages.

TABLE III.

Analyses of Samples of Estuary Water collected during the last two hours of the Ebb (Neap Tide), March 9th, 1900.

(High-water at 4·55 a.m. Weather very dry and calm; no rain for the previous seven days, with light E. and N.E. winds. Temperature of water at surface, 8° C.)

No.	SURFACE AND BOTTOM SAMPLES. Where collected; description.	Time kept.	Gaseous constituents expressed as volumes at N.T.P. per 1000 volumes of water.				Other constituents as parts by weight per 100,000 parts of water.						
			Carbon Dioxide.	Oxygen.	Oxygen in per cent. of saturation.[1]	Nitrogen.	Nitrogen as			Chlorine.	Solids in solution.	Solids in suspension.	
							Ammonia.	Nitrates.	Organic.			In-organic	Organic
	Sewage from Penstock, .	3 hrs.	113·73	3·83	0·00	16·75	·300	·750	·130	191	446	1·135	3·365
1	Over Outfall[2] at 9.5 a.m.,	4 ,,	85·05	5·27	68·84	15·31	·160	·340	·060	837	1651	1·285	0·715
2	10 yds. below Outfall in path of sewage, and 2 ft. below surface, at 9.9 a.m., ...	5 ,,	53·73	6·24	89·76	13·90	·004	·051	·086	1575	3057	Traces.	
3	Ditto at surface, at 9.12 a.m., ...	6 ,,	63·20	5·95	82·22	14·47	·042	·158	·088	1295	2527	Traces.	
4	50 yds. below Outfall, and 2 ft. below surface, at 9.14 a.m., in path of sewage, ...	30 ,,	54·27	6·15	36·74	14·17	·015	·013	·045	1554	3066	Traces.	
5	Ditto at surface, at 9.17 a.m., ...	31 ,,	60·96	5·77	79·72	14·48	·042	·083	·010	1313	2565	Traces.	
6	100 yds. below Outfall, and 4 ft. below surface, in path of sewage, at 9.19 a.m., ...	7 days.	52·97	5·35	76·32	14·02	·012	·028	·042	1617	3135	Traces.	
7	Ditto at surface, at 9.22 a.m., ...	7 ,,	61·27	4·80	67·32	14·26	·032	·086	·038	1348	2614	Traces	

8	Mid-way between Outfall and mouth of Harbour, near the S. Wall, 7 ft. below the surface, at 9.30 a.m., ...	10	,,	50·47	6·11	87·54	13·96	·006	·016	·054	1663	3280	Traces.
9	Ditto at surface, at 9.32 a.m., ...	10	,,	59·27	4·37	61·29	14·26	·015	·035	·064	1400	2711	Traces.
10	Mid-way between Outfall and mouth of Harbour, and a little to N. of path of sewage, 7 ft. below the surface, at 9.34 a.m., ...	10	,,	50·27	5·79	83·43	13·88	·001	·012	·036	1694	3295	Traces.
11	Ditto at surface, at 9.37 a.m., ...	10	,,	56·93	4·83	67·41	14·30	·004	·028	·058	1400	2742	Traces.
12	In deep channel near Lightbuoy 1, 21 ft. below the surface, at 9.40 a.m., ...	11	,,	48·97	6·49	92·45	14·04	·007	·014	·016	1768	3457	Traces.
13	Ditto at surface, at 9.53 a.m., ...	11	,,	57·85	4·77	67·56	14·13	·016	·031	·040	1335	2670	Traces.
14	100 yds. above Outfall mid-way between S. Wall and deep-water channel, 7 ft. below the surface, at 10.10 a.m., .	11	,,	55·12	5·11	72·69	14·07	·017	·026	·038	1523	2904	Traces.
15	Ditto at the surface, at 10.13 a.m., ...	11	,,	65·51	3·16	43·23	14·62	·034	·055	·048	1155	2742	Traces.

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[1] The figures in this column and in the similar column of the succeeding Table have been calculated on the basis that the volume of oxygen required for saturation was equal to half the volume of the nitrogen in them.

[2] The Rathmines and Pembroke Outfall Works.—Sample 2 was collected perpendicularly over the Outfall when it was covered by about 2 feet of water.

TABLE IV.

Analyses of Samples of Estuary Water collected during the last two hours of the Ebb (Spring Tide), March 2nd, 1900.

(Weather fine, no rain during the preceding forty-eight hours; light N.-W. winds. High tide, 11·32 a.m. Temperature of water at surface, 10° C.)

No.	SURFACE AND BOTTOM SAMPLES. Where collected; description.	Time kept.	Gaseous constituents expressed as volumes at N.T.P per 1000 volumes of water.				Other constituents as parts by weight per 100,000 parts of water.						
			Carbon Dioxide.	Oxygen.	Oxygen in per cent. of saturation.[1]	Nitrogen.	Nitrogen as Ammonia.	Nitrogen as Nitrates.	Nitrogen as Organic.	Chlorine.	Solids in solution.	Solids in suspension. Mineral	Solids in suspension. Organic
	Sewage from Penstock chamber. Very turbid,	23 hrs.	129·80	0·00	0·00	18·50	1·13	·82	·270	172	414	4·47	9·93
16	Over Outfall,[2] at 4.5 p.m. Turbid; odourless, . .	19 ,,	125·80	1·01	11·69	17·25	1·00	·80	·150	210	486	3·97	6·03
17	100 yards above Outfall, near Buoy 2, in mid-channel, 15 feet below surface, 4.10 p.m. Clear; odourless, . .	4 days.	51·41	6·60	91·92	14·35	·000	·024	·062	1631	3169	5·14	1·265
18	Ditto, at the surface. Distinctly turbid; odourless, ...	4 ,,	62·07	4·70	60·72	15·48	·003	·065	·071	921	1829	Traces.	
19	100 yards below Outfall, near the S. Wall, at 4.20 p.m., in shallow water. Turbid; odourless, ...	20 hrs.	69·41	5·21	69·34	15·03	·080	·420	·170	980	1906	2·47	1·73

20	Below Outfall, midway between the S. Wall and the Light-buoy 1, 14 in. below surface, at 4.28 p.m. Turbid; odourless, ...	3 days.	55·12	5·73	76·60	14·96	·003	·088	·037	1267	2484	1·28	0·32
21	Ditto, at surface, at 4.30 p.m. Turbid; odourless, ...	3 ,,	56·53	5·19	70·04	14·83	·004	·056	·060	1250	2411	0·63	0·00
22	Mid-channel, near Light-buoy 1, 14 feet below the surface, at 4.35 p.m. Clear; odourless, ...	4 ,,	51·03	6·67	93·29	14·30	·002	·024	·034	1503	3151	2·885	2·215
23	Ditto, at surface, 4.37 p.m. Slightly turbid; odourless, ...	4 ,,	55·96	5·98	89·59	14·84	·004	·026	·034	1330	2602	Traces.	
24	Above Outfall, mid-channel, opposite Pigeon House Harbour, 14 feet below surface, at 5.22 p.m. Faintly turbid; odourless, ...	5 ,,	51·34	6·18	86·37	14·31	·018	·007	·036	1579	3098	3·885	1·715
25	Ditto, at surface, at 5.26 p.m. Turbid; odourless, ...	5 ,,	72·61	0·82	9·90	16·48	·120	·070	·130	459	929	Traces.	

Solids in Suspension.—The solids in the bottom water samples were of a light granular character; those in the surface water samples were of a very fine granular character with occasional pieces of light flocculent matter.

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[1] See footnote 1, Table III.

[2] See footnote 2, Table III.

After the references I have made to the two preceding tables it will be unnecessary to make any detailed reference to these further tables. I need only remark that the application of the aëration method to sea water is attended with results quite as definite and as valuable as those obtainable when applied to the examination of fresh waters.

The "outfall" referred to in the tables is, I should explain, situated a few yards to the north of the South Wall, and about half a mile below the Pigeon House Harbour.

These analyses, besides illustrating the value of the aëration method when applied to the analysis of sea-waters, will be found, on careful examination, to afford some valuable evidence upon the question of the disposal of sewage matters from which the heavy solid matters have been previously separated by discharging them into tidal waters. It will be seen from the analyses that the effect of the liquid and the lighter solid sewage matters discharged from so populous a city as Dublin and its neighbouring districts is confined in calm weather to the surface waters of the estuary, the bottom waters being but slightly affected even at low tides. Thus in samples 9 and 10, Table IV., the percentage of oxygen found in a sample of the surface water, collected at low spring tide opposite the Pigeon House Harbour, and in calm weather, was 9·9, after it had been kept for five days out of contact with air, while the percentage of oxygen found in the sample collected at the same spot, but 14 feet below the surface, was 86·37.

ERRORS ARISING WHEN THE OXYGEN ONLY OF THE DISSOLVED GASES IS DETERMINED.

One further point which these analyses illustrate, and which must be here emphasized, is the nature and extent of the error to which I referred in the earlier part of this paper as more or less seriously affecting the results obtained by volumetric methods for dissolved oxygen.

The practice hitherto amongst analysts for the estimation of the dissolved oxygen in a water when such has been necessary, has been to adopt one of the volumetric methods, and to employ, for the purpose of calculating the quantities of oxygen found into percentages of saturation, tables giving the maximum quantities of oxygen which distilled water holds in solution when saturated, at different temperatures.

Although it is well known that accurate determinations of the actual quantity of oxygen dissolved in the water may be made, within certain limiting conditions, by Schützenberger's, or by Thresh's, volumetric method, a serious difficulty arises when it comes to the question of the standard of oxygen saturation to be taken for the purpose of calculation. This becomes evident immediately it is remembered that the composition of the dissolved gases in still water alters very slowly with alterations of temperature, so that samples of a good fresh river water may be, and probably always are, either over-saturated or under-saturated with oxygen for the temperatures of the water at the times of collection.

When it happens that the waters examined are pure sea water, or mixtures of sea and river waters, such as in tidal rivers, the error becomes still more serious, since the solubility of atmospheric oxygen is very much less in sea water than in fresh, temperature for temperature.

If, however, the dissolved nitrogen, as well as the oxygen, be determined, we have thereby the means of calculating whether the volume of dissolved oxygen found does actually represent the state of oxygen saturation for the conditions to which the water had been subjected at the time it was collected, or of calculating, if it does not, its exact amount below that state.

The truth of these statements will be apparent from the following table, showing the solubility of atmospheric nitrogen and oxygen at different temperatures in distilled and in sea waters:—

The gases are expressed in c. cs., at N.T.P., per 1000 c. cs. of water.

Temperature.	Sea-water.[1]		Distilled water.[2]		Sea-water.	Distilled water.
	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.		
10° C.	12·47	6·45	15·47	7·87	$O_2 = \frac{N_2}{1·933}$	$\frac{N_2}{1·966}$
15° C.	11·34	5·83	13·83	7·09	$O_2 = \frac{N_2}{1·945}$	$\frac{N_2}{1·951}$
20° C.	10·41	5·31	12·76	6·53	$O_2 = \frac{N_2}{1·960}$	$\frac{N_2}{1·954}$
25° C.	9·62	4·87	11·81	5·97	$O_2 = \frac{N_2}{1·975}$	$\frac{N_2}{1·978}$

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[1] Dittmar, "Challenger" Reports, p. 224.

[2] Roscoe and Lunt, Journ. Chem. Soc., 1889, 552.

XXVI.

NOTES ON TEMPERATURE OBSERVATIONS MADE AT DUNSINK OBSERVATORY DURING THE ECLIPSE OF THE SUN ON MAY 28, 1900. By C. MARTIN.

(Plate XXI.)

[Read June 20; Received for Publication June 22; Published October 17, 1900.]

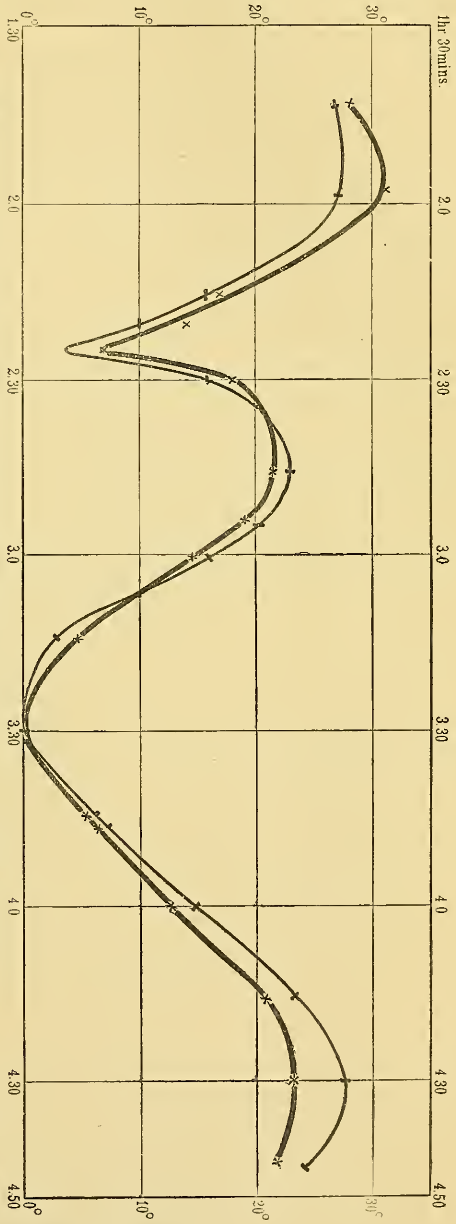
Observations of temperature were made at Dunsink Observatory during the recent eclipse of the Sun. The observations were taken with two heat radiation thermometers, one with a black bulb, and the other with a white bulb, kindly lent to the Observatory by Professor Fitz Gerald. These thermometers were mounted about an inch apart on a post a little over six feet high. The post was painted black, the bulbs of the thermometers being 6 inches away from any part of the woodwork, and pointed directly towards the Sun.

It was intended at first to take readings every fifteen minutes, but owing to clouds the readings were sometimes made oftener. Observations were started at 1.45; but from that time till 2.30 there were a good many clouds about which obscured the Sun every few minutes, so the readings at that time are not of much value; but from 2.45 to the time the observations were discontinued at 4.45, the Sun was free from clouds, and the observations seem very good. From the curves drawn (see Plate XXI.), it will be seen that about eight minutes after the middle of the eclipse the temperature was at its lowest, and began to rise rapidly as the portion of the Sun eclipsed became less. It will also be noticed that as the Sun became more eclipsed the temperature fell quickly. The highest reading before the eclipse began was 63°·7, and the lowest 35°·7, showing a drop of 28° with the black bulb thermometer; with the white bulb the highest reading was 15°·6, and the lowest 3°, showing a drop of 12°·6.

Experiment was made by shading the thermometers to find how they were affected. It was found that on an average the black bulb thermometer fell 6°·4 after being in the shade for one minute, and the white fell 2°·7 in the same time.

On annexed figure are given two curves showing the comparison of the two thermometers used. These were made by taking the lowest reading of each instrument from each of the other readings. The sums of these differences were taken, and the sum for the white bulb divided into that for the black bulb, thus finding the factor necessary to reduce white to black. The differences of the readings of the white bulb from the lowest reading were then multiplied by this factor, and the results were plotted down. The thick curve refers to the white bulb, and the other curve to the black bulb. From these two curves it will be seen that, if anything, the white bulb thermometer moved less quickly than the black, and is the least sensitive of the two instruments.

The temperature in the meridian room was recorded on a thermograph, but owing to the small scale of the sheet, no difference of temperature was noticeable.



The barometer also did not vary, the curve on the barograph sheet for several days before and after the eclipse showing a curve indicative of thunder.

Owing to clouds the first contact of the Moon with the Sun could not be seen, the last contact, however, was seen particularly well, and notwithstanding the error in the Nautical Almanac as to the duration of the time of totality of the eclipse, the time of the last contact agrees well with the time given in the Nautical Almanac. The Nautical Almanac time of the last contact is $4^h\,26^m{\cdot}6$, and the time observed at Dunsink $4^h\,26^m\,35^s{\cdot}7$, this observation was made on the chronograph with the Dent sidereal time clock, the error of this clock was determined on the same night.

Readings of Thermometers made during the Eclipse of May 28th, 1900, at Dunsink Observatory.

Dunsink Mean Time.	Black Bulb Therm.		White Bulb Therm.		Notes.
	Min.	Max.	Min.	Max.	
$1^h\,45^m$	63°·4	120°·9	14°·7	79°·8	Windy.
2 0	63 ·7	122 ·6	15 ·6	81 ·5	Cloudy for 9 minutes before these readings were taken, though the Sun was shining when readings were made.
2 15	51 ·8	—	9 ·8	—	Cloudy for 11 minutes before these readings were taken, the Sun was hidden in clouds when readings were made.
2 20	45 ·7	—	8 ·8	—	Clouds hid the Sun from last readings.
2 25	38 ·7	—	5 ·3	—	Cloudy all the time.
2 30	52 ·0	—	10 ·3	—	The Sun was hidden for the first $1\frac{1}{2}$ minutes; the remainder of the time it was clear.
2 45	59 ·1	—	11 ·9	—	The Sun was hidden by clouds for the first 9 minutes, the remaining 6 minutes the Sun was showing clearly.
2 55	56 ·0	—	10 ·7	—	The Sun was hidden by clouds for the first $1\frac{1}{2}$ minutes, the last $8\frac{1}{2}$ minutes the Sun was showing clearly.
3 0	52 ·4	—	9 ·1	—	No clouds over Sun.
3 15	38 ·3	—	4 ·6	—	,, ,,
3 30	35 ·7	—	3 ·0	—	,, ,,
3 45	41 ·8	—	5 ·3	—	,, ,,
3 47	43 ·3	—	5 ·9	—	,, ,,
4 0	50 ·0	—	7 ·9	—	,, ,,
4 15	59 ·0	—	11 ·5	—	,, ,,
4 30	63 ·4	—	12 ·6	—	,, ,,
4 45	58 ·9	—	11 ·8	—	,, ,,

The wind was blowing rather strongly from the time the observations were started till 3.30, when it began to drop; there was hardly any wind from 3.45 till 4.15, when it began to rise again.

XXVII.

ACTINOMETRIC OBSERVATIONS OF THE SOLAR ECLIPSE.

BY SAMUEL ROBERT BENNETT, SCH. T.C.D.

[Read JUNE 20; Received for publication, JUNE 29; Published OCTOBER 17, 1900.]

INTRODUCTION.

IN order to determine the decrease in the Sun's actinic power during the first period of the eclipse, *i.e.* up to the moment of greatest phase, and the increase of the same during the second period (which were naturally to be expected to take place), the following experiments were made under the surveillance of Professor G. F. Fitz Gerald, F.R.S. It was to be anticipated also that the increase in actinic effect during the second period would be modified by the Sun's decrease in altitude. But by eliminating the latter cause, the effect of the eclipse alone could be found.

INSTRUMENT USED.

The method adopted to measure the actinic effect at any instant during the eclipse was to have a piece of sensitised paper exposed to daylight, until darkened to a certain standard shade. This was effected by means of an actinometer. It consists of a circular disc of sensitised paper, enclosed in a light-proof case like a watch, one small sector of the dial of which is absent; so that a small piece of the paper can be exposed and compared with two standard colours, one on either side of this slit.

OBSERVATIONS.

By this means the following set of 54 observations were made, notes as to percentage of clouds and state of the sky being also taken. In the first column is given the mean time of the commencement of the exposure; in the second, the net time of exposure; and in the third, notes on the state of the sky, &c.

TABLE OF ACTINOMETRIC OBSERVATIONS.

Mean time.		Exposure in seconds.	NOTES.
H.	M.	S.	
2	12	52	⊙ clear, sky cloudy, about 60 per cent. clouds present.
2	15	56·6	⊙ clear, but not too strong.
2	17	57	Cloud over Sun, 2^h 17^m; clearing, 2^h 17^m 15^s; clear till 2^h 17^m 35^s; dark, 2^h 17^m 40^s to 2^h 17^m 50^s; clearing, 2^h 17^m 50^s.
2	20	58·4	⊙ bright, 2^h 20^m; darkening, 2^h 20^m 35^s; dark to end of observation.
2	26	60	⊙ dark at first, cleared slightly at 2^h 26^m 25^s, dark rest of time.
2	38	71·4	⊙ dark all the time.
2	43	80·8	⊙ dark all the time, 90 per cent. clouds.
2	46	84·6	⊙ dark all the time, about 60 per cent. clouds.
2	49	82·4	⊙ dark till 2^h 50^m 10^s, when it cleared; 10 per cent. clouds.
2	52	88	⊙ dark, 30 per cent. clouds.
2	55	85	⊙ clear till 2^h 55^m 30^s; dark rest of time.
2	59	69·2	⊙ clear throughout.
3	2	71	,, ,,
3	4	72·2	,, ,,
3	7	81	,, ,,
3	11	83	⊙ clear, but sky cloudy.
3	17	88·2	⊙ clear, but dark at the end.
3	20	86·2	⊙ dark till 3^h 20^m 45^s; clear to end; about 10 per cent. clouds.
3	23	91·8	⊙ clear all the time; sky almost clear.
3	25	100·6	⊙ and sky quite clear.
3	27	99·8	,, ,,
3	30	2	,, ,,
3	34	92	,, ,,
3	36	97 8	,, ,,
3	41	101·6	,, ,,
3	44	109·2	,, ,,

Mean time.		Exposure in seconds.	NOTES.
H.	M.	S.	
3	49	103·4	⊙ and sky quite clear.
3	52	100·6	,, ,,
3	55	102·2	,, ,,
4	1	93·4	,, ,,
4	3	90·5	,, ,,
4	5	95	,, ,,
4	8	92·8	,, ,,
4	10	93·5	,, ,,
4	13	92·7	,, ,,
4	15	89·5	,, ,,
4	17	90·4	,, ,,
4	19	90·8	⊙ and sky clear.
4	21	104	Till dark shade in standard colour.
4	24	74·8	,, light ,, ,, ,,
4	26	105	Till same as dark standard.
4	30	79·6	,, ,, light ,,
4	32	79	Sun and sky clear.
4	34	84	,, ,,
4	36	90	,, ,,
4	39	84·4	,, ,,
4	44	90	,, ,,
4	46	106	,, ,,
4	48	102·6	,, ,,
4	50	102	,, ,,
4	52	111	,, ,,
4	54	99	,, ,, [read rather soon.]
5	0	130	,, ,,
5	3	126·4	,, ,,

It may be mentioned that it would be quite easy to make an error of 10 per cent. in recording the proper exposure. From 4 hours 17 minutes to the end of the observations, a friend of mine held the stopwatch and marked the time when I considered the action completed to the usual colour, as it was of importance that the observer's judgment should be wholly uninfluenced by not knowing the previous watch-readings. We finished the observations at $5^h\ 5^m$, as the tendency was an increase in the time of exposure with the Sun's decrease in altitude.

The quick rise in time of exposure at $5^h\ 0^m$ was due to the Sun's rays becoming parallel to the side of the building, in which was situated the window where the observations were made.

GRAPHIC REPRESENTATION OF RESULTS.

To represent these results graphically the observations were plotted to rectangular axes. The ordinate of a point is the time of exposure in seconds required at the mean time represented by the corresponding abscissa. On describing the most probable curve satisfying these points, taking into account the state of the sky in estimating the value of each observation it was found to be of the form represented in fig. 1. This shows that, owing to the combined effect of the eclipse and the Sun's decrease in altitude, the time of exposure increased rapidly from 52^s at about $2^h\ 12^m$ represented by the point *A*, till about $3^h\ 40^m$, when the time of exposure attained a maximum value 101^s, represented by the point *B*. After this a decrease took place till a minimum value 86^s was reached at $4^h\ 26^m$, corresponding to the point *C*. It will be also noted that the rate of decrease *B* to *C* is more rapid than that of increase from *A* to *B*. After $4^h\ 26^m$ the branch rises rapidly from *C* to *D*. According to the Nautical Almanac, the

Eclipse commenced at	2^h	$12^m{\cdot}6$	Dublin mean time ;
Assumed greatest phase at	3	22	
Ended at	4	26 ·6	

thus the abscissæ of the points *A* and *C* are coincident with the times of beginning and end of the eclipse, but *B* is attained 18^m later than the moment of greatest phase. This was to be expected as the decrease in time of exposure, for a short time after $3^h\ 22^m$, due to the eclipse, would likely be counterbalaced by the increase due to the approach of evening.

DEDUCTION OF ALTITUDE CURVE.

To separate out the eclipse effect it was necessary to plot a similar curve to the above when there was no eclipse, *i.e.* to get the curve representing the decrease in actinic effect of the Sun's rays due to decrease in altitude alone. This was done in two ways. One curve was found by drawing freely a curve, the continuation of the branch of the observed curve before it reached *A*, and after it passed *C*. This is the continuous curve *AFCD* in fig. 1.

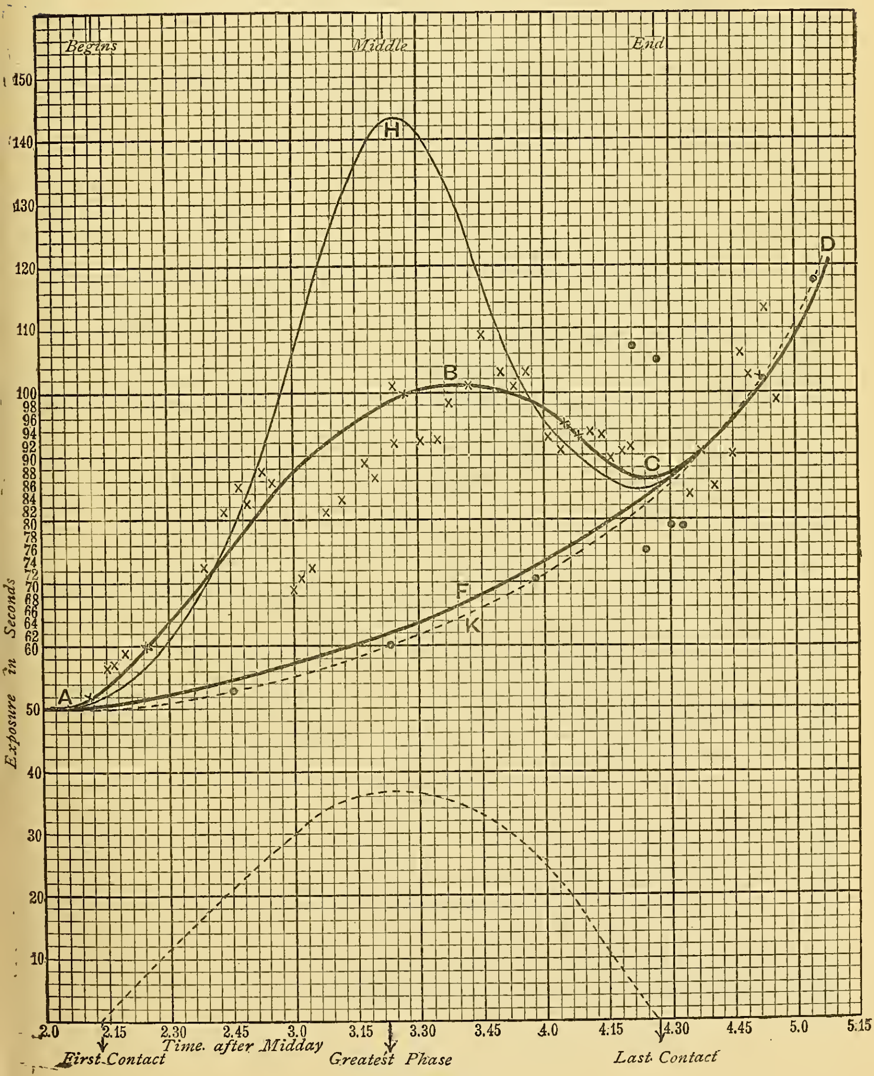


Fig. 1.

Another was obtained from theoretical considerations as follows:—When a ray of light is transmitted through a layer of an absorbing medium a certain fraction of it is absorbed, and it is assumed that this fraction is independent of the intensity of the incident beam.

If Q_0 denotes the intensity of the incident beam, then Q_0a will be the intensity after transmission through a layer of unit thickness, where a is the *coefficient of transmission.*

Similarly, $(Q_0a)a = Q_0a^2$ will be the intensity after transmission through two layers of unit thickness.

$\therefore$ for a layer of thickness l,

$$Q = Q_0a^l = Q_0e^{-\mu l}, \tag{1}$$

since a is a proper fraction; also $\mu = -\log a = \log\left(\frac{1}{a}\right)\cdot$

Now let SRZ (fig. 2) be the plane through the Sun S, the place of observation R, and the centre of the Earth. Then, if RR' be the surface of the Earth, QQ', approximately a circle parallel to RR', will be the limiting height of atmosphere.

Also let

$SRT = \alpha =$ altitude of the Sun.

Then we have

$RQ = RN$ cosec α approximately.

But the beam of light reaching R from the Sun passes through a layer of thickness RQ; hence we may write in (1),

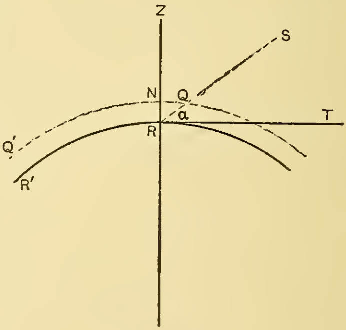


Fig. 2

$$l = h \text{ cosec } \alpha,$$

thus

$$Q = Q_0e^{-h\mu \operatorname{cosec}\alpha}.$$

Let

$$h\mu = h \log\left(\frac{1}{a}\right) = k,$$

where k is a constant which is always positive and depends only on our atmosphere.

Then

$$Q = Q_0e^{-k \operatorname{cosec}\alpha}, \tag{2}$$

where Q_0 and k can be determined by two observations; and they can be so determined that $Q = \frac{1}{y}$ where y is the ordinate of a point on the required curve.

Thus if

$$Q_1 = Q_0 e^{-k \operatorname{cosec} a_1},$$

and

$$Q_2 = Q_0 e^{-k \operatorname{cosec} a_2},$$

then

$$k \doteq \frac{\log\left(\dfrac{Q_1}{Q_2}\right)}{\operatorname{cosec} a_2 - \operatorname{cosec} a_1}; \qquad (3)$$

and substituting this value of k in either of the above given equations, we find Q_0.

Again the altitude of the Sun is given in terms of the hour angle (h) by the formula

$$\sin a = \sin \phi \sin \delta + \cos \phi \cos \delta \cos h, \qquad (4)$$

where

$$\phi = \text{latitude of Dublin} = 53^\circ\ 23',$$

and

$$\delta = \text{declination of Sun on May 28th} = 21^\circ\ 26'{\cdot}5 \text{ approx.}$$

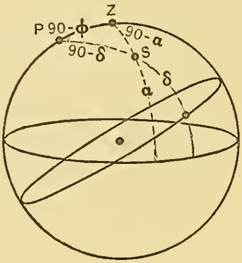


Fig. 3.

Thus at the beginning of the eclipse

$$h = (2^h\ 13^m) \times 15 = 33^\circ\ 15',$$

and

$$\therefore \quad a_1 = 48^\circ\ 45'.$$

Again for the time $4^{\mathrm{h}}\ 37^{\mathrm{m}}$, $h = 69^\circ\ 15'$,

and

$$\therefore \quad a_2 = 29^\circ\ 15'.$$

Thus

$$\begin{cases} \frac{1}{50} = Q_0 e^{-k \operatorname{cosec} 48^\circ\ 15'} & \text{for the point } A, \\ \frac{1}{90} = Q_0 e^{-k \operatorname{cosec} 29^\circ\ 15'} & \text{for a point near } C. \end{cases}$$

Hence

$$Q = \tfrac{1}{50}\, e^{\frac{133 - 100 \operatorname{cosec} a}{282}} = \frac{1}{y}. \qquad (5)$$

This then is the equation of the theoretical curve.

By taking different values of a the following points on this curve were found :—

Sun's altitude.	Theoretical ordinate.	Abscissa (mean time).
		H. M.
48° 45′	50	2 12·6
45°	53·56	2 46·3
40°	60·11	3 22·6
35°	70·05	3 58
29° 15′	90	4 37
25°	116·6	5 5·4

This curve is represented in fig. 1 by the dotted curve *AKCD*, and it will be seen that it comes remarkably close to that drawn freely as the continuation of the branches unaffected by the eclipse in the observed curve.

Another curve representing the decrease in actinic effect with the Sun's altitude could be obtained by exposing the actinometer on a day of like atmospheric conditions to the day of the eclipse and under similar circumstances as far as possible.

Curve of Eclipse Effect.

Having now found these two curves, viz. the observed curve during the eclipse and the theoretical curve of decline of actinic power, if a curve be plotted whose abscissæ are the mean time and ordinates the ratios of the ordinates of the observed curve to the corresponding ordinates of the theoretical curve above mentioned, this will be the curve representing the eclipse effect alone. For equation (2) is

$$\frac{1}{y} = Q = Q_0 e^{-k \operatorname{cosec} \alpha},$$

while if only a portion s of the area S of the Sun's disc be exposed we have

$$\frac{1}{\eta} = q = \frac{s}{S} Q_0 e^{-k \operatorname{cosec} \alpha}, \tag{6}$$

where η is an ordinate of the theoretical curve for the actinic power of the Sun at any instant during the eclipse.

Equation (6) is the curve *AHCD* in fig. 1, and is what the observed curve *ABCD* should have been to agree with the theory that the amount of light given out by the Sun during an eclipse is proportional to the fraction of his disc exposed.

From these two equations, by division, we get

$$\frac{\eta}{y} = \frac{Q}{q} = \frac{S}{s}. \tag{7}$$

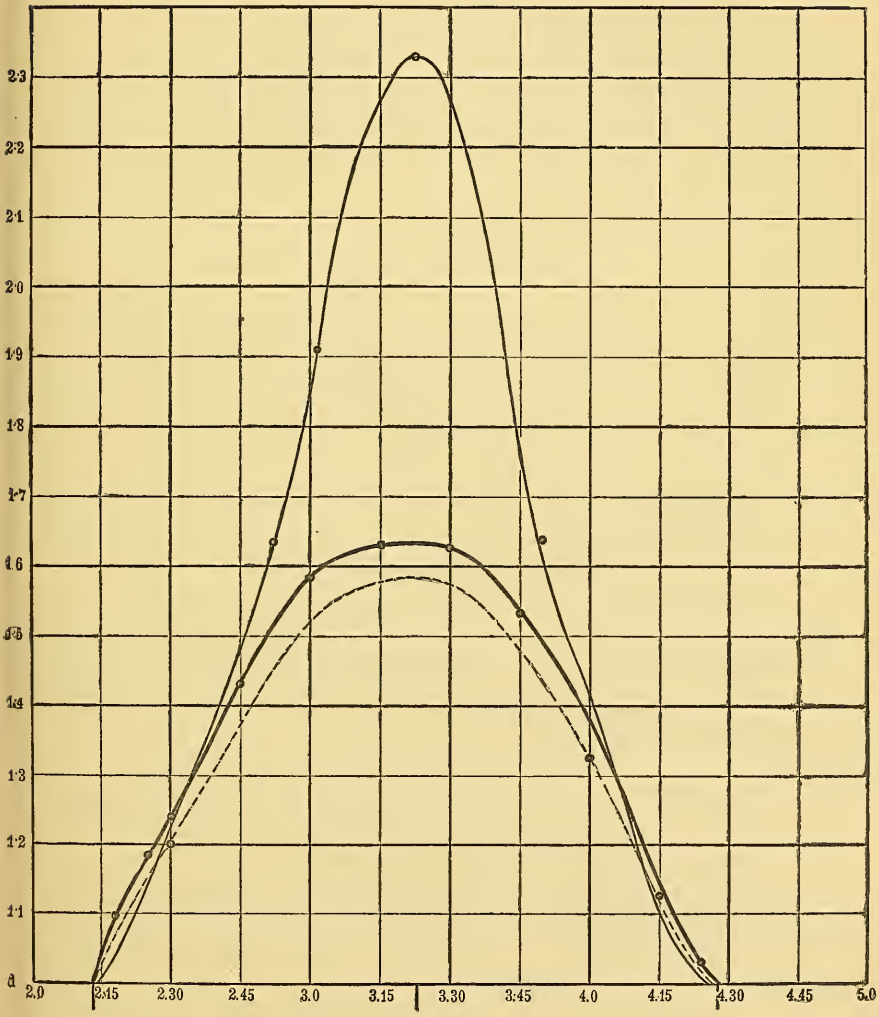


Fig. 4.

This then is the relation which should hold between the magnitude of the eclipse at any instant, and the actinic power of the Sun's rays at the same instant.

The curve whose abscissæ are the mean time, and ordinates $\frac{\eta}{y}$ as found from observations, was plotted and is the thick-lined curve shown in fig. 4 (p. 373).

It was now necessary to determine the curve $\frac{S}{s}$.

The Sun's semi-diameter on May 28th, 1900, at mean noon, was 15′ 48·15″, and the Moon's was 15′ 58·15″ at the same time, according to the Nautical Almanac. We may then assume them equal. If θ be the angle COP, fig. 5, which the line joining their centres at any instant makes with the radius of either to a point of intersection, we easily find

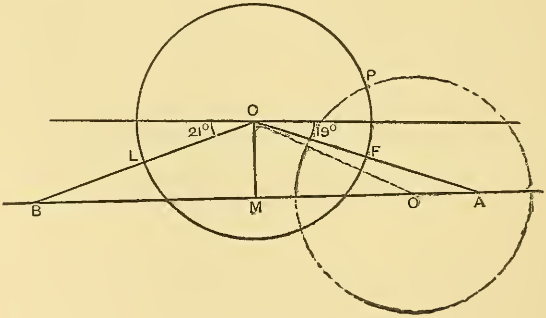


Fig. 5.

$$\frac{S}{s} = \frac{\pi}{\pi - 2\theta + \sin 2\theta}. \tag{8}$$

Again, taking either radius to be unity, we have the distance between their centres

$$\left.\begin{aligned} OC &= 2 \cos \theta \\ \text{and} \quad OM^2 &= OC^2 - MC^2 \end{aligned}\right\}. \tag{9}$$

Thus for any value of θ, $\frac{S}{s}$ is found from equation (8), and the point O is determined on AB from equations (9).

Also A corresponds to $2^{\text{h}}\ 12{\cdot}6^{\text{m}}$ mean time

M „ „ 3 22 „

B „ „ 4 26·6 „

The Nautical Almanac also gives angle from North point of

$$\begin{Bmatrix}\text{first contact } 109^\circ \text{ towards the West} \\ \text{last contact } 111^\circ \text{ towards the East}\end{Bmatrix}$$

for direct image, that is

$$ACM = MCB = 70^\circ,$$

and magnitude of eclipse (Sun's radius = 1) 1·352,

thus

$$CM = {\cdot}648 \text{ (radius)}.$$

If then we assume that AB is described *uniformly* in 134^{m}, the ratio $\frac{AO}{OB}$ determines the mean time for the value of $\frac{S}{s}$ so found.

Thus the following points on the $\frac{S}{s}$ curve were found:—

θ	Corresponding mean time.		$\frac{S}{s}$
	H. M.	H. M.	
0°	2 12·6	4 26·6	1
30°	2 22	4 16	1·061
45°	2 35	4 4	1·222
60°	2 52	3 46·5	1·642
70°	3 22	—	2·343

This is the tall curve in fig. 4.

CONCLUSION.

It is apparent, from inspection of figure 4, that the curves

$$\frac{\eta}{y} \text{ and } \frac{S}{s}$$

do not coincide, even approximately. In fact the observations indicate that, at $3^h\ 22^m$ the moment of greatest phase, more light was received from the Sun than should have been theoretically in the ratio of 2·343 to 1·63. It is difficult to propound a satisfactory explanation of this inconsistency[1] between theory and experiment.

Experiments were made to test if the time of exposure of the actinometer used obeyed the "Photographic Law," and was really inversely proportional to the intensity. This was done by measuring the variation in actinic power of the light from an arc lamp at different distances.

If

I_0 = the intensity of the light at unit distance

and

I = " " " distance D,

then

$$I = \frac{I_0}{D^2}.$$

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[1] An inconsistency in the direction found would take place if the Sun's disc were not uniformly intense, and if the edge were more powerful in actinic effect than the centre. This might be tested by taking an under-exposed photograph of the Sun, and would be verified if the edge of the Sun were more clearly defined than his centre. Also an error in the calculated distance of the Moon from the Earth making it less than it actually was, or the existence of an atmosphere on the Moon would tend to have the same effect. But none of them would cause a discrepancy of such magnitude as that observed. The eclipse was actually found to last some 5 seconds less than was expected in Spain.

To prove the photographic law $IT = \text{const.}$ where T is the time of exposure corresponding to the intensity I, we should have

$$\frac{T}{D^2} = \text{const.}$$

The experiments made with this object justified, within the errors of observation, the use of the above law in the experiments during the eclipse.

XXVIII.

INFLUENCE OF PRESSURE ON THE SEPARATION OF SILICATES IN IGNEOUS ROCKS.

By J. JOLY, M.A., D. Sc., F.R.S; Hon. Sec. Royal Dublin Society; Professor of Geology and Mineralogy in the University of Dublin.

[Published October 25, 1900.]

The application of the thermo-dynamical formula connecting pressure and melting-point with the formation of silicates in certain igneous rocks—as more especially Mr. C. E. Stromeyer has lately indicated in his interesting Paper "On the Formation of Minerals in Granite"[1]—calls for some comment.

It should not, in the first place, be forgotten that the question at issue is not simply the transformation of the particular silicate from a state of fluidity to a state of solidity. The silicate has been built up, molecule by molecule, in the crystalline form in the rock. It never at any time existed as a fluid glassy aggregate. That it did not is obvious from many considerations, as well as from the observed presence of lines of growth and such like phenomena.

Prior to the existence of the crystal the molecules comprising it were diffused throughout the magma. The influence of pressure here would be exerted in virtue of the total volume-change arising in the magma due to the segregation and orderly arrangement of the molecules attending crystallization. Is this volume-change measured by observation on the transformation of the crystal at the temperature of its formation into the melted glass at the same temperature? It does not follow. In fact it very certainly is not; for the segregation of the molecules and their consequent withdrawal from solution is very probably attended with a considerable volume-change affecting the magma. We might, moreover, expect from analogy with known cases that this volume-change

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[1] Manchester Literary and Philosophical Society, vol. 44, Part III.

will be positive in sign—a change of increase—and will thus, under the influence of pressure, act in opposition to the negative change of volume, probably occurring on crystallization. We are not, however, *sure* that the volume-change of withdrawal from solution will be positive. As the withdrawal from solution and assumption of the crystalline form are accomplished simultaneously the algebraic sum of the volume-changes is what concerns the final result. The change in volume attending solution, or withdrawal from solution, is often very considerable in known cases. We are ignorant of what its amount may be in the case of silicates dissolving in a silicious magma at temperatures near their melting points. Experimental investigation presents considerable difficulties.

But this is not all. We are hardly justified in assuming without question that the silicate molecule is first formed upon its crystallization. That in short the crystal is built up by successive additions of the more stable sub-molecules, such as CaO, Al_2O_3, SiO_2, adding themselves independently to the crystal. We are, indeed, *prima facie* entitled to assume that molecules of the particular silicate were first formed in the magma, or were so in some cases. If this is the first stage in the order of events, the pressure influence must be considered here also. The formation of such combinations as possess small molecular volumes would be favoured. Pressure might decide between two contending combinations, conferring greater stability upon the one, and hence causing it to grow at the expense of, or to the exclusion of, another.

It must also be borne in mind that, according to Maxwell and others, at every stage of temperature the viscous silicate-glasses would contain macro-molecules of various magnitudes, accounting for their partly solid, partly liquid state.

Every petrologist has had the extreme complexity of the phenomena of rock formation forced upon him with the extension of his studies. I would here enter a word of warning against applying without very full consideration a formula, applicable to reversible processes only, to the very complex conditions (chemical and physical) attending volume change on the formation of silicates in igneous rocks. The extreme uncertainty introduced into the computation by indefinite melting points, slow changes of volume, and latent heat, phenomena extending over a wide range of temperature, are a further reason for caution in this connexion. Again, the latent heat—as a quantity of heat involved in the progress of certain physical changes—is in nature complicated by such thermal changes as accompany the attainment of the crystallized state. Experiments made by cooling in a calorimeter a mass of the melted glass do not take this into account. The magnitude of the error involved may be small, but is unknown.

Until something is known respecting the molecular events which precede the formation of the crystal, it appears to me that the evaluation of all these quantities and the thermo-dynamical consideration of the entire matter are hampered by grave difficulties.

I may add that whether my views as to the influence of the silica percentage on the order of solidification of the silicates are generally confirmed or not, the results on quartz fibres certainly remove all difficulty from the occurrence of residual quartz. I have found more recently that quartz fibres show a steady viscous extensibility even to a temperature so low as about 735° C. Of course this does not preclude the possibility of the silica crystallizing at a higher temperature under conditions of repose, but it relieves us of any difficulty in explaining why it does not crystallize at 1400° C. or for that matter at considerably lower temperatures.

With reference to crystallized silica—rock crystal—I may observe that the temperatures inducing rapid melting, as given both by myself[1] and by Mr. Ralph Cusack,[2] are also far above the melting temperatures under conditions of prolonged heating, as can be conclusively shown when the latter is specially looked for. Finely powdered rock crystal folded in strong platinum sheet, and exposed for twenty-four hours or even considerably less in the flame of an ordinary Bunsen burner will be found to have adhered in a fine dust of minute slagged and rounded particles which cannot be wiped off. A prismatic vertical illuminator, used with a No. 7 Leitz, shows these blebs most clearly.

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[1] "The Melting Points of Minerals." Proc. Royal Irish Academy, vol. ii., ser. iii., p. 38, 1891.

[2] *Ibid.*, vol. iv., p. 339, 1896.

The temperature here is a bright red, and not over 1200° as judged by comparison with the luminosity and colour of a meldometer ribbon of platinum. But more accurate observations can be effected on the meldometer. I find that finely powdered rock-crystal spread on the meldometer ribbon, and exposed for one hour to a temperature of 1180° C. leaves an adherent residue of slagged and rounded particles, showing their slow fusion in the most unmistakeable manner. But even at a temperature which varied but little from 1100° C., an exposure of four hours produced a like result.

Finally I may mention here the result of a comparison of olivine, hornblende, and augite with rock crystal on the meldometer under condition of prolonged heating. The powders were all reduced to fine flour and spread thinly in adjacent patches. The temperature varied between the limits of 1085° C. and 1105°. The exposure was for 2 hours and 10 minutes. When examined by a Leitz No. 5, and vertical illuminator, it was found that *the quartz alone gave conclusive evidence of slagging.* As in the previous cases it was visibly rounded in small particles, while no such appearance could be certainly detected in the case of the other bodies. There were some colour changes apparent. The olivine had assumed a pale reddish hue; the hornblende inclined to a rusty brown. The augite showed little change. These changes, I may observe, also attend the ordinary experiments, such as have been recorded by Mr. Cusack and myself, and which fix the temperature at which these bodies slag rapidly—as olivine, 1342°–1378°; hornblende, 1187°–1200°; augite, 1187°–1199°.[1] Whether the colour changes observed, indicate any alteration such as would affect the melting point it is difficult to say. An experiment in which the meldometer was completely immersed in carbon dioxide and the temperature maintained at 1080° C. for 2½ hours showed less coloration, and gave the same results as regards appearance of melting.

Experiments on the behaviour of the previously melted silicates are in hand, but these results as they stand confirm the theoretical views[2] which I have already had the honour to bring before the

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[1] Cusack, *loc. cit.*

[2] "Theory of the Order of Formation of Silicates in Igneous Rocks." Proc. Royal Dublin Soc. Vol. ix. (N.S.), p. 298, 1900.

Society, that when properly investigated the softening points of the rock-forming minerals would be found to be such as would remove much of the difficulty which has been raised as to the order of solidification of minerals in certain igneous rocks.

It has been suggested that platinum may chemically effect silica. I may say, I have seen no sign of such an effect on the meldometer. Moreover the low softening temperature of quartz-fibre fully confirms the experiments just quoted, and, in the case of the fibre, there is no contact between platinum and silica.

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XXIX.

A CONTRIBUTION TO THE THEORY OF THE ORDER OF CRYSTALLIZATION OF MINERALS IN IGNEOUS ROCKS.

By J. A. CUNNINGHAM, A.R.C.Sc.I., B.A.

(Plates XXII. and XXIII.)

[COMMUNICATED BY PROFESSOR GRENVILLE A. J. COLE, M.R.I.A., F.G.S.]

[Read June 20 ; Received for Publication Nov. 23, 1900 ; Published May 7, 1901.]

I might fairly be expected to offer some apology for bringing this Paper before the Royal Dublin Society, since it is only so recently as March 21st of the present year that the subject was discussed and a theory put forward by no less distinguished an authority than Dr. John Joly, F.R.S.[1] But after considering the matter carefully, I cannot help thinking that the experiments on which Dr. Joly's theory was based are capable of a very different interpretation. In the present Paper I have therefore attempted to reinterpret them, and to correlate them with other experimental data, and to show how they point towards another theory which was formulated by Bunsen[2] in 1850.

The facts which demand a theory in order to reconcile their apparent inconsistencies can be briefly stated. By the study of thin sections of rocks petrologists have been able to determine with comparative ease and certainty the order in which their constituent minerals have consolidated. This order can, in general, be expressed in terms of Rosenbusch's[3] Law as being the inverse of the order of basicity of the minerals concerned. Thus, in particular, quartz is always last to crystallize in deep-seated plutonic rocks. This order was at once seen to be almost exactly the reverse of what one would expect from the relative fusibilities of the rock-

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[1] J. Joly, "Theory of the Order of Formation of Silicates in Igneous Rocks," Proc. Roy. Dublin Soc., vol. ix. (N.S.), pt. iii. (1900), p. 298.

[2] R. Bunsen, "Ueber den Einfluss des Drucks auf die chemische Natur der plutonischen Gesteine," Pogg. Ann. Phys. u. Chem. 81 (1850), p. 562.

[3] Rosenbusch, N. Jahrb. Min. Geol. u. Pal. (1882), Bd. vi., p. 1.

forming minerals. When Dr. Joly[1] and Mr. Ralph Cusack[2] made accurate determinations of the melting points of the minerals, the incompatibility of the two sets of facts in no sense disappeared. Here, then, was just the sort of material which demanded a theory to endow the facts with an intelligible meaning.

As an experimental foundation for his "theory," Dr. Joly took what Professor C. V. Boys[3] had named a "quartz fibre," and stretched it by a force amounting to a little less than two tons per square inch.[4] This fibre was surrounded by a platinum trough which was mounted as the ribbon of a meldometer, so that its temperature could be raised to a known degree. The elongation of the fibre was observed by means of two micrometer microscopes. Under these conditions the fibre was found to stretch at a temperature estimated at about 800° C.

Now, I venture to submit the following remarks on this experiment for consideration :—

1. In the first place, as was pointed out by Professor Grenville Cole at the March meeting of this Society, the so-called "quartz fibres" experimented upon by Professor Joly are not quartz at all, but amorphous silica, as was proved by their optical inactivity between crossed nicols. In fact, so far as I am aware, quartz once fused alone at atmospheric pressure has never been found to recrystallize as quartz. If rapidly cooled after fusion the density of the resulting silica is 2·2. If maintained for long at a high temperature its density increases to 2·3.[5] The conditions under which quartz fibres are produced (*i.e.* by shooting an arrow the tail of which has been dipped in fused silica) are evidently such as to insure rapid cooling. In fact, the elasticity and strength of the

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[1] J. Joly, "On the Determination of the Melting Points of Minerals," Proc. Roy. Irish Acad., Ser. III., vol. ii. (1891), p. 38.

[2] R. Cusack, "On the Melting Points of Minerals," Proc. Roy. Irish Acad., 3rd Ser., vol. iv. (1896), p. 399.

[3] C. V. Boys, "On the Production, Properties, and some suggested Uses of the Finest Threads," Proc. Phys. Soc., 9 (1887–88), p. 8.

[4] It may be well to point out an obvious misprint in Dr. Joly's paper (p. 299, l. 28):—

For "Stress . . . 293 × 10³ kilogrames per sqr. cm,"
read "Stress . . . ·293 × 10³ kilogrammes per sqr. cm."

[5] Frémy, Encyclopédie Chimique, T. II., Sect. 3^e, 6, p. 142. Paris, 1884.

fibres depend on rapid cooling, and are destroyed by annealing.[1] The physical properties of quartz are in many respects so peculiar and evidently so closely connected with a particular molecular arrangement,[2] that it is a peculiarly unsafe thing to infer its behaviour from experiments on amorphous silica which presents more normal characters. It would be as safe to infer the physical properties of the diamond from experiments on graphite or gas carbon. The refractive index of quartz for the D line is 1·5442, that of amorphous silica 1·4587 (according to a communication from Prof. C. V. Boys). The density of quartz is 2·66; that of amorphous silica 2·22. Hence, in the latter, the average distance of the molecules of SiO_2 may be supposed to be greater, and hence the intermolecular forces will be less; we should not then be surprised to find that amorphous silica is not so rigid under stress as quartz. It is well known that the physical properties of the useful metals are profoundly altered by their method of preparation and previous treatment, although the actual difference of molecular structure is probably much less in such cases than between quartz and amorphous silica. I may quote an example of this taken from the work of Dr. Carl Barus[3] as being connected with the subject in hand in more ways than one. He plots curves exhibiting the results of experiments on hard and soft steel. It will be seen at a glance how much greater is the viscosity of soft steel than of hard steel, and how much more rapidly it increases with time in the former case than in the latter. In fact only at the end of a considerable interval of time does the absolute viscosity of hard steel attain to that of soft specimens at the outset of the experiment. At the same time we may note that there can be no doubt that the soft steel is actually the more ductile, *i.e.* it can be stretched more easily without breaking.

2. This naturally leads me to a second point. Prof. C. V. Boys[4]

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[1] M. Gaudin, "Seconde lettre sur les propriétés du cristal de roche fondu." Comptes Rendus 8 (1839), p. 711; and C. V. Boys, Proc. Phys. Soc. 9 (1887–88), p. 17.

[2] Kelvin, "On the Piezo-electric Property of Quartz," Phil. Mag. [v.] 36 (1893), p. 331.

[3] C. Barus, "The Change of the Order of Absolute Viscosity encountered on passing from Fluid to Solid," Phil. Mag. [v.] xxix. (1890), p. 337.

[4] C. V. Boys, "On the Production, Properties, and some suggested Uses of the Finest Threads," Proc. Phys. Soc. 9 (1887–88), p. 17.

showed that his "quartz fibres" retained any desired form (*e.g.* a coiled form when so held in a box) when raised above the melting point of copper (1050°), but refused to do so below that temperature. By increasing the distorting force Dr. Joly has lowered the temperature of permanent deformability to 800°. To my mind Professor Joly's experiment simply proved that amorphous silica is ductile at 800°. Ductile is, of course, only a relative term; but I wish to imply that the phenomenon observed was one of ductility, and not one of melting in the usual sense.

For practical purposes it is often convenient to observe the melting of a solid by means of optical tests, or by noticing the instant at which gravitational and surface tension forces belonging to the liquid state overcome the forces of rigidity which are characteristic of the solid state of aggregation. For rough practical purposes, I have said, these are convenient and sufficiently accurate methods, but if carried to an extreme they may lead to serious error, and for accurate purposes they are wholly inadequate. Dr. Carl Barus who has recently been awarded the Rumford medal by the American Academy of Arts and Sciences, for his researches on heat, and who has a good right to speak with authority,[1] says:—"My results have long since shown that in a comprehensive study of this question the crude optical and other methods hitherto used as criteria of fusion (criteria which have no inherent relation to the phenomenon to be observed) must be discarded. In their stead the striking volume changes which nearly always accompany change of physical state, in a definitely constituted simple substance, are to be employed." Workers on the fusion of metals have, on the other hand, very generally employed the evolution of heat at the moment of consolidation as the criterion.[2] This is exhibited on the cooling curves, so commonly drawn by metallurgists, by a horizontal line indicating a constant temperature for a certain interval of time. These two phenomena probably occur simultaneously; as, for instance, was proved by

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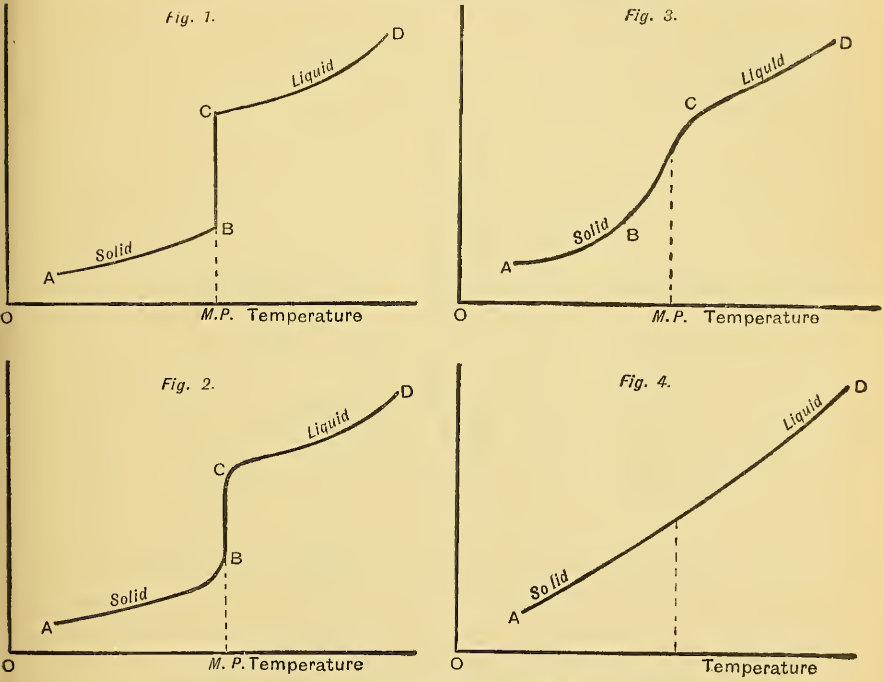
[1] C. Barus, "The Continuity of Solid and Liquid," Amer. Jour. of Science III.° 42 (1891), p. 125.

[2] Cf. W. C. Roberts-Austen, Report to the Alloys Research Committee. Proc. Institution of Mechanical Engineers (1891), p. 569.

M. W. Spring[1] in the case of certain metallic alloys. Both of these criteria when plotted as curves to a suitable scale exhibit in general pretty much the same characters. Thus, if in the accompanying curves, figs. 1 to 4, we represent temperatures by abscissæ, and volumes by ordinates, then the slope of the curve at any point represents the coefficient of expansion $\left(\frac{dV}{d\theta}\right)$ at that temperature. At the melting point (MP) we have a sudden expansion while the temperature remains constant. The passage from solid to liquid may be sudden which would be indicated by sharp corners at B and C (fig. 1), or it may be more or less gradual, indicated by one or both corners being rounded (figs. 2 and 3). The vertical height BC represents the volume change on passing from solid to liquid which is usually an expansion as in the



Figs. 1–4.—Curves showing the connexion between Temperature and Physical Properties in passing from Solid to Liquid.

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[1] M. W. Spring, Bull. Acad. R. des Sciences, des Lettres, et des Beaux-Arts de Belgique, 2° Séries, T. xxxix. (1875), p. 548.

diagram, but may be a contraction as in the familiar case of ice. The amount of this volume change varies greatly according to the substance under examination. In the extreme case the corners B and C may be so much rounded off that there is no longer any vertical line (fig. 3). We can include both these cases if we define the melting point of a simple substance as "that temperature at which its coefficient of expansion is a maximum." This definition only breaks down in the extreme case when the curve flattens out to one continuous line. But this is only the usual difficulty of applying a general law to the limiting case; and it is doubtful if such a limiting case occurs in nature (*i.e.* among actual substances), and if it did occur, it would be legitimate to say that such a substance had no melting point. As examples of the behaviour of a number of different substances I may refer to the beautiful curves of Kopp.[1] Barus says they are too seldom quoted.

Similar descriptions will apply to the above curves (figs. 1 to 4), if we let the ordinates represent quantities of heat. The slope of the curve at any point now shows the specific heat $\left(\frac{dH}{d\theta}\right)$ for that particular temperature, and the vertical height of the steeper portion measures the "latent heat" of fusion. From this point of view we might define the melting point as "that temperature at which specific heat is a maximum." So far as I know, these two definitions are consistent, *i.e.* they would both lead to the same melting temperature for the same substance. This seems to me to be the only satisfactory way of drawing a sharp line of distinction between solid and liquid; and I can see no objection to drawing such a sharp distinction in theory, at least, even though our imperfect means of working may render it impossible to do so in practice for some time to come.

Now it is extremely probable, and in the absence of any data to the contrary it seems fair to assume, that many other physical properties also change suddenly, and in a similar manner, at the same temperature. If we say that a substance does not melt suddenly at any one temperature, we mean that its coefficient of expansion and specific heat increase gradually as it approaches its melting temperature, and finally attain a maximum at that

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[1] H. Kopp, "Ueber die Volumänderung einiger Substanzen beim Erwärmen und Schmelzen," Liebig's Ann. d. Chem. u. Pharm., vol. xciii. (1855), pp. 129–232.

temperature, and then begin to diminish again, also, perhaps, more or less gradually. We assume that a number of other properties also change more or less gradually at the same time. Thus, if we could measure the viscosity of such a substance as we gradually raised its temperature, we should probably find that its viscosity began to diminish at first slowly, then more rapidly until its rate of decrease of viscosity with rise of temperature $\left(\frac{-d\eta}{d\theta}\right)$ attained a maximum at the melting temperature. Its viscosity would then begin to diminish less rapidly with rise of temperature, as it passed into the liquid state. A perceptible "softening" may thus be taken to indicate the first upward bending of the corner B, figs. 2 and 3, which may now be looked upon as curves showing the relation between general properties (ordinates) and temperature (abscissæ) to a suitable scale.[1] It must be remembered that a gradual passage from solid to liquid (fig. 3) is highly characteristic of amorphous substances,[2] whereas a sudden change from solid to liquid (figs. 1 and 2) is characteristic of crystalline bodies.[3] Indeed, we know that quartz does undergo such a sudden volume change on melting as indicated by the observation of Moissan,[4] and by the density of quartz. Hence, I infer that the other physical properties of quartz also change suddenly on melting. Further, the fact that molten silica may be quenched in cold water without developing a single crack,[5] and will cool down as the amorphous substance, with

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[1] Of course certain properties will diminish with rise of temperature, but then we can think of these curves (figs. 1 to 4) as having the reciprocal of such properties for ordinates. It is the *rate* of increase or decrease of the physical properties which concerns us here.

[2] The gradual expansion of amorphous silcates is illustrated by Dr. Joly's experiments on mineral glass beads: ("On the volume Change of Rocks and Minerals attending Fusion," Trans. Roy. Dublin Soc., Ser. ii., vol. vi. (1897), p. 283). The expansion curves show very much rounded corners corresponding to B, fig. 3., but they lack the upper portion C. The volume changes obtained by Dr. Joly's method do not, of course, exhibit the volume changes that go on in rocks when crystallizing, but probably only a small part of them.

[3] Cf. Preston's "Theory of Heat," pp. 270 and 286. London, 1894.

[4] M. H. Moissan, "Le Four Électrique," p. 50. Paris, 1897. Id. "Sur la volatilisation de la silice," &c. Comptes Rendus, 116 (1893), p. 1222.

[5] Cf. Shenstone and Lacell, "Working Silica in the Oxy-gas Blowpipe Flame," Nature, vol. lxii., p. 20. (3rd May, 1900); and C. V. Boys, "Quartz Fibres," Nature, vol. xlii. (1890), p. 605.

density 2·2, without exhibiting any observed phenomena indicating a state of strain, seems to suggest that such silica comes very near to the above-mentioned limit, where the curve indicating volume change flattens out (fig. 4). But I have to return to this matter again later. Only in the meantime I wish to point out that we cannot safely infer that the melting phenomena of quartz are the same as those of amorphous silica, although the actual melting point, as defined above, of the two substances may be nearly identical.[1] It would be interesting to know if any difference in the rate of melting or period of softening of quartz and amorphous silica could be detected on the meldometer.

I therefore contend that quartz must exhibit a sudden volume change on melting which is, in all probability, accompanied by a sudden absorption of heat, and a sudden change of other physical properties (fig. 2, and Plate XXII.). M. Pionchon[2] measured the heat absorption of quartz up to 1185° C., and found an increase of specific heat in the neighbourhood of 400°, but from that up to nearly 1200° the specific heat was constant. This, I believe, indicates that the melting point of quartz is certainly above 1200°.

3. Professor Joly introduces viscosity (as indicated by ductility) as a criterion of melting. Dr. C. Barus[3] again deserves to be heard on the subject of viscosity in liquids and solids:—"In a liquid or a viscous fluid under moderate stress the instabilities are supplied by the mere thermal agitation at ordinary temperatures, at the same rate in which they are used in promoting viscous motion. Hence viscosity is constant at a given temperature. In a solid under stress the instabilities are expended at a rate decidedly greater than the small rate of continuous supply. Thus viscosity decidedly increases with time." Or, again, in referring[4]

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[1] Cf. R. Cusack, "On the Melting Points of Minerals," Proc. Roy. Irish Acad., Ser. III., vol. iv. (1896-98), p. 407. It is quite certain that the melting points of polymorphic bodies are not in general identical, although it is conceivable that in certain cases they may be. Cf. Van 't Hoff, Lectures on Theoretical and Physical Chemistry, pt. ii., p. 134. London (1899).

[2] M. Pionchon, "Sur la variation de la chaleur spécifique du quartz avec la température." Comptes Rendus, 106 (1888), p. 1344.

[3] C. Barus, Phil. Mag. [v.], xxix. (1890), p. 354.

[4] C. Barus, "Isothermals, Isopiestics, and Isometrics relative to viscosity," Amer. Journ. Sc., III.° 45 (1893), p. 88.

to this, he restates it rather more briefly:—"I defined a fluid (liquid or gas) as a body which, under constant conditions of pressure, temperature, and stress, shows constant viscosity as to time. In a solid, *cœteris paribus*, viscosity markedly increases with the time during which stress is brought to bear." An examination of the data given by Dr. Joly (*loc. cit.*, p. 299) shows that his fibre was solid according to this definition. Thus during the first fifty-five minutes the extension was found to be 0·076 cm., and during the next thirty-five minutes only 0·039, instead of 0·048 cms., which it would have been had viscosity been constant. But, on the contrary, viscosity increased, as is quite characteristic of the flow of solids.

4. Dr. Joly does not, indeed, state that the "melting point" of quartz is as low as 800°, but unless he intends to imply as much it is difficult to understand his meaning. For instance, he writes (*loc. cit.*, p. 301) of the silica entering "as an influence retarding crystallization and prolonging the viscous properties downwards in the scale of temperature. CaO, MgO, Al_2O_3, on the other hand, are crystallizers at high temperature," the contrast being apparently between these and silica, a crystallizer at low temperature. It certainly is the crystallizing temperature which concerns us in the present discussion.

Joubert,[1] in 1878, measured the rotatory power of quartz through a wide range of temperature, and found that, "De −20 à 1500 degrés, le pouvoir rotatoire du quartz augmente, d'une manière continue, avec la température." And further, using both right- and left-handed specimens, he found that, on allowing each specimen to cool down again, its rotatory power returned to its original amount. Now silica, which has once been really fused, has lost for ever this rotatory power. This question was fully discussed and put to experimental tests by Gaudin[2] and

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[1] M. J. Joubert, "Sur le pouvoir rotatoire du quartz et sa variation avec la température." Comptes Rendus, 87 (1878), p. 497. The author marks the 1500° with a ?, but states that it was the softening point of porcelain. Frémy quotes the figures into his "Encyclopédie Chimique," and omits the ?, evidently satisfied with the estimate.

[2] M. Gaudin, "Sur les propriétés du cristal de roche fondu." Comptes Rendus, 8 (1839), pp. 678, 711.

Biot,[1] the latter of whom refers to the work of Brewster and Sir John Herschel. The conclusion arrived at was that this rotatory power was a property characteristic of silica crystallized as quartz. I therefore submit that quartz is certainly not decrystallized, even in the neighbourhood of 1500°. It cannot, then, I think, be regarded as a crystallizer at low temperature. In fact, I see no reason for lowering the melting point of quartz as given by the meldometer, *i.e.*, 1425°.

It may here be well briefly to consider the melting points of the mineral silicates.[2] In the absence of more complete data one would hesitate to go beyond the indications of the meldometer, as given by Dr. Joly[3] and Mr. Ralph Cusack.[4] They certainly remain the best measurements that we have got. But in the paper under discussion, Dr. Joly seems almost inclined to rob them of all value by suggesting that the ordinary gravitational and surface tension forces may not be sufficient to make melting apparent. But how are we to know when they are sufficient and when not? Of what use, in fact, is the meldometer?

Mendeléeff,[5] as Dr. Joly points out, has likened the silicates to metallic alloys, regarding them as "alloyed" oxides—CaO, Al_2O_3, SiO_2, etc. Now, so far as I know, it is characteristic of the majority of metallic alloys to have a melting point decidedly below the mean of the melting points of the constituent metals. The curves[6] illustrated on pp. 393 and 396 (figs. 5 and 6) exhibit this in a striking manner. They are a few convenient examples, taken from Landolt and Börnstein. In many cases the melting point is far below that of either constituent. Two curves (Pt and Au,

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[1] M. Biot, "Sur la cause physique qui produit le pouvoir rotatoire dans le quartz cristallisé." Comptes Rendus, 8 (1839), p. 683.

[2] *Vide* Nature, vol. lxii., p. 368 (16th August, 1900).

[3] J. Joly, *loc. cit.*

[4] R. Cusack, *loc. cit.*

[5] D. Mendeléeff, "Principles of Chemistry." Translated by Kamensky and Lawson, vol. ii., p. 117. New York, 1897.

[6] Plotted from data collected in Landolt and Börnstein's Physikalisch-chemische Tabellen, pp. 159–161, and copied into Gray's Physical Constants (Smithsonian Institution, Contributions to Knowledge).

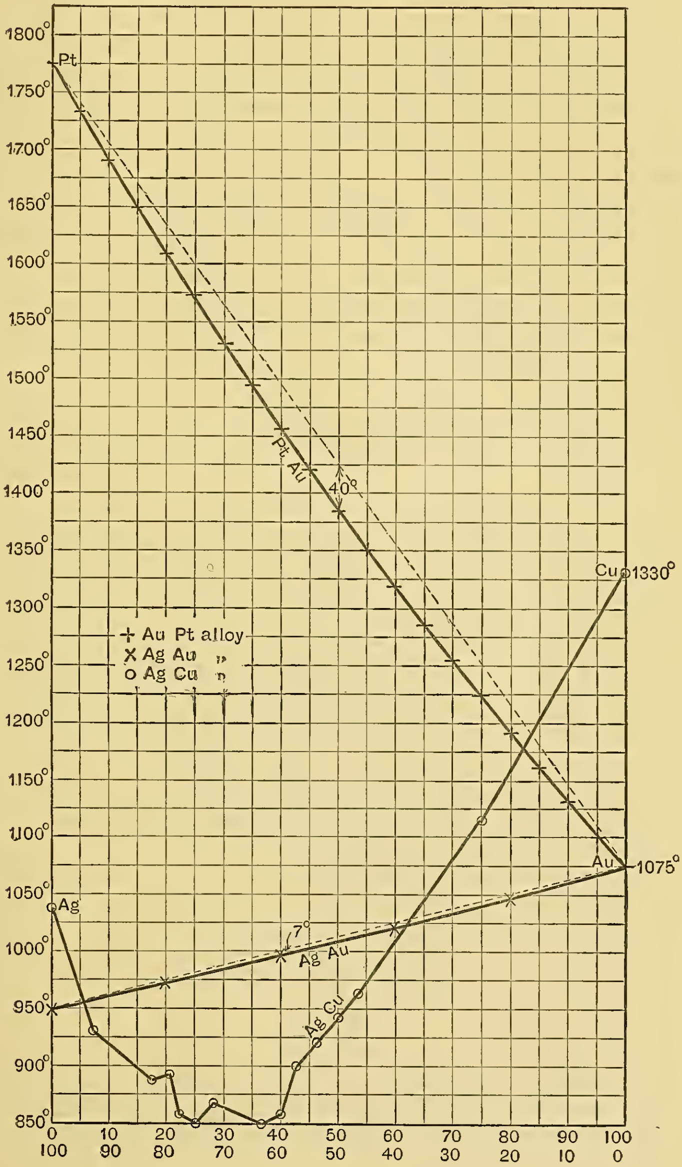

FIG. 5.—Curves showing the Melting Points of certain Metallic Alloys.

Au and Ag, fig. 5) illustrate the case where the depression below the mean is regular but least marked. The only instance given in Landolt and Börnstein, where the melting point of the alloy is above the mean of the melting points of its constituents, is that of white brass (half copper, half zinc), whose melting point is 912°, or slightly above the mean of the melting points of its constituents.[1] I do not know if the number of such examples could be increased by searching the works of metallurgists. M. Léo Vignon[2] has investigated the melting points of mixtures of organic substances, many of which he finds to be below the mean of the melting points of the constituents, and often far below the melting point of the most fusible constituent, and more particularly so where some feeble chemical combination can be traced. In those cases where the melting point is above the mean of the constituents no chemical affinity can be detected. Analogies are, however, never perfect,

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[1] 29*th June*, 1900.—Since the above was written I have obtained access to curves drawn by M. Gautier as reproduced in Sir W. C. Roberts-Austen's "Introduction to the Study of Metallurgy," 4th Edition (1898), although it is to be regretted that the Bulletin in which the original paper was published is apparently not to be had in Dublin. An examination of these curves shows that of the twenty-six examples of binary alloys given, nine of the melting point curves are entirely below the mean line (which would show the melting point of the alloy if it was affected by each constituent in proportion to the mass of that constituent in the alloy); nine of the curves pass both above and below the mean line, whereas eight are entirely above the mean line. So the "majority" mentioned in the text is a narrow one (9–8) for these particular curves. On combining these with those given by Landolt and Börnstein the majority becomes 16 to 8. Moreover, all the examples of ternary and quaternary alloys given in the latter tables show a marked depression of melting point on the additions of a third and fourth constituent. The most important rock-forming mineral silicates are certainly ternary and quaternary alloys.

In connexion with the melting point of alloys I may mention that in only one of the examples given is the melting point of the alloy above that of the least fusible constituent, whereas in numerous cases the alloy melts at a lower temperature than either of the constituents.

But as I have said in the text, science cannot be built up by analogy, and therefore it is more fruitful for the present purpose to examine the available data for the alloyed oxides themselves (fig. 7). Then, if we knew nothing else about the melting point of quartz, we could not be blamed for putting it at least as high as 1400° C.

[2] M. L. Vignon, "Point de fusion de certains systèmes binaires organiques (carbures d'hydrogène)."—Comptes Rendus, 113 (1891), pp. 133, 471.

Cf. A. Matthiessen, "On Alloys," Jour. Chem. Soc., v. (1867), p. 207.

and so it is more to the point to look for data regarding the behaviour of the oxides which enter into the composition of rock-forming minerals when mixed. Moissan[1] found that mixtures of CaO and Al_2O_3 (also of CaO and Fe_3O_4, and CaO and Cr_2O_3) were far more easily fusible than either of the oxides alone. It is familiar to the practical metallurgist that the addition of lime renders a siliceous slag much more fluid at the temperature of the furnace.[2] On the other hand, if a metallurgist[3] wants a highly refractory material, as a rule he prefers a pure oxide, either CaO, MgO, or SiO_2, etc., but he avoids a mixture, the exceptions being cases of similar oxides, and where, in consequence, the chemical union is weak, as, for instance, Fe_2O_3 and Al_2O_3 in Bauxite, and certain clays (Al_2O_3 and SiO_2). We cannot, then, be surprised to find the melting points of the various silicates (which are certainly crystalline chemical compounds) distinctly below that of quartz or any of the constituent oxides. In fact, if we draw a few curves (fig. 7, p. 397) for such "alloys" they are quite similar to those previously shown for the metallic alloys (fig. 6, p. 396). The melting points of CaO and Al_2O_3 are according to the estimates of Moissan.[4]

5. Finally, in any measurements of the melting points of quartz and silica, it is necessary to make sure that the specimens experimented with are pure SiO_2, and contain no alkalies in particular, even a trace of which would certainly lower the melting point very considerably. Prof. W. A. Shenstone and Mr. H. G. Lacell[5] found that quartz very commonly contained sodium and lithium.

It may be noted that all previous observers state that quartz does not melt at the temperature of a furnace. Moissan and Gaudin both found that the boiling point of silica was very little above its melting point. Mendeléeff says[6]:—"But silica fuses and volatilises (Moissan) in the heat of the electric furnace, about 3000°. SiO_2 is also partially volatile at the temperature

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[1] M. H. Moissan, "Le Four Électrique," pp. 32, 35, and 38.

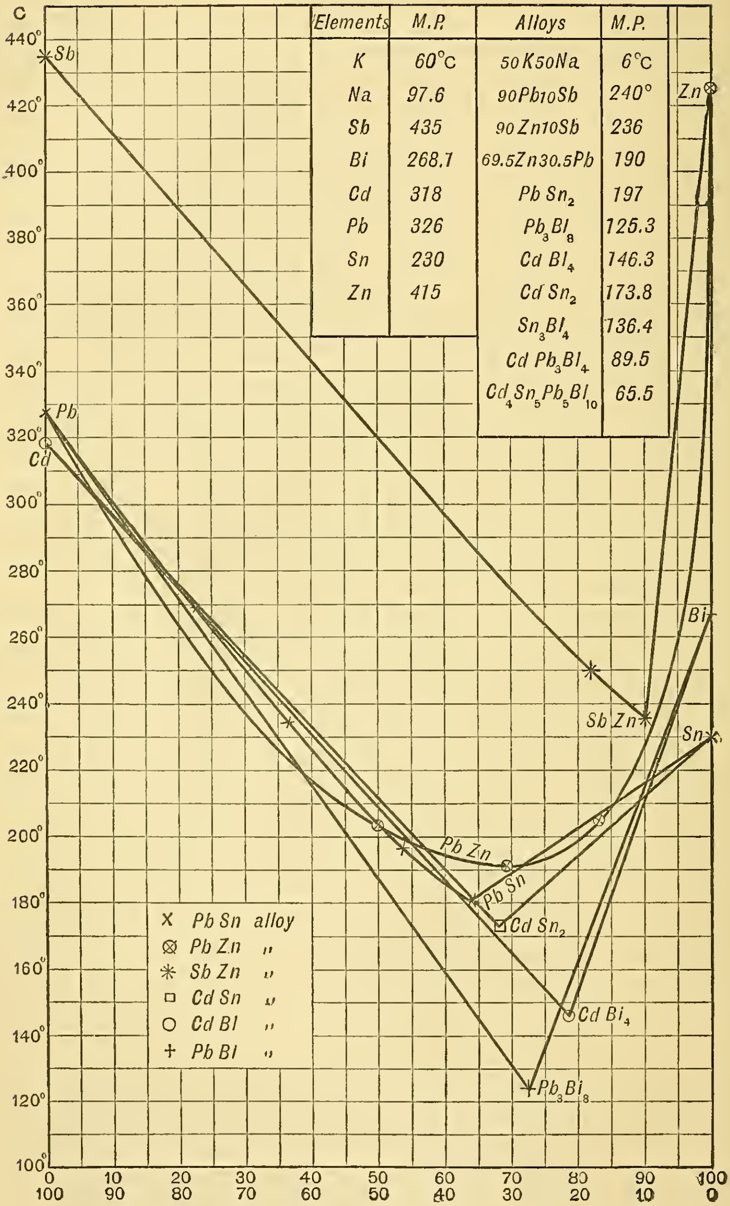
[2] Cf. Mendeléeff, "Principles of Chemistry," chap. XVIII., p. 120, note 25.

[3] Cf. M. L. Gruner, "Traité de Métallurgie," vol. i., pp. 196 *et seq.*, Paris, 1875.

[4] M. H. Moissan, "Action d'une haute température sur les oxydes métalliques." Comptes Rendus, 115 (1892), p. 1034.

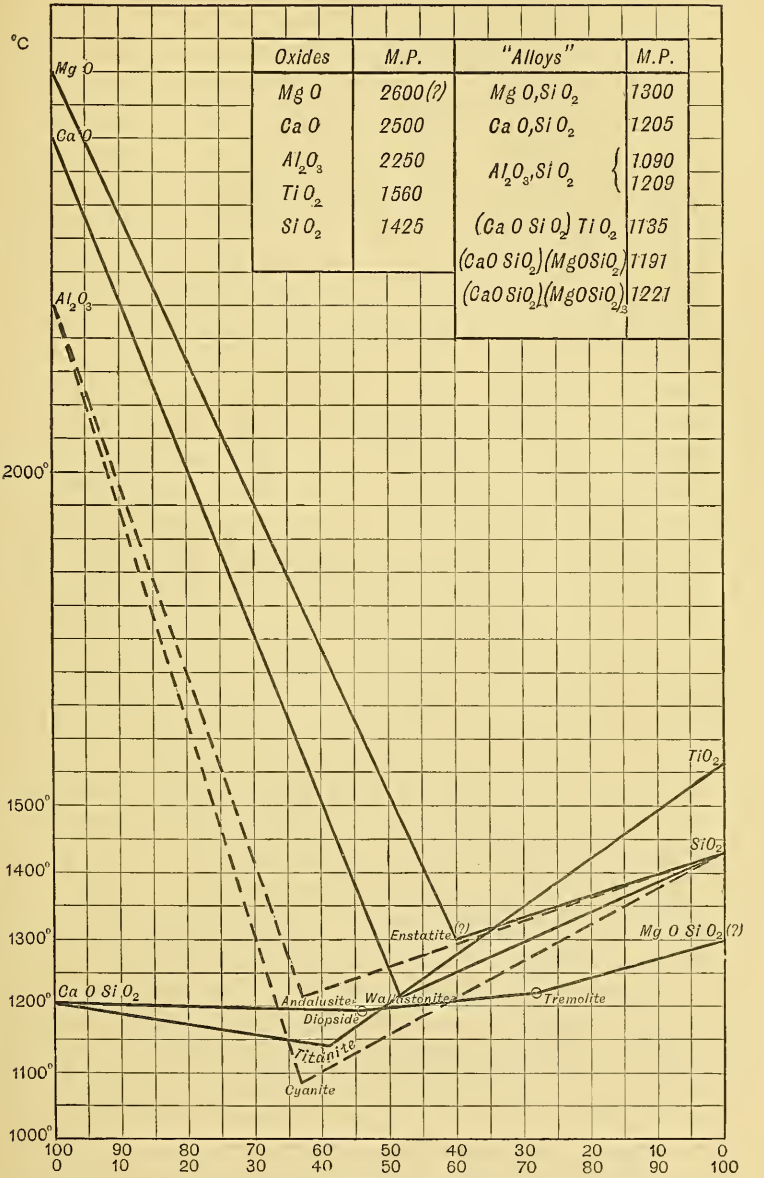
[5] "Working Silica in the Oxy-gas Blowpipe Flame," Nature, 62 (1900), p. 20.

[6] *Loc. cit.*, p. 100, n. 1 *bis*.



Elements	M.P.	Alloys	M.P.
K	60°C	50K50Na	6°C
Na	97.6	90Pb10Sb	240°
Sb	435	90Zn10Sb	236
Bi	268.7	69.5Zn30.5Pb	190
Cd	318	$Pb\,Sn_2$	197
Pb	326	Pb_3Bi_8	125.3
Sn	230	$Cd\,Bi_4$	146.3
Zn	415	$Cd\,Sn_2$	173.8
		Sn_3Bi_4	136.4
		$Cd\,Pb_3Bi_4$	89.5
		$Cd_4Sn_5Pb_5Bi_{10}$	65.5

Fig. 6.—Curves showing the Melting Points of certain Metallic Alloys.



Oxides	M.P.	"Alloys"	M.P.
MgO	2600(?)	MgO,SiO_2	1300
CaO	2500	CaO,SiO_2	1205
Al_2O_3	2250	Al_2O_3,SiO_2	1090 1209
TiO_2	1560	$(CaO\,SiO_2)\,TiO_2$	1135
SiO_2	1425	$(CaO\,SiO_2)(MgO\,SiO_2)$	1191
		$(CaO\,SiO_2)(MgO\,SiO_2)_{2/3}$	1221

FIG. 7.—Curves showing the Melting Points of certain "Alloyed" Oxides which occur as Rock-forming Minerals.

attained in the flame of detonating gas (Cremer, 1892)." Prof. C. V. Boys[1] says that silica retains its form at a temperature at which platinum is as liquid as water.

Admitting that the true melting and crystallizing point of quartz is above that of felspar, it might be urged (as is indeed suggested in Dr. Joly's paper) that the "softening point" of quartz is below that of felspar (to confine our attention to one particular crystallizing pair), and that although the quartz had actually crystallized before the felspar, yet when the latter crystallized it became rapidly more rigid than the former, and so was able to squeeze it out of shape, or was in some way able to perfect its own crystalline form at the expense of that of the quartz. But if this were the true explanation of what happens when quartz and felspar crystallize together, how is it that quartz is sometimes idiomorphic and the felspar moulded on it?

In the first place this fact (?) wants demonstrating by experiments on both quartz and felspar. (By these names I mean the crystalline compounds. The use of the name "quartz" for all forms of silica can only lead to confusion, and is therefore to be deprecated.) Nor is it sufficient to find the lowest temperature at which any particular substance yields to a definite distorting force under ordinary or reduced pressure. The rigidity and certainly the viscosity is pretty sure to vary with pressure as well as with temperature. Barus[2] has put this to the test of experiment in the case of marine glue, and exhibits the results as curves. The isothermals show how markedly viscosity increases with increase of pressure at constant temperature. The isopiestics show how the viscosity decreases with rise of temperature at constant pressure. But it is to the isometrics (lines of constant viscosity) that I wish to draw particular attention. They are seen to rise rapidly at first, and are then convex to the axis of temperature (temperature and pressure increase together). They are all similar for the same substance, only displaced parallel to the axis of temperature. If now we devise an experiment with a definite distorting force and gradually raise the temperature until we observe a particular

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[1] C. V. Boys, "Quartz Fibres" (Lecture to Brit. Assoc., 1890), reported in Nature, XLII., p. 604 (Oct. 16, 1890).

[2] C. Barus, "Isothermals, Isopiestics, and Isometrics relative to Viscosity," Amer. Jour. Sc., III.° 45 (1893), p. 87.

rate of yielding, we obtain a single point on a particular isometric corresponding to the pressure at which the experiment is conducted. But without making at least one other experiment under a different external pressure we can get no idea of the slope of this particular isometric, and therefore we cannot even guess what the viscosity would be under such enormous pressure as those to which minerals would be subjected when crystallizing in the depths of the earth. In fact we must determine the isometrics for both felspar and quartz before we can know which[1] will deform the other if crystals of the two minerals are conceived to be pressed together during the consolidation of a rock magma.

In the second place this idiomorphic "crystallizing force" is—so far as I know—purely hypothetical, or at any rate such a crystallizing force is of incomparably smaller dimensions than the mechanical force necessary to distort a viscous crystal. It is in fact opposed to the principle of Professor James Thomson,[2] "*that stresses tending to change the form of any crystals in the saturated solutions from which they have been crystallized must give them a tendency to dissolve away, and to generate, in substitution for themselves, other crystals free from the applied stresses or any equivalent stresses.*"

Now the slow rate of cooling, and therefore the enormous time at its disposal will make this "tendency" all important in the case of a mineral crystallizing in a molten magma. In other words, a crystal will grow round any obstacle, no matter how trivial, rather than push aside the obstacle in order to develop its perfect crystalline form. This is abundantly demonstrated in the case of minerals which constantly grow round microscopic crystals rather than remove them by overcoming the small surface tension and viscous forces which hold the obstacles in position. Is it possible then to conceive of a growing felspar deforming a quartz crystal? Professor Boys[3] found that the force necessary to draw out "quartz fibres" at the temperature of the oxy-hydrogen blowpipe to be perceptibly greater than the force necessary to do the same for any of the silicates, including felspar. Further, if a long period of high viscosity during fusion is to be regarded as an

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[1] Cf. Boys, Proc. Phys. Soc. 9 (1887–88), p. 13, &c.

[2] James Thomson, "On Crystallization and Liquefaction, as influenced by Stresses tending to change of form in the Crystals," Proc. Roy. Soc., xi. (1861), p. 474.

[3] Proc. Phys. Soc. 9 (1887–88), p. 13, &c.

indication of deformability, we have direct petrological evidence to show that such an hypothesis of soft crystals deforming one another is untenable. Olivine is a mineral melting at 1371° C. (therefore below quartz) and exhibiting (according to Mr. Ralph Cusack)[1] a far longer period of viscosity during fusion than any other mineral. The melting period of olivine as observed on the meldometer was 84° (1323°–1407°), that of quartz only 34° (1406°–1440°). If then the slow melting of quartz be regarded as accounting for its appearing in allotriomorphic shapes then *a fortiori* olivine should always be allotriomorphic. But this is exactly what we never find. Olivine is always idiomorphic with regard to the other silicates in the rocks in which it occurs.[2]

A possible factor in the problem may perhaps be the "melting hysteresis," or want of agreement between the melting and freezing temperature of a substance. This has often been noticed in the case of certain organic substances, but has been fully demonstrated by Dr. C. Barus,[3] and is illustrated by a series of curves. These illustrate the "volume lag" in isothermal fusion, and from these curves the isopiestic volume lag could readily be deduced. *E. g.* under a pressure of about 600 atmospheres naphthalene melts at 100° and solidifies at 90°. Barus also points out that there is a perfectly definite amount of lag. It is conceivable that quartz might crystallize at a lower temperature than its melting-point.

There are then several more purely chemical aspects of the subject which probably all enter to a greater or less extent in the building up of a complete theory. Indeed, a complete theory could only be developed from a consideration of all the connected phenomena included under the Theory of Solution. All molten rock magmas were probably once true solutions. Thus, for instance, Bunsen[4] dwelt on the important influence on the melting-points of both solvent and dissolved substance exerted on each by the presence of the other. It is well known that the order of crystallization of

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[1] *Loc. cit.*, p. 405.

[2] Cf. J. J. H. Teall, "British Petrography," p. 53.

[3] C. Barus, "The Continuity of Solid and Liquid," Am. J. of Sc., III.° v. 42 (1891), p. 125.

[4] R. Bunsen, "Ueber die Bildung des Granites," Zeitschrift d. deut. geol. Ges. Bd. XIII. (1861), p. 61.

Cf. H. C. Sorby, "On some Peculiarities in the Arrangement of the Minerals in Igneous Rocks," Brit. Assoc. Report, 1858 (pt. 2), p. 107.

a salt and its solvent can be inverted by varying the relative proportions of the two substances. Several workers have obtained various eutectic mixtures by using proper proportions. Since Bunsen's time this side of the subject has received particular attention, and seems to be very generally recognised by geologists. It is therefore unnecessary for me to dwell upon it at length. I may, however, remark that it is very difficult to make direct experiments on the behaviour of mineral substances in this respect; and the theory of such behaviour is apparently not yet sufficiently advanced to make it possible to predict what it would be for the silicates from any of their other more easily measureable chemical or physical properties.[1]

I am at present concerned with a more physical aspect of the theory which then leads me to the discussion of some interesting chemical measurements. So long ago as 1850 (the year after Professor James Thomson's[2] famous development of the theory of the influence of pressure on the melting-point of ice) Bunsen[3] undertook a series of experiments on the influence of pressure on the melting-points of spermaceti and paraffin, for the express purpose of illustrating the crystallization of igneous rocks. I have plotted his results, which are very interesting (see fig. 8, p. 402). They show that while at ordinary atmospheric pressure spermaceti consolidates at a higher temperature than paraffin, yet at pressures above ninety-five atmospheres the order of consolidation would be reversed. At ninety-five atmospheres the melting-points of the two bodies are identical, and so they should consolidate simultaneeously and exhibit a "graphic" structure. The great master chemist then modestly draws his conclusion:—"Obgleich das physikalische Gesetz der Abhängigkeit des Schmelzpunktes vom Druck aus diesen wenigen *vorläufigen* Versuchen nicht einmal

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[1] *8th Aug.*, 1901.—Since the above was written, a Paper on the present subject by Prof. W. J. Sollas, F.R.S., has appeared in the Geol. Mag. for July, 1900, in which the author dwells upon the possible importance of included water. The frequent secondary origin of such inclusions, as well as the small and variable quantity of the included water in similar rocks, makes it difficult to draw general conclusions as to its influence on the order of crystallization in actual rocks. Cf. J. Morozewicz, Tschermak's Min Mittheil. xviii. (1898) 1–90, 105–240, and Min. Mag. xii. p. 313–315. See also A. Lagorio, *id.* viii., p. 421 (1887).

[2] James Thomson, Trans. Roy. Soc., Edinb., vol. xvi. (1849), p. 575.

[3] R. Bunsen, "Ueber den Einfluss des Drucks auf die chemische Natur der plutonischen Gesteine," Pogg. Ann., 81 (1850), p. 562.

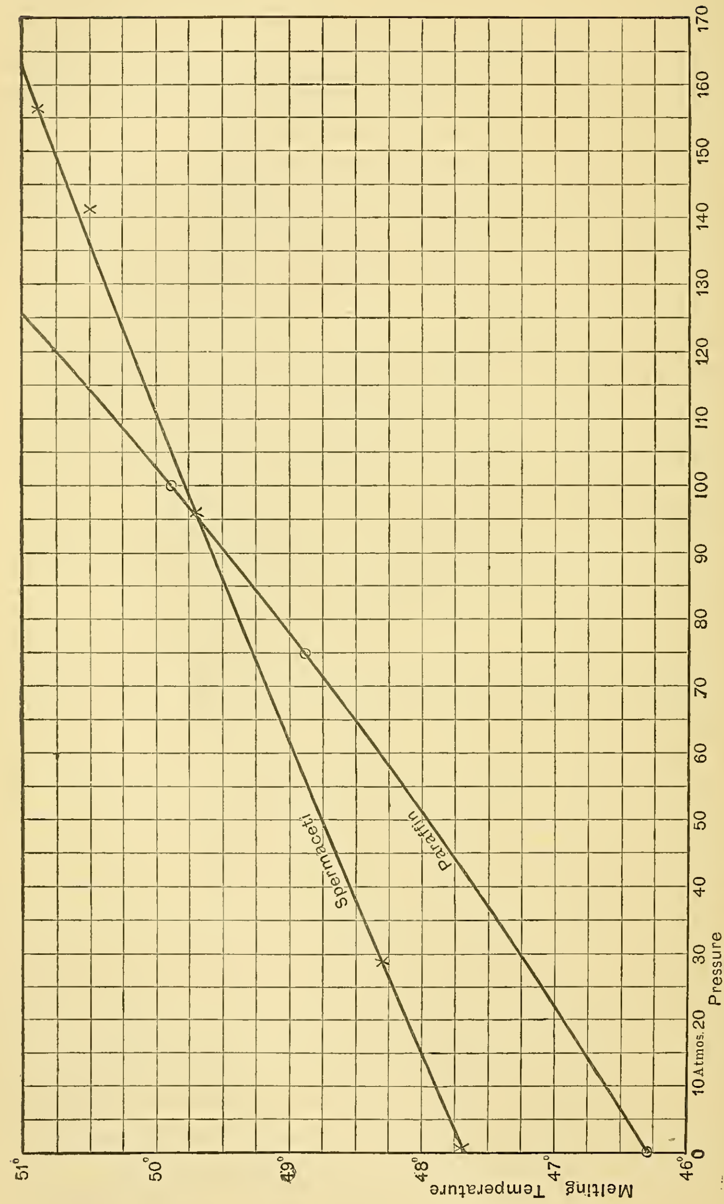

Fig. 8.—Curves showing the Variation with Pressure of Melting Points of Paraffin and Spermaceti.

annähernd ersichtlich ist, so lässt sich doch daraus bereits soviel mit Bestimmtheit abnehmen, dass ein Körper bei Druckdifferenzen von kaum 100 Atmosphären seinen Schmelzpunkt um mehrere Centesimal-grade ändern kann. Hält man nun die schon nicht weniger als 400 bis 500 Atmosphären betragende Pressung, welche ungefähr zur Sprengung der 3 Millimeter dicken Wandung einer 2 Millimeter weiten Glasröhre erfordert wird, mit jener gewaltigen Druckkraft zusammen, welche die Feste ganzer Continente erschüttert oder emporhebt, und sich in meilenlangen Lavaströmen und Aschenstrahlen an dem Vulcanen Bahn bricht, so wird man die Ueberzeugung nicht abweisen können, dass *solche* Kräfte sich nur nach Tausenden von Atmosphären messen lassen. Dann aber müssen auch nothwendig die solchen Druckeinwirkungen ausgesetzten feuerflüssigen Gesteine, je nach dem Wechsel des Drucks, ihre Erstarrungstemperatur um Hunderte von Graden ändern können. Man begreift daher leicht, dass Feldspath, Glimmer, Hornblende, Augit, Olivin, etc., welche unter einem bestimmten Druck bei einer gewissen Temperatur aus dem silicatischen Lösungsmittel erstarren, unter verändertem Druck bei ganz anderen Temperaturen auskrystallisiren werden. Und wenn die Verrückung des Schmelzpunktes, wie es obige Versuche bereits andeuten, bei verschiedenen Körpern für gleiche Druckdifferenzen eine verschiedene ist, so wird sich unter Umständen selbst die Reihenfolge der Ausscheidungen, ja es werden sich diese Ausscheidungen selbst, ihrer chemischen Constitution nach, durch den blossen Druck ändern können.

"Man wird es daher als ausgemacht betrachten dürfen, dass der Druck auf das Festwerden der plutonischen Gebirge und auf die chemische Constitution der darin auftretenden Gemengtheile einen grossen, vielleicht noch grösseren Einfluss ausgeübt hat, als selbst die Verhältnisse der Abkühlung."[1]

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[1] I may mention that Sir Henry Roscoe in his Bunsen Memorial Lecture to the Chemical Society quite misstates the extent of Bunsen's theory. Its essential feature was the explanation of different mineral structure in rocks of the same total chemical composition. (Jour. Chem. Soc., 77–78 (1900), p. 513).

Cf. H. C. Sorby "On the Comparative Structure of Artificial and Natural Igneous Rocks," Brit. Assoc. Rep., 1862 (pt. ii.), p. 96, in which the author shewed (by thin sections) that a "fused basalt" contained the same minerals as the original "which, nevertheless, are developed and arranged in such a very different manner that it is easy to understand why this fact has been overlooked. Indeed the difference in general structure is so considerable that probably other causes besides a slower cooling were

Precisely the same ground has been covered in greater detail by Mr. C. E. Stromeyer,[1] in a paper read before the Manchester Literary and Philosophical Society in January last (referred to by Dr. Joly on March 21st). I need not recapitulate all his arguments which appear on the whole to be sound, though occasionally somewhat loosely stated. The well-known formula connecting the rate of change of melting point and pressure[2] is—

$$\frac{d\theta}{dp} = \frac{\theta(v_2 - v_1)}{L},$$

where $\frac{d\theta}{dp}$ = rate of rise of melting point with pressure;

θ = the melting point on the absolute scale of temperature;

$(v_2 - v_1)$ = the volume change on melting;

L = the latent heat of melting (in mechanical units).

In order to apply this to the particular cases of the rock-forming minerals, we want certain experimental data. Dr. Joly and Mr. Ralph Cusack have supplied us with the melting points of the most important minerals (θ). But the all-important items are the different values of the ratio $\frac{v_2 - v_1}{L}$ for these minerals (not, as Mr. Stromeyer states (l. c. p. 4), simply the volume changes; for, although the latent heats of the minerals may be small (l. c. p. 10), yet their relative magnitudes are quite as important as the volume changes). Now, these two quantities (volume change and latent heat of melting) are extremely difficult to measure directly in the case of bodies melting at such high temperatures as do the mineral silicates.

The most important part of the volume change on melting is

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instrumental in producing the peculiar characters of the natural rocks." Evidently any purely chemical theory is quite incapable of explaining this phenomenon. The influence of pressure at once suggests itself.

Cf. also H. C. Sorby, "On the Direct Correlation of Mechanical and Chemical Forces," Proc. Roy. Soc., xii. (1862–63), pp. 538-550.

[1] C. E. Stromeyer, "The Formation of Minerals in Granite," Mem. Manchester Lit. and Phil. Soc., vol. 44, pt. iii. (1900), No. vii.

[2] M. A. Battelli tested the applicability of this formula to the melting points of a number of organic substances, some of which melted gradually. ("Influence de la Pression sur la Température de Fusion," Journal de Phys., tom. vi. (1887), p. 90). The agreement between the calculated and the found is very approximate.

supplied us by the difference of the densities of the crystallized mineral and of its glass, *i.e.* on the assumption that the coefficient of expansion of the substance is the same in the two states. This assumption is of course not really a safe one to make; but the coefficients of expansion are not, in all probability, very different. They are, moreover, comparately simple, physical measurements to make; and, knowing them, together with the volume change on melting of the mineral glass as supplied us by such experiments as those of Dr. Joly,[1] our knowledge of the volume change of the crystalline mineral on fusion would be complete. Thus, to take a specific example, I have drawn a diagram (Plate XXII.) to show the expansion of quartz on melting. I have got from available experimental data the coefficient of expansion of quartz, taken as 0·00004,[2] (slope of DB) the melting temperature, and the densities of quartz and amorphous silica at 0° C. Now, if I also knew the coefficient of expansion of fused silica (slope of EF) and its behaviour on fusion, I should know all that is necessary. For reasons given above (p. 389), I have assumed that there is little or no sudden volume change on melting amorphous silica. The slope of EF in the diagram (Plate XXII.) is a pure assumption. However, it seems likely that the volume change on melting is not very different from the difference of specific volumes of the two bodies at ordinary temperatures. I have rounded the corners at B and F in accordance with the observations of Mr. Ralph Cusack.[3] I have inserted a line to represent provisionally the behaviour of the form of silica obtained by Moissan[4] by distillation in his electric furnace. The density of this substance is stated to be 2·4, and the little spherules exhibited dimples owing to sudden contraction on solidification. I had hoped to have obtained specimens of these spherules, and to have measured the volume change (DF) on consolidation, assuming that the dimple was caused by the molten spherule forming a solid skin which was adapted to contain its melted volume, but was too large for the contracted solid volume. This contraction, together with

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[1] J. Joly, "On the Volume Change of Rocks and Minerals attending Fusion," Trans. Roy. Dublin Soc., Ser. II., vol. VI. (1897), p. 283.

[2] Kopp, "Ueber die Ausdehnung einiger fester Körper durch die Wärme," Ann. Chem. Pharm., 81 (1852), 1. Pogg. Ann., 86, 156.

[3] *Loc. cit.*, p. 407.

[4] M. H. Moissan, "Le Four Électrique," p. 50.

the coefficient of expansion of the third material, would be interesting data for the completion of my diagram.

The same sort of construction would also afford us the latent heat of fusion. But before entering into details in this subject I would wish to point out a rough method of obtaining an idea of the relative latent heats of the minerals. It is the common experience of practical mineralogists that certain minerals are more "easily fusible" than others; and yet in many cases when put to the test of the meldometer it is not always the more easily fusible which has the lower melting point. Thus, orthoclase which is only with difficulty fusible before the blow-pipe (5 on Von Kobell's scale of fusibilities) melts, according to Joly, at 1175° (Cusack finds 1166° for adularia); whereas labradorite with melting point at 1229° is "easily fusible at 3" on the same scale. Now, this is in itself a very remarkable result. In the example here given, the conductivities of the two minerals cannot be very different, and the cleavage fragments introduced into the blow-pipe flame will be closely similar. What, then, is the proper explanation of these apparent discrepancies?[1] It seems to me that it may be looked for in the latent heats of the minerals. It must be remembered that the temperature of the blowpipe flame is not much higher than the melting points of the minerals concerned, that the loss of heat by radiation is enormous, and that the minerals themselves are all very bad conductors of heat. Under these circumstances the supply of heat to the interior of the mineral grain will be very slow. We have then, evidently, a very sensitive arrangement for detecting the rate of absorption of heat by the substance under examination. I therefore submit that rate of melting or "fusibility" has to do with latent heat as well as melting point. There is, in fact, the same sort of connexion between "rate of fusion" and "melting temperature," as there is between "diffusivity" and "conductivity." We shall, in future, want two terms for what has hitherto been vaguely included under "fusibility," in order to distinguish clearly between "melting-point" and "rate of fusion."

There are, I fear, as yet no exact determinations of the rate of fusion for the silicates. The cooling curves, so commonly

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[1] Cf. J. Joly, "On the Determination of the Melting Points of Minerals," Proc. Roy. Irish Acad., Ser. III., vol. ii. (1891), p. 39.

given for metals, are the graphic representations of their rates of consolidation. Their case is simplified by the high conductivity of the metals. Von Kobell's numbers, of course, only pretend to be purely empirical, and they may or may not give us an idea of the true relative rates of melting. So, in general, they cannot be used at present for calculation. But in particular cases we may, with a high degree of probability, infer which of two minerals has the larger latent heat. Thus, if the above reasoning be correct, there can be no doubt that the latent heat of orthoclase is distinctly greater than that of labradorite. Similarly augite and hornblende are more easily fusible, but have higher melting points than orthoclase, and, therefore, their latent heats are smaller. At the same time the volume-change of augite, as here deduced from its loss of density on fusion, is distinctly greater than that of orthoclase. There can then be no doubt that the value of the ratio $\frac{v_2 - v_1}{L}$ is greater for augite than for orthoclase. That is, the rate of increase of melting-point with increase of pressure $\left(\frac{d\theta}{dp}\right)$ is evidently greater for augite than for orthoclase (fig. 9). If this relative position of these two minerals may be

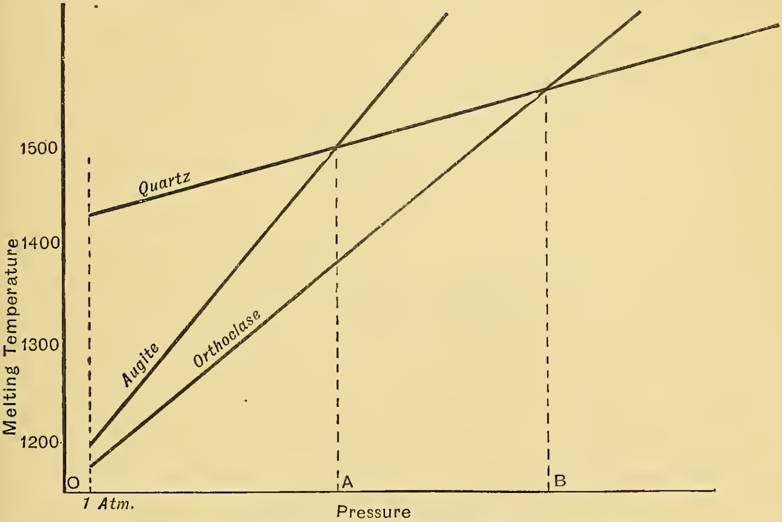

FIG. 9.—Diagram showing the Variation with Pressure of the Melting Points of Quartz, Orthoclase, and Augite.

taken as an indication of the general order with respect to the basicity of the minerals concerned, it follows that Rosenbusch's order of crystallization is at once explained for deep-seated rocks. From an examination of the accompanying table,[1] it will be seen that the same relative positions could be established for the basic felspar oligoclase and the acid orthoclase.

Name.	Density.		Difference of Specific Vols. $v_2 - v_1$.	Melting Point °C.	Fusibility (Von Kobell).	$\frac{M.P.}{F.}$	Scale of Relative Latent Heats.
	Crystal. ρ_1.	Glass. ρ_2.					
Quartz, .	2·663	2·228 (D.)	0·0733	1425	7·00	204	8
Orthoclase, .	2·574	2·328 (R.)	0·0411	1175	5·00	235	7
Albite, .	2·604	2·041 (R.)	0·1059	1175	4·00	294	6
Labradorite, .	2·689	2·525 (D.)	0·0241	1229	3·00	410	2
Oligoclase, .	2·66	2·258 (R.)	0·0669 (Max.)	1220	3·50	349	5
Anorthite, .	2·75	—	—	—	5·00	—	—
Sodalite, .	2·22	—	—	1130	3·75	301	6
Epidote, .	3·409	2·984 (R.)	0·0418	965	3·25	297	6
Hornblende, .	3·216	2·826 (D.)	0·0428	1194	3·00	398	3
Augite, .	3·267	2·804 (D.)	0·0505	1191	3·00	397	3
Wollastonite,	2·85	—	—	1205	5·00	241	7
Spodumen, .	3·133	2·429 (R.)	0·0925	1173	3·50	335	5
Olivine, .	3·381	2·857 (D.)	0·0543	1371	7·00	196	8
Garnet (Almandine),	3·784	3·052 (Th.)	0·0634	1265	3·00	422	1
Cyanite, .	3·62	—	—	1090	7·00	156	9
Vesuvianite,	3·40	2·937 (Ch.)	0·0464	1030	3·00	343	5

In the seventh column I have divided melting-point by Von Kobell's scale-number, but, of course, do not pretend that the numbers obtained indicate even a general relative position,

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[1] Compiled from Roth's Allgemeine u. Chemische Geologie, B. II., p. 52, and Dana's Mineralogy. Capital letters in the third column refer to the original observers:—(D.) = Ch. Ste.-Claire Deville; (R.) = Rammelsberg; (Th.) = Thoulet; (Ch.) = Church.

much less any relative magnitude of the latent heat. Thus if we try to compare oligoclase and augite, we find the available data insufficient for our purpose. For we cannot safely compare their latent heats until we have actual numerical data over and above Von Kobell's scale. Much less would it be safe to compare the values of the ratio $\frac{v_2 - v_1}{L}$ in such cases. But let us confine our attention to the examples of augite and orthoclase as typical, and for which the above comparison is, I believe, reliable. It is apparently the general opinion that the latent heats of the minerals are small.[1] I shall show directly that the latent heat of quartz is very large, certainly much greater than the latent heat of ice (the greatest previously on record). Hence we might be led to expect that the less silica a mineral contains, the smaller was its latent heat.[2] This is certainly not contradictory to my statement of the order of the values of $\frac{d\theta}{dp}$ for the minerals; *i.e.* its value for quartz is least, for orthoclase rather greater, for augite the greatest of the three. The diagram (fig. 9) on p. 407 shows this relation. We have the curve for augite, crossing that for quartz at a pressure corresponding to OA; and the orthoclase line crossing the quartz line at a pressure corresponding to OB. Then in a rock formed under any pressure greater than OB, augite and orthoclase will crystallize before quartz; at any pressure greater than OA, augite will crystallize before quartz; but at pressures less than OA, quartz must crystallize before both augite and orthoclase. We may call OA and OB the "eutectic pressures" for quartz and augite, and quartz and felspar respectively. It is unfortunate that we do not know the melting-point of any of the micas, although their fusibilities are known to be low. However, in the meantime we may class them with augite as typical ferro-magnesian minerals. And so the crystallization of an ordinary granite is explained at once.

Let us conceive of a rock magma kept liquid by reason of its high temperature, in spite of great pressure. Now, if the pressure is maintained while the temperature gradually falls, the rock will

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[1] Cf. C. E. Stromeyer, *loc. cit.*, p. 10.

[2] This agrees with the observation that the amount of thermal metamorphism is in general greater round an acid than round a basic magma.

consolidate according to the plutonic or Rosenbusch's order of crystallization. If, on the other hand, the pressure is relieved (*e.g.* by rising nearer to the surface), and then, owing to expansion or otherwise, the temperature falls, we have the surface, or melting-point order of crystallization, with quartz coming out first. And if the pressure be suddenly or rapidly relieved by the magma rising in the neck of a volcano, while the temperature also falls, we should expect to have the minerals of high melting-point rapidly crystallizing out as large porphyritic crystals. Mr. J. J. H. Teall says[1]: "The first fact that strikes one is that the granular texture is especially characteristic of plutonic (*i. e.* deep-seated); the porphyritic texture of volcanic (*i. e.* surface) masses." Also the numerous inclusions and many other imperfections of such porphyritic crystals may be partly accounted for by rapidity of growth.

Mr. C. E. Stromeyer in his Paper has given several examples, illustrating the way in which this theory explains cases of exceptional order of crystallization. That relating to the so-called "pegmatite" veins should appeal to members of the Royal Dublin Society who are familiar with the veins in the granite at Rochestown and Stillorgan, where idiomorphic prisms of quartz may be seen imbedded in crystals of felspar. I may add the example of the graphic structure, owing to simultaneous crystallization of quartz and felspar, exhibited in certain granites. Now it is certainly often the case that this graphic structure is associated with drusy cavities, apparently due to diminished pressure, near the tops of granite domes (*e. g.* in the granite of the Mournes and at St. David's). We have, in fact, got down to the "eutectic pressure" of quartz and felspar (*OB* on the above diagram). At greater depths in the same granite boss, we have an increased pressure (greater than *OB*), and, therefore, the felspar has crystallized before the quartz, as is usual with deep-seated plutonic rocks. If a molten magma comes so near the surface as to be only covered by a thin layer of rock, we may have so little pressure on its upper portions that the quartz will crystallize first and give rise to a quartz porphyry. If the fluid mass was of sufficient dimensions, we should be able to trace the different types of crystallization down through the graphic into the true granitic type. Professor Grenville Cole tells me that the Slieve Gallion mass

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[1] J. J. H. Teall, "British Petrography," p. 55. London, 1886–1888.

affords evidence of all three types of crystallization. Nor is it wonderful that the above, as well as Mr. Stromeyer's examples, are only the exceptions, for certainly the majority of igneous rocks must have crystallized at great depths, where the pressure would be enormous (greater than OB).

The exception proves the rule. It will be evident that Dr. Joly's, as well as any of the other theories alone, breaks down in face of these exceptions. Thus, if, according to Dr. Joly, the softening point of quartz is actually below that of felspar, and hence the felspar crystals are able to develop their proper form at the expense of the quartz crystals, then why was this not always the case? In the same way (as Bunsen saw long ago) the theories depending on the different proportions of the chemical elements could not possibly explain differences of crystallization in rocks of the same chemical composition.

As an appendix, I shall now take the example of quartz, and examine how its latent heat, and similarly the latent heats of the other minerals, may be deduced from simple chemical and physical measurements (Plate XXIII).

In the case of quartz, then,[1] we know the specific heat, up to 1185° C. (slope of OB), and we know that the specific heat of amorphous silica is somewhat greater. Dr. Joly[2] measured the specific heat of opal. The density of this substance varies from 2·1 to 2·22, and it contains a variable quantity (13 to 2 per cent.) of water, which would be a factor tending to increase its specific heat. The values obtained varied from 0·2379 to 0·2033. I have adopted the value 0·20 as a fairly safe minimum for anhydrous SiO_2. This affords us the slope of EF. In order to err on the side of the minimum I have further assumed the specific heat constant up to the melting point. For most solids and liquids the specific heat increases with rise of temperature.[3] Further, it is highly probable that the specific heat of an amorphous substance is greater than that of the crystalline modification.[4] If we assume the *same* mean specific heat for silica as has quartz, we get a curve like EF' to represent the heat absorption of amorphous silica. But we do not yet know how far apart to place these two lines, or, in other words, where to

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[1] Pionchon, *loc. cit.*

[2] J. Joly, "On the Specific Heats of Minerals," Proc. Roy. Soc., xli. (1886) p. 250.

[3] Preston, "Theory of Heat," p. 212.

[4] J. Joly, *loc. cit.*, p. 254, &c.

take the point *E*. The height of *E* will evidently represent the difference of the heats evolved by the solution of amorphous silica and quartz in hydrofluoric acid or other suitable reagent. I have, therefore, undertaken some experimental measurements on the subject. The difficulty of the determination will be at once apparent; for, especially in the case of quartz, the reaction is so slow at ordinary temperatures that it is practically impossible to measure any rise of temperature that may occur. There is also the additional inconvenience that one's thermometer must be covered with wax to prevent its being attacked by the hydrofluoric acid. Mr. J. B. Mackintosh[1] found that only 1·56 per cent. of powdered quartz was acted upon by a 9 per cent. solution of hydrofluoric acid in an hour, while in the same time 77·28 per cent. of similarly powdered opal was dissolved by the same acid. This in itself looked promising for a final result, if only the difficulties of slowness could be overcome. I determined to make use of Lavoisier's form of ice calorimeter. A leaden crucible was obtained (platinum was too expensive) to fit the inner chamber of the calorimeter. This being half filled with the aqueous hydrofluoric acid, and the calorimeter carefully packed with ice and allowed to stand until the temperature had fallen inside, the powdered silicate was then introduced into the crucible and the calorimeter rapidly closed. A weighed flask was then placed in position, and the whole allowed to stand for from two to five hours, according to the velocity of the reaction. This ice calorimeter is at best a very rough apparatus, and it seems impossible to prevent some external heat entering the inner chamber, which has, therefore, to be estimated and allowed for in the final result. I have unavoidably been engaged on other work, and my experiments in this direction are really only in their preliminary stage. I hope to be able to give a full account of my work when it is completed. I may, however, say that I have got distinct indications of the large latent heat (or pseudo-latent heat at 0°, as I may call it,) in the case of quartz. This "latent heat" of adularia is also distinctly measurable, but I cannot, up to the present, get any appreciable difference between the heat generated by fused and unfused augite. I admit that my method is a rough one, perhaps too rough to give very trustworthy numerical results; but I hope it may be capable of improvement.

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[1] J. B. Mackintosh, "The Action of Hydrofluoric Acid on Silica and Silicates," School of Mines Quarterly, vol. vii., p. 384, and Chem. News 54 (1886), 102.

It will, I am sure, be more satisfactory to show how I can obtain a safe lower limit for the latent heat of quartz (Plate XXIII.) from the results of other more experienced workers. Frémy in his "Encyclopédie Chimique," states that quartz is dissolved in hydrofluoric acid with the evolution of no heat. Amorphous silica, on the other hand, when added to fuming aqueous hydrofluoric acid, evolves so much heat that the liquid boils. I have therefore assumed that a weighed quantity of silica is added to the least possible relative proportion of the strongest possible hydrofluoric acid at 20°, and that the heat evolved is only just able to warm up the liquid to 100° C.

The reactions which take place are:—

$$3\{SiO_2 + \overbrace{4HF + 7{\cdot}9H_2O}^{36\%\ HF}\} = 3\{SiF_4 + 2H_2O + 7{\cdot}9H_2O\} \ . \ . \ . + Q \text{ cal.}$$

and $$3SiF_4 + 2H_2O = 2(2HF,\ SiF_4) + SiO_2 \ . \ . \ . + 48 \text{ ,,}$$

(Mean of Hammerl & Guntz.)

Combining these two we obtain for the final result of the reaction:—

$$3\{SiO_2 + 4HF + 7{\cdot}9H_2O\} = 2(2HF,\ SiF_4) + SiO_2 + 27{\cdot}7H_2O + (Q + 48) \text{ cal.}$$

Then, according to Frémy's statement, this quantity of heat $(Q + 48)$ is more than sufficient to raise the products of the reaction to the boiling-point, let us assume from 20° to 100° C. We do not know the specific heat of these products, but they may be fairly safely deduced from Dulong and Petit's Law, according to the following table, the known data being supplied from Landolt und Börnstein's "Physikalisch-Chemische Tabellen" (p. 339):—

Substance.	Mol. Weight.	Specific Heat.	*M. W.* × *S.H.* (= const.)
HI, . .	128·0	0·055	7·04
HBr, . .	81·0	0·082	6·64
HCl, . .	36·4	0·194	7·06
HF, . .	20·0	0·346 (?)	(6·92)
$SiCl_4$, . .	169·6	0·132	22·42
SiF_4, . .	104·0	0·216 (?)	(22·42)

Then we have :—

					Cal.
Heat necessary to raise	80·0 grms. of	HF	through 1° C. =	80·0 × ·346 =	27·7
,, ,, ,,	208·0 ,,	SiF_4	,, ,, =	208·0 × ·216 =	44·9
,, ,, ,,	60·0 ,,	SiO_2	,, ,, =	60·0 × ·188 =	11·3
,, ,, ,,	498·6 ,,	H_2O	,, ,, =	498·6 × 1 =	498·6
,, ,, ,,	846·6 ,,	products	=		582·5

Heat necessary to raise 846·6 grms. of products from 20–100° = 582·5 × 80 = 46600·0

i.e.	heat generated by solution of	180 grms. of SiO_2 (Amorphous) in 36 % HF	>	46600·0
	,, ,, ,,	1 ,, ,, ,, ,, ,,	>	258·9
and	,, absorbed in warming	1 ,, ,, ,, from 20°–1425°	>	281·0
	,, ,, ,,	1 ,, ,, ,, along OEF	>	539·9
	,, ,, by solution of	1 ,, ,, (Quartz) in HF (Fremy)	=	0·0
	,, ,, in warming	1 ,, ,, ,, from 20°–1425° (Pionchon)	=	404·6
∴	,, ,, in fusing	1 ,, ,, ,, at 1425° (Latent Heat)	>	135·3
	,, ,, in warming	1 ,, ,, ,, along OBF	>	539·9

Thus we arrive at the remarkable number 135·3 calories as a safe minimum value for the latent heat of quartz. How much greater it may be we cannot at present say. As I have said, the specific heat of amorphous silica is probably greater than that of quartz. If we assume that it has the same mean value as quartz from 0° to 1425° we obtain the much greater value 258·9 as the minimum latent heat for quartz.

The above serves as an example of how we may arrive at the latent heat of any mineral, with a high degree of probability, by means of two determinations of specific heat, and two determinations of the heat of solution. The latter are at present difficult in the case of the silicates on account of their slowness. But the difficulty should not be insurmountable.

In conclusion, I have to express my indebtedness to Professor C. V. Boys, F.R.S., and to Professor W. A. Shenstone, F.R.S., for much valuable information about fused silica. To several of the Professors of the Royal College of Science for Ireland I am very deeply indebted.

XXX.

ON THE THEORY OF THE STRATIFIED DISCHARGE IN GEISSLER TUBES.

By H. V. GILL, S.J., Clongowes Wood College, Co. Kildare.

[COMMUNICATED BY PROFESSOR W. F. BARRETT, F.R.S.]

[Read February 7; Received for Publication February 22; Published June 5, 1901.]

In a somewhat recent number of the "American Journal of Science"[1] I published an article dealing with the stratified discharge, in which I suggested a possible explanation of this curious phenomenon. As the question is an interesting one, I hope I may be allowed to state briefly the result of a further consideration of the matter.

In the Paper referred to I gave some reasons for supposing that the strata were due to certain mechanical disturbances caused in the body of the gas by the explosion of the spark. A number of experiments were described which went to establish a relation between the stratified discharge and the well-known experiment of Kundt, in which the position of nodes is shown by heaps of a light powder which are formed at certain places in the tube, when the column of air inside it is made to vibrate by some source of sound waves. When the length of the tube is an exact multiple of the half wave-length[2] of the note the powder collects at the nodes. In addition to the true nodal lines there are also other short transverse lines which Lord Rayleigh[3] thus describes:—"Perhaps the most striking of all the effects of alternating aerial currents is the rib-like structure assumed by cork filings in Kundt's experiment. Close observation, while the vibrations are in progress, shows that the filings are disposed in thin laminæ transverse to the tube and extending upwards to a certain distance from the bottom." Tyndall, and in fact all who have studied the experiment, have remarked the fact that these lines do not appear in Kundt's experiment when the tube is an exact multiple of the

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[1] Vol. v., 4th Ser., June, 1898, pp. 399–417.

[2] Lord Rayleigh, "Sound," vol. ii., p. 58.

[3] *Ibid.*, p. 45.

half-wave-length of the note. An example of the same phenomenon is found in the case of a glass rod caused to vibrate longitudinally by being rubbed with a damp cloth. The residue of water on the rod is seen to divide up into little rings very near to each other, and such rods have frequently been found to divide up into little glass discs, showing that this formation was due to the vibrations of the rod. In general, bodies in a state of longitudinal vibration seem to show a like state of division and subdivision.

In the paper already alluded to I suggested the theory that the striæ might be the true nodes formed by the explosive effect of the spark, and illuminated by the light of the same spark :—"Having proved that there are gas waves in the Geissler tube, we can deduce the existence of the stratified discharge. Since the gas is strongly electrified the discharge takes place between the molecules (or, as some hold, between the atoms) : these inter-molecular discharges produce the illumination in the body of the gas. Add now the effect of waves in the gas : the gas at a condensation will be in a different condition from that at a rarefaction. When the molecules are crowded together at a condensation the number of inter-molecular discharges will be very much greater than at a rarefaction. There will hence be a greater illumination at a node ; this is a stratum, but as the state of condensation at a node is intermittent the illunination will be so too."[1]

The first part of that paper dealt with the mechanical effects produced by the explosion of the spark. The chief among these is the strongly-marked sound wave which proceeds from the seat of the disturbance. I then described some experiments showing the similarity between the "Kundt-tube" effect produced by sparks and the stratified discharge.

The object of this note is to state the results of some further experiments, and to show the connexion between the results and some of the results obtained in Kundt's experiment. We have seen that in addition to the well-marked nodes which correspond to the wave length of the note, there are also a series of dust heaps which are independent of the note period. Now a further consideration of the conditions of the stratified discharge make it

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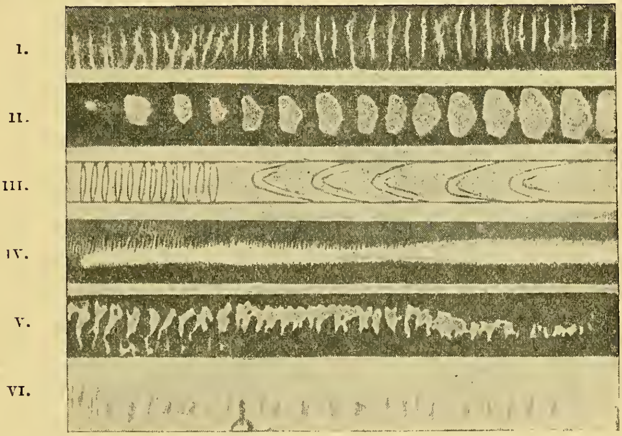
[1] *Loc. cit.* p. 415.

evident that the strata can also be attributed to the presence of the causes which produce this "rib-like" structure described by Lord Rayleigh. That is to say, that while in certain cases the strata may be explained as being due to the Kundt-tube effect, in others it seems necessary to attribute them to this secondary Kundt effect. So that the present note is not to be taken as a change in the explanation already suggested, but as a more developed form of the same.

In the present Paper I propose to describe some ways in which this rib-like appearance is produced. Some of these I have already noticed elsewhere, and some are new.[1]



I. Effect produced on powder when a reed pipe was sounded at its open end.
II. Stiff paper stretched tightly over the end of the tube and tapped.
III. Sketch of the effect produced on smoke in a tube when a reed pipe was sounded at its extremity.
IV. Result produced by passing an electric spark near the extremity of a tube in which some powder had been sprinkled.
V. Effect due to a small spark inside a tube in which the pressure of the air was about 10 mm.
VI. This drawing represents the formation of the rib-like powder heaps in a Geissler tube in *which the discharge which produced them was stratified.*

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[1] The records of the effects thus produced, shown in the figure, were obtained as follows:—A strip of photographic paper was placed inside the tube, and some lycopodium was sprinkled over its surface. When the effect of the spark was obtained, the whole was exposed to the light, and the trace of the powder was thus registered. Nos. III. and VI. are sketches. The various strips of photographic paper were then all mounted together, and a photograph was taken of the whole, thus giving a record of the results, which is practically full-size.

A spark about 5 mm. long, from a coil connected to Leyden jars, was passed in front of a tube open at both ends in which a light powder had been placed. The first spark caused the powder to arrange itself in little ridges, and at each succeeding spark the powder at these places was seen to jump up and settle down in the same places. When the tube was of small diameter the powder ascended quite to the top of the tube at each spark. The tube was thus effected throughout its entire length (about 4 feet), and I could reflect into a second tube the air disturbance, causing a like effect in the other tube. The same effect could be produced in the open air, in which case the powder sprinkled on a card was observed to form rings round the place where the spark passed (IV.).[1]

The same result was obtained by sharply tapping a membrane such as a piece of paper or indiarubber which had been tightly stretched over one end of a tube. In this case the heaps were separated by longer intervals (II.).

In the above methods the shocks necessarily followed each other with comparative slowness, so that the effect was of short duration. By causing the air to vibrate by means of a reed-pipe a continuous effect was produced. In this case the far end of the tube had to be closed. With a small free reed-pipe, giving about 1000 vibrations per second, beautiful laminæ were produced. These were often seen to move *en masse*, just as the striæ are often observed to do; this was owing to the fact that the intensity of the note was not quite constant, and also because the tube was not quite horizontal. On remedying these defects the laminæ remained quite steady. Of course when the note ceased the powder fell down to the bottom of the tube. These laminæ rose up a considerable height in the tube, and when its diameter was small they often reached quite to the top, so that when the sound was kept constant they appeared like so many little paper discs attached to the interior of the tube. The distance between the successive laminæ was not quite constant, but was fairly so. It is evident that these laminæ did not correspond to the nodes from the fact that the distance between them was nothing like what the formula ($v = nl$) would have demanded. Also the distance between them depended on the intensity of the note (I.).

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[1] These numbers refer to the figure on p. 417.

These results seemed to prove that the cause of this curious formation, whatever it might be, was something more than the effect produced by air currents simply *passing over the powder*. In order to ascertain if this was really the case I repeated the experiment already described, having replaced the powder by smoke. The tube I made use of was 30 inches long and ¼ inch in diameter. When the reed-pipe was made to sound at one end, the other end being closed, the smoke was seen to acquire the same formation as the powder. The ridges or strata of smoke were ¼ or ½ inch apart, and sometimes nearer. They were not all the same distance apart, but it was to be remarked that while one series consisting of, perhaps, a dozen, were separated by more or less equal distances, another series were, though at equal distances, not separated by intervals of the same length as in the first series. It required a strong steady note to produce these smoke strata. The instant the note ceased there was a rapid movement of less than an inch in the direction from which the sound was proceeding, just as if a pressure had been removed. This experiment, which I have not seen noticed before, seems to show that there are "rib-like" formations produced in the body of the gas. The resemblance to the stratified discharge is striking (III.).

Finally, I endeavoured to procure the powder strata in a Geissler tube, by means of a spark discharge, which was itself stratified. In order to obtain this result, it was necessary to employ a strong discharge. On former occasions I was unable to obtain this effect. However, on connecting the discharging pillars of a coil, giving in air, a six-inch spark with the insides of Leyden jars, the outsides of the jars being also in connexion, I obtained a discharge in a Geissler tube which was stratified. There was some lycopodium powder in this tube, which, by its movements, showed that the disturbance caused by the spark was considerable. The powder was arranged evenly along the tube, and, after a few sparks, it was found to be divided up into the usual "rib-like" strata. These powder-heaps were not the same distance apart as were the luminous strata. The tube was so made that one of the electrodes was placed about 3 inches from the extremity of the tube, with the object of seeing the effect of the discharge on the powder not in the direct line of discharge. The powder in this space was influenced by the discharge in the same manner as that along the tube. This result proves, at least, that along with the luminous discharge, there exist air disturbances, such as, I suppose, to be the cause of the strata (VI.).

Taking all these facts in connexion with those already stated in my former paper, I venture to put forth the following line of argument:—Electric sparks have been shown to produce certain mechanical effects which, in appearance, present a remarkable similarity to the stratified discharge. These effects are shown to be due to the air disturbances caused by the electric sparks, which are of the same nature as the "alternating" currents mentioned by Lord Rayleigh. These latter effects have also been shown to be due to modifications in the body of the gas itself. We have further seen that they are present in the case of the stratified discharge itself. These modifications consist of node-like collections of gaseous matter, at regular intervals, throughout the length of the tube. These collections of gas particles, illuminated by the discharge which is actually passing between them, would in the present theory, be a series of strata. As far as the general theory goes, the strata might be either true nodes or the "rib-like" lines. The latter would appear to be the more easily produced.

This theory would explain many difficulties which other more elaborate ones fail to explain; such, for example, as the general movement of the strata, often mentioned by those who have written on this subject.

There is one point which might present a difficulty. If the strata are, as I suggest, a mechanical production, it is, at first sight, difficult to understand how they could be illuminated by the spark which causes them. I think this objection can be met by considering that the gas, at this instant, is in a state of electrification, and that this, of itself, would be a reason why the disturbance would be propagated with great velocity. Again, the origin of the disturbance is not confined to any one point in the tube, but seems to take place throughout its whole length, in which case the formation of the "gas-strata" would be practically simultaneous with the discharge. Again, the tubes remain illuminated an appreciable time after the discharge has passed.

I think I have given ample evidence to show the existence of the gas disturbances demanded in this theory. It does not, therefore, appear unreasonable to suppose that the real cause of the strata may be of this nature.

With regard to the actual cause of the rib-like formation in Kundt's experiment, there appears a good deal to be proved. A discussion of the question will be found in Lord Rayleigh's "Sound." It is interesting to note that the method of Kundt has been applied to the determination of the wave-length of notes with a period as high as 170,000 vibrations per second (Edelmann, Ann. d. Physik, Bd. II., Heft 3, Juli, 1900, p. 469).

XXXI.

PROSPECTING FOR GOLD IN CO. WICKLOW, AND AN EXAMINATION OF IRISH ROCKS FOR GOLD AND SILVER.

By E. ST. JOHN LYBURN, A.R.C.Sc.I., F.G.S., Mining Engineer, Pretoria.

(Plates XXIV. and XXV.)

[communicated by professor w. n. hartley, f.r.s.]

[Read December 19, 1900; Received for Publication February 6, 1901; Published May 8, 1901.]

The existence of gold in Ireland has been known for many years, and papers have been read before this Society dealing with the history and occurrence of the metal; however, the following passages from Lewis's "Topographical Dictionary of Ireland" and Calvert's "Gold Rocks of Great Britain" appear to have escaped attention.

Lewis writes thus (1837)—"The mountain of Croghan Kinshelagh, towards the close of the last century, became an object of intense interest from its supposed production of native gold. A peasant fishing in one of the streams which descended from it discovered, at different times, small particles of gold, which for about twelve years he continued to sell privately to a goldsmith, till, in September, 1796, the discovery became known, and thousands of persons engaged in the search for this precious metal. Several masses of extraordinary size were found, one of which weighed nine, another eighteen, and a third twenty-two ounces; and so great was the number of the peasantry allured to the spot by the hope of enriching themselves that in the short space of six or seven weeks, during which the washing of the sand was continued, not less than 2666 ounces of pure gold were obtained, which were sold for £10,000.

"After the people had continued their searches for a little more than six weeks, Government took possession of the mine, and stationed a party of the Kildare Militia to prevent further encroachment; an Act of Parliament was passed for working it, and

Messrs. Weaver, Mills, & King were appointed directors of the operations. Stream works were established on several rivulets which descended from the mountains, and from this time till May, 1798, when the works were destroyed in the insurrection of that disturbed period, the total quantity of gold found was 944 oz. 4 dwts. and 15 grains, which was sold for £3675 8s. In 1801, the mining operations were resumed, and, on the representation of the directors, Government was induced to extend the search upon a more systematic principle; the stream works were continued to the heads of the several streams, and the solid mass of the mountain was more minutely examined, by cutting trenches in every direction down to the firm rock. The veins already known, and such as were afterwards discovered by the process of trenching, were more extensively explored, and their depth minutely ascertained by means of a gallery or level, driven into the mountain at right angles to the general range of their direction. The mineral substances thus obtained were subjected to a rigid chemical analysis, but in no instance, was a single particle of gold discovered. The result of these operations convinced Government that no gold existed as an inherent ingredient in any of the veins which traversed the mountain, and the works were consequently abandoned."

Again, Calvert writes—"The extent of these diggings have never been ascertained, nor is the amount of the produce well known. About £10,000 was obtained previous to the rebellion, and probably £100,000 since. The produce seems to be about £2000 yearly." I do not place much confidence in this statement, but, undoubtedly, at the present time, panning for gold is secretly carried on in Wicklow, and is apparently lucrative to those interested.

The object of this communication is to afford information, gathered from six months' prospecting in Wicklow, during which time about seventy samples of quartz, &c., were taken and subjected to fire assay in duplicate. In addition to these samples, thirty were supplied me by Her Majesty's Geological Survey, which were supposed to be more or less auriferous. In April, 1899, a report was published in the *Independent* newspaper of gold being found near Killaloe. I proceeded to that town with the object of reporting on the supposed discovery. Seven samples of grit were taken, assayed, and found to be barren in gold; the eighth sample, galena, contained 12 grains of gold per ton, and

7 oz. 12 dwts. of silver. (See Table of Assay Results and Assay Plan, Plate xxv., Plan C.) This sample was found lying on the surface, and was probably washed down from a lode. I spent some days prospecting for this lode, but was unable to locate it.

With regard to Wicklow, a fair chance of testing the gold mines valley and Croghan Kinshelagh was not afforded me, owing to an objection which the owner of the estate had to prospecting, orders being given to those in charge to have me turned off and prosecuted if found on the estate. However, before being informed of this, I had obtained some samples, the highest assay being four dwts. per ton (No. 65, Table of Assay Results and Assay Plan, Plate xxiv.). This sample was taken from a quartz vein eight inches wide. The length of the outcrop was not obtainable; it is situated near the summit of Croghan Kinshelagh, and in the immediate vicinity of the old Government workings. This I believe to be the highest assay as yet obtained from vein quartz in Ireland. The assay was performed in triplicate, the fluxes at the same time being assayed and found to contain no gold.

It was the intention of Mr. John Howard Parnell, M.P., and myself to erect an experimental washing plant in the vicinity of this lode, but permission was refused by the owner of the estate. I now beg to refer to the paper contributed by Mr. George H. Kinahan "On the possibility of gold being found in quantity in Co. Wicklow."[1] He states:—

"From the explorations in different portions of the world it has been learned that in connexion with a Placer mine, gold may be found —first, in the mother rock (reefs or veins); second, in the higher shallow alluvium of the valley (shallow placers); third, in the lower deep alluvium of the valley (deep placers); fourth, in the alluvium of the beds of the high, now dry, supplementary streams of the ancient or primary valley (dry gulch placers); and fifth, in the shelves, or high level flats, on the sides of valleys (shelf, reef, or bar placers), the latter being the relics or records left of the floor of the ancient primary valley—they proving that prior to the present time the gold was, in the first instance, deposited in a comparatively wide shallow valley, while the alluvium of the present stream is the rewashed drift of the ancient valley mixed

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[1] Sci. Proc. Roy. Dublin Soc., vol. iv., 1883–1885, p. 39.

with newer detritus. Now, in modern times, in none of the valleys of Co. Wicklow has gold been found, or even looked for, except in the first, second, and fourth cases." Mr. Kinahan then goes on to state the localities where gold has been found in the gold mines valley, and concludes thus—"That to me it appears rash to give an opinion on the non-existence of gold, while the miles of alluvial ground now enumerated still remain unexplored, or while no attempt has been made to explore the shelves of the valley."

Again, Mr. Gerrard A. Kinahan, in his paper on "The Mode of Occurrence and Winning of Gold in Ireland,"[1] concludes:—

"We may consider what probabilities there are as to any quantity of gold remaining undisturbed in the county. In the recognised auriferous valleys the peasants worked in the shallow deposits, and all subsequent explorers appear to have been unwilling to break new or deeper ground, while Weaver was directed only to continue the workings till the covering became deep enough to prevent the peasants working it profitably. It appears to me that there are yet places in the county where trials might well be undertaken with a fair chance of success, such as—

"(1). The shallow deposits or gravels (shallow placers of the Californian diggers) on the tributaries of the Ovoca River:—It appears remarkable that Weaver did not seek after some of these in connexion with his mine (Cronebane), although portions of the lode were known to be auriferous. His trials round the summit of Croghan Kinshelagh, and his choice of the streams of Croghan Moira,[2] seem to suggest that he had some peculiar idea as to the occurrence of the gold.

"(2). The 'bench diggings,' *i.e.*, placers on the narrow benches on the slopes of the valleys above the present level of the rivers:—These have not been looked for in any of the valleys of this district, nor are there many places where they could exist.

"(3). The deep gravels in the Ovoca River and its tributaries the Daragh Water and Gold Mine River:—These deep gravels have never been explored, although Frazer, in his Statistical Survey (1801), recommended the estuarine flat above Arklow as a proper place for a trial. Higher up the rivers there are, however, places more favourably situated for such explorations.

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[1] Sci. Proc. Roy. Dublin Soc., vol. iii., 1880–82, p. 263.

[2] See Assay Plan.

"(4). Quartz reefs in the Croghan Kinshelagh district and other favourable localities:—It has already been pointed out that no auriferous vein or lode has been found, the explorations only having narrowed the limits of its possible occurrence. If one lode or vein were proved auriferous, it would show to what system the auriferous lodes belong, and remove the difficulty of concluding whether they be auriferous continually or only locally."

I entirely concur with these conclusions, and as a part proof I must refer to Assay No. 65; Croghan Kinshelagh; four dwts. per ton.

Mr. George H. Kinahan, referring to the valley from Mucklagh Brook to the Darragh Water (over six miles in length), says this valley has not been explored. Bearing this in mind, I spent some four days in prospecting and panning the river; eighty pannings were made, of which thirty-two were found to be blanks, the remainder containing very fine gold, proving his theory to be correct.

In conclusion, Wicklow may be considered from a miner's point of view "unscratched" and worthy of further attention. I may perhaps be permitted to say that where the same prospects present themselves in South Africa we would leave "no stone unturned" to bring the matter to a conclusion one way or the other. The portion worthy, in my opinion, of attention is the Croghan Kinshelagh Mountain, more especially at the junction of the diorite rocks, and the Silurian formation. It is well known throughout gold mining that the presence of diorite is indicative of gold, and the gold matrix is always richer in that metal in the immediate vicinity of diorite. From my own experience on the Witwatersrandt, the banket[1] becomes highly impregnated with gold at the junction of the banket and a diorite fault or dyke. In the Barberton District, Transvaal, a highly decomposed diorite, existing more or less as a sheet, contains gold in payable quantity. I quote this as an example in order to prove that the dioritic rocks should not be overlooked. Undoubtedly, it can be argued that owing to the samples all more or less containing a certain amount of gold, natural concentration has taken place. This, I should consider worthy of support, provided the district had been properly

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[1] Conglomerate.

prospected and proven to be valueless. As this has not been done, it still remains open to question if Wicklow contains payable gold or not. It is a matter of regret to me that I was unable to give Croghan Kinshelagh the thorough search which it deserves. The accompanying Table of Assay Results describe the nature of the matrix, locality, formation, &c., representing 110 assays or analyses in duplicate. In 1898, the Department of Science and Art, London, upon the recommendation of the Council of the Royal College of Science, awarded me a Research Scholarship. The foregoing paper is the outcome of the work then undertaken. Samples of the quartz obtained have been presented by me to the Science and Art Museum, Dublin.

Note.—The Assay Surveys have been plotted on the one-inch geological maps of the Geological Survey of Ireland.

[Table of Assay Results.

TABLE OF ASSAY RESULTS.

Date.	No. Sample.	Nature of Matrix.	Formation.	County.	Locality.	Gold Assay Value.	Silver Assay Value.	Remarks.
1889						oz. dwt. grs.	oz. dwt. grs.	
March	1	Mispickel, ...	..	Cork,	Bantry, ...	0 2 0	86 0 0	
		.. .. ..	..	..	.. .. ..	--	87 16 0	Duplicate.
	2	Duplicate, ..	..	..	.. .. ..	0 2 0	86 16 0	Triplicate.
	2	Sheared Grit, ..	..	Mayo,	6″ Sheet, No. 69. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	3	Hornblende Schist, ..	..	Mayo,	Callon R.C. Church, 6″, No. 61.	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	4	Sheared Felsite, ..	..	Mayo,	Bohenhill, ...	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	5	Diorite, ...	..	Tyrone,	Scalp Mountain, Pomeroy,	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	6	Quartz Schist, ..	..	Mayo,	Corelaig, 6″, No. 17, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	7	Sheared Quartzite, ..	..	Mayo,	Ross, East, 6″, No. 70, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	8	Amphibolite, ..	..	Tyrone,	Clare Rock, outer, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	9	Sheared Grit, ..	..	Mayo,	Achilbeg, N. Shore, 6″, 75,	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	10	Sheared Grit, ..	..	Mayo,	Achilbeg, N. Shore, 6″, 75,	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	11	Vein Quartz with Pyrites,	..	Cork,	Bearhaven S. Mine, ..	Traces.	0 2 12	
		Duplicate, ..	..	..	.. .. ..	—	—	
	12	Quartzite, ...	..	Mayo,	Ross, East, 6″, 75, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	13	Chlorite Schist, impregnated with Pyrites,	..	Galway,	Rahoon Mine, ...	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	14	Separated Iron Pyrites,	..	Galway,	Rahoon Mine, ...	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	14	Vein Quartz, ..	..	Mayo,	Ross, East, 6″, No. 75, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	15	Quartz with Dolomite, ..	..	Cork,	Roeska Bantry Mine,	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	

		Siderite,	..	Cork,	Bantry Mine, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	18	Quartzose Conglomerate,	..	Mayo,	North of Castlebar, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	19	Mica Schist, ..	..	Sligo,	½ North Cartran Hill, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	20	Sheared Grit, ..	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	2 Miles E. of Westport, ..	—	—	
	21	Hornblende Schist, ..	..	Wexford,	Saltee Island, ...	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	22	Eurite, ...	..	Donegal,	West Derryneagh, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	23	Sheared Felsite, ..	..	Mayo,	Bohen Hill, 98/4, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	24	Sheared Grit, ..	..	Mayo,	River Conloen Bridge, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	25	Sheared Grit, ..	..	Mayo,	1½ Miles N. W. Castlebar, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	26	Diorite, ...	..	Tyrone,	Glencollip Burn, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	27	Diorite, ...	..	Derry,	Churchtown, Moneymore, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	28	Breccia, ...	..	Galway,	Waterfall, 39/3, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	29	Quartz Schist, ..	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
April.	30	Vein Quartz, slightly Ferruginous,	Lower Silurian, ..	Wicklow,	Croghan Moira or Connary Gold Mine,	Traces,	—	Assay Plan[1].
		Duplicate, ..	..	..	.. .. ..	—	—	
	31	.. .. ..	..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	32	.. .. ..	..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	33	.. .. ..	..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	34	Vein Quartz, Ferruginous,	Lower Silurian, ..	Wicklow,	Ballyarthur, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	

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[1] Unless otherwise indicated, the large "Assay Plan" is referred to.

TABLE OF ASSAY RESULTS.

Date.	No. Sample.	Nature of Matrix.	Formation.	County.	Locality.	Gold Assay Value.	Silver Assay Value.	Remarks.
1889 March						oz. dwt. grs.	oz. dwt. grs.	
	1	Mispickel, ...	..	Cork,	Bantry, ...	0 2 0	86 0 0	
		.. .. ..	..	..	.. .. ..	--	87 16 0	Duplicate.
	2	Duplicate, ..	..	..	.. .. ..	0 2 0	86 16 0	Triplicate.
	2	Sheared Grit, ..	..	Mayo,	6″ Sheet, No. 69. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	3	Hornblende Schist, ..	..	Mayo,	Callon R.C. Church, 6″, No. 61.	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	4	Sheared Felsite, ..	..	Mayo,	Bohenhill, ...	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	5	Diorite, ...	..	Tyrone,	Scalp Mountain, Pomeroy,	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	6	Quartz Schist, ..	..	Mayo,	Corelaig, 6″, No. 17, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	7	Sheared Quartzite, ..	..	Mayo,	Ross, East, 6″, No. 70, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	8	Amphibolite, ..	..	Tyrone,	Clare Rock, outer, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	9	Sheared Grit, ..	..	Mayo,	Achilbeg, N. Shore, 6″, 75, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	10	Sheared Grit, ..	..	Mayo,	Achilbeg, N. Shore, 6″, 75, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	11	Vein Quartz with Pyrites,	..	Cork,	Bearhaven S. Mine, ..	Traces.	0 2 12	
		Duplicate, ..	..	..	.. .. ..	—	—	
	12	Quartzite, ...	..	Mayo,	Ross, East, 6″, 75, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	13	Chlorite Schist, impregnated with Pyrites,	..	Galway,	Rahoon Mine, ...	—	—	
		Duplicate, ..			.. .. ..			
	14	Separated Iron Pyrites,	..	Galway,	Rahoon Mine, ...	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	14	Vein Quartz, ..	..	Mayo,	Ross, East, 6″, No. 75, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	15	Quartz with Dolomite, ..	..	Cork,	Roeska Bantry Mine, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	16	Quartz with Pyrites, ..	..	Cork,	Bearhaven Mine, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	17	Quartz Rock, Mispickel Siderite,	..	Cork,	Roeska Bantry Mine, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	18	Quartzose Conglomerate,	..	Mayo,	North of Castlebar, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	19	Mica Schist, ..	..	Sligo,	½ North Cartran Hill, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	20	Sheared Grit, ..	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	2 Miles E. of Westport, ..	—	—	
	21	Hornblende Schist, ..	..	Wexford,	Saltee Island, ...	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	22	Eurite, ...	..	Donegal,	West Derryneagh, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	23	Sheared Felsite, ..	..	Mayo,	Bohen Hill, 98/4, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	24	Sheared Grit, ..	..	Mayo,	River Conloen Bridge, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	25	Sheared Grit, ..	..	Mayo,	1½ Miles N. W. Castlebar, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	26	Diorite, ...	..	Tyrone,	Glencollip Burn, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	27	Diorite, ...	..	Derry,	Churchtown, Moneymore, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	28	Breccia, ...	..	Galway,	Waterfall, 39/3, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	29	Quartz Schist, ..	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
April.	30	Vein Quartz, slightly Ferruginous,	Lower Silurian, ..	Wicklow,	Croghan Moira or Connary Gold Mine,	Traces,	—	Assay Plan[1].
		Duplicate, ..	..	..	.. .. ..	—	—	
	31	.. .. ..	..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	32	.. .. ..	..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	33	.. .. ..	..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	34	Vein Quartz, Ferruginous,	Lower Silurian, ..	Wicklow,	Ballyarthur, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	

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[1] Unless otherwise indicated, the large "Assay Plan" is referred to.

Assay Results—*continued.*

Date.	No. Sample	Nature of Matrix.	Formation.	County.	Locality.	Gold Assay Value.	Silver Assay Value.	Remarks.
						oz. dwt. grs.	oz. dwt. grs.	
1899 April.	35	Vein Quartz, Ferruginous,	Lower Silurian, ..	Wicklow,	Ballyarthur, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	36	Quartz (road metal), Ferruginous and Chloritic,	..	Wicklow,	Woodenbridge, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	37	Quartz Boulder, Ferruginous and Chloritic,	Drift, ...	..	Ow River, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	38	Quartz (road metal), Ferruginous,	..	..	Aughrim, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	39	Vein Quartz (from Dump) Slickensided,	Lower Silurian, ..	..	Ballymurtagh, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	40	Vein Quartz, slightly Ferruginous,	Lower Silurian, ..	Wicklow,	Connary Gold Mine, ..	Traces,	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	41	Vein Quartz, with Pyrites,	..	..	Rattlebox Lode, Connary, ..	Traces,	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	42	Gossan and Quartz from Dump,	..	..	Connary Gold Mine, ..	Traces,	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	43	Ochre, ...	..	..	Cronbane, ...	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	44	Copper Pyrites, ..	..	..	Ballygahan Copper Mine, ..	0 0 12	2 12 0	
		Duplicate, ..	..	..	.. .. ..	—	—	Assay Plan.
	45	Vein Quartz, Dump crushed Ore,	..	..	Connary Gold Mine, ..	Traces.	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	46	Pebbles, washings from Pannings,	Drift, ...	..	Ow River, Aughrim, ..	—	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	47	North Copper Lode, ..	Lower Silurian, ..	..	Ballymurtagh, ...	Traces,	4 18 0	
		Duplicate, ..	..	..	.. .. ..	—	—	

		Pyrites,						
		Duplicate, ..	..	..	.. .. ..	—	—	
	49	Kilmacooite, ..	..	..	Connary, ...	0 0 12	15 16 0	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	50	Ferruginous Quartz (Road Metal), selected,	..	Wicklow,	Aughrim, ...	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	51	Quartz, slightly Ferruginous,	Drift, ...	..	Sugar Loaf (Mr. Pollock), ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	52	Quartz, Ferruginous Chloritic,	Drift, Ordovician Slates (?)	Dublin,	Dodder River (Mr. Seymour),	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	53	Quartz, ...	Drift, ...	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	54	Grit, ...	..	Clare,	Killaloe, ...	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	55	.. .. ..	..	..	.. .. ..	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	56	.. .. ..	..	..	.. .. ..	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	57	.. .. ..	..	..	.. .. ..	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	58	.. .. ..	..	..	.. .. ..	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	59	.. .. ..	..	..	.. .. ..	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	60	Grit, ...	..	Clare,	Killaloe, ...	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	61	Galena, surface find, ..	Drift, ...	..	.. .. ..	0 0 12	7 12 0	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	62	Quartz Boulder, Honeycombed Ferruginous,	Drift, ...	Wicklow,	Gold Mines Valley, ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	63	Quartz Vein, ..	Lower Silurian, ..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	64	Fractured Quartz Boulder,	Drift, ...	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	

Assay Results—*continued.*

Date.	No. Sample	Nature of Matrix.	Formation.	County.	Locality.	Gold Assay Value.	Silver Assay Value.	Remarks.
						oz. dwt. grs.	oz. dwt. grs.	
1899 April.	35	Vein Quartz, Ferruginous,	Lower Silurian, ..	Wicklow,	Ballyarthur, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	36	Quartz (road metal), Ferruginous and Chloritic,	..	Wicklow,	Woodenbridge, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	37	Quartz Boulder, Ferruginous and Chloritic,	Drift, ...	..	Ow River, ...	Traces,	—	Assay Plan.
		Duplicate. ..	..	..	.. .. ..	—	—	
	38	Quartz (road metal), Ferruginous,	..	..	Aughrim, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	39	Vein Quartz (from Dump) Slickensided,	Lower Silurian, ..	..	Ballymurtagh, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	40	Vein Quartz, slightly Ferruginous,	Lower Silurian, ..	Wicklow,	Connary Gold Mine, ..	Traces,	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	41	Vein Quartz, with Pyrites,	..	..	Rattlebox Lode, Connary, ..	Traces,	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	42	Gossan and Quartz from Dump,	..	..	Connary Gold Mine, ..	Traces,	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	43	Ochre, ...	..	..	Cronbane, ...	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	44	Copper Pyrites, ..	..	..	Ballygahan Copper Mine, ..	0 0 12	2 12 0	
		Duplicate, ..	..	..	.. .. ..	—	—	Assay Plan.
	45	Vein Quartz, Dump crushed Ore,	..	..	Connary Gold Mine, ..	Traces.	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	46	Pebbles, washings from Pannings,	Drift, ...	..	Ow River, Aughrim, ..	—	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	47	North Copper Lode, ..	Lower Silurian, ..	..	Ballymurtagh, ...	Traces,	4 18 0	
		Duplicate, ..	..	..	.. .. ..	—	—	
	48	Slickensided Quartz with Pyrites,	..	..	Connary, ...	Traces,	3 6 0	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	49	Kilmacooite, ..	..	..	Connary, ...	0 0 12	15 16 0	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	50	Ferruginous Quartz (Road Metal), selected,	..	Wicklow,	Aughrim, ...	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	51	Quartz, slightly Ferruginous,	Drift, ...	..	Sugar Loaf (Mr. Pollock), ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	52	Quartz, Ferruginous Chloritic,	Drift, Ordovician Slates (?)	Dublin,	Dodder River (Mr. Seymour),	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	53	Quartz, ...	Drift, ...	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	54	Grit, ...	..	Clare,	Killaloe, ...	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	55	.. .. ..	..	..	.. .. ..	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	56	.. .. ..	..	..	.. .. ..	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	57	.. .. ..	..	..	.. .. ..	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	58	.. .. ..	..	..	.. .. ..	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	59	.. .. ..	..	..	.. .. ..	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	60	Grit, ...	..	Clare,	Killaloe, ...	—	—	Assay Plan C.
		Duplicate, ..	..	..	.. .. ..	—	—	
	61	Galena, surface find, ..	Drift, ...	..	.. .. ..	0 0 12	7 12 0	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	62	Quartz Boulder, Honeycombed Ferruginous,	Drift, ...	Wicklow,	Gold Mines Valley, ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	63	Quartz Vein, ..	Lower Silurian, ..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate. ..	..	..	.. .. ..	—	—	
	64	Fractured Quartz Boulder,	Drift, ...	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	

ASSAY RESULTS—*continued.*

Date.	No. Sample	NATURE OF MATRIX.	FORMATION.	COUNTY.	LOCALITY.	Gold Assay Value.	Silver Assay Value.	REMARKS.
						oz. dwt. grs.	oz. dwt. grs.	
1899 April.	65	Quartz Vein, Ferruginous,	Lower Silurian, ..	..	Gold Mines Valley, Croghan Kinshelagh,	0 4 0	Trace,	*Duplicate 4 dwts. *Triplicate 4 dwts.
		Duplicate, ..	..	..	.. .. ..	—	—	” ”
	66	Schistose Grit, Country Rock, Debris Dump,	Lower Silurian, ..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	67	Ferruginous Quartz Boulder, ..	Drift, ...	..	Avonmore River, Avondale,	Traces,	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	68	Fractured Quartz Vein,	Lower Silurian, ..	..	Gold Mines Valley, ..	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	Assay Plan A.
	69	Ferruginous Quartz Boulder, ..	Drift, ...	..	Avondale, Avonmore River,	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
May.	70	Fine Sand, ..	Drift, ...	Wicklow,	Earl of Meath's Sand Pit, Aughrim,	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	71	Coarse Sand, ..	Drift, ...	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	72	Quartz Lode with Galena,	..	..	Seven Churches Old Mining Co.'s Lode,	Traces,	Traces,	Assay Plan B.
		Duplicate, ..	..	..	.. .. ..	—	—	
	73	Iron-stained Quartz Boulder, ..	Drift, ..	..	Wynne's Wood, Seven Churches, ..	—	—	Assay Plan B.
		Duplicate, ..	..	..	.. .. ..	—	—	
	74	Iron-stained Quartz Leader Chloritic Slickensided,	Mica Schist, altered Silurian,	..	Aughrim, Aughavanagh, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	75	Micaceous Vein Quartz,	Mica Schist, altered Silurian,	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	76	Dull White Vein Quartz,	Mica Schist, altered	..	.. .. ..	—	—	

		Duplicate, ..	..	..	.. .. ..	—	—	
	78	Ferruginous Manganiferous Vein Quartz, Ferruginous, ..	Lower Silurian, ..	..	Mount Avon, Avondale, ..	—	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	79	White Quartz Boulder, ..	Drift, ...	..	Avondale, Avonmore River,	—	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	80	Slickensided Shale, ..	..	Wicklow,	Railway Cutting, Avondale,	—	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	81	Country Rock Grit, ..	Lower Silurian, ..	..	Gold Mines Valley, ..	—	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	82	Schistose Grit, ..	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	83	Footwall of No. 65, ..	Lower Silurian, ..	..	Gold Mines Valley, Croghan Kinshelagh,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	84	Ferruginous Quartz Boulder, ..	Drift, ..	..	Gold Mines Valley, ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	85	Schist Country Rock, ..	Lower Silurian, ..	..	Aughrim, ...	—	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	86	Chloritic Quartz Boulder,	Drift, ..	..	Aughrim, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	87	Eurite, ...	..	..	Ow River, Aughrim, ..	—	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	88	Shaly Grit, Country Rock,	Lower Silurian, ..	..	Gold Mines Valley, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	89	Decomposed Diabase Boulder, ..	Drift, ..	..	Avondale, Avonmore River,	—	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	90	Ferruginous Quartz Boulder, ..	Drift, ...	Wicklow,	Ballykillagear, Hagan's Farm, Gold Mines Valley,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	91	Ferruginous Quartz Boulder, ..	..	..	.. .. ..	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	92	Decomposed Dolerite, ..	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	

* Highest Assay.

Assay Results—*continued.*

Date.	No. Sample	Nature of Matrix.	Formation.	County.	Locality.	Gold Assay Value.	Silver Assay Value.	Remarks.
1899 April.						oz. dwt. grs.	oz. dwt. grs.	
	65	Quartz Vein, Ferruginous,	Lower Silurian,..	..	Gold Mines Valley, Croghan Kinshelagh,	0 4 0	Trace,	*Duplicate 4 dwts. *Triplicate 4 dwts.
		Duplicate, ..		..	.. .. ..	—	—	” ”
	66	Schistose Grit, Country Rock, Debris Dump,	Lower Silurian,..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	67	Ferruginous Quartz Boulder, ..	Drift, ...	..	Avonmore River, Avondale,	Traces,	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	68	Fractured Quartz Vein,	Lower Silurian,..	..	Gold Mines Valley, ..	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	69	Ferruginous Quartz Boulder, ..	Drift, ...	..	Avondale, Avonmore River,	Traces,	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
May.	70	Fine Sand, ..	Drift, ...	Wicklow,	Earl of Meath's Sand Pit, Aughrim,	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	71	Coarse Sand, ..	Drift, ...	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	72	Quartz Lode with Galena,	..	..	Seven Churches Old Mining Co.'s Lode,	Traces,	Traces,	Assay Plan B.
		Duplicate, ..	..	..	.. .. ..	—	—	
	73	Iron-stained Quartz Boulder, ..	Drift, ..	..	Wynne's Wood, Seven Churches, ..	—	—	Assay Plan B.
		Duplicate, ..	..	..	.. .. ..	—	—	
	74	Iron-stained Quartz Leader Chloritic Slickensided,	Mica Schist, altered Silurian,	..	Aughrim, Aughavanagh, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	75	Micaceous Vein Quartz,	Mica Schist, altered Silurian,	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	76	Dull White Vein Quartz,	Mica Schist, altered Silurian,	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
1899 May.	77	Iron-stained Vein Quartz,	Mica Schist, altered Silurian,	..	Mucklagh Brook, Aughavanagh,	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	78	Ferruginous Manganiferous Vein Quartz, Ferruginous,	Lower Silurian,..	..	Mount Avon, Avondale, ..	—	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	79	White Quartz Boulder,..	Drift, ...	..	Avondale, Avonmore River,	—	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	80	Slickensided Shale, ..	..	Wicklow,	Railway Cutting, Avondale,	—	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	81	Country Rock Grit, ..	Lower Silurian,..	..	Gold Mines Valley, ..	—	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	82	Schistose Grit, ..	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	83	Footwall of No. 65, ..	Lower Silurian,..	..	Gold Mines Valley, Croghan Kinshelagh,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	84	Ferruginous Quartz Boulder, ..	Drift, ..	..	Gold Mines Valley, ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	85	Schist Country Rock, ..	Lower Silurian,..	..	Aughrim, ...	—	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	86	Chloritic Quartz Boulder,	Drift, ..	..	Aughrim, ...	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	87	Eurite, ...	..	..	Ow River, Aughrim, ..	—	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	88	Shaly Grit, Country Rock,	Lower Silurian,..	..	Gold Mines Valley, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	89	Decomposed Diabase Boulder, ..	Drift, ..	..	Avondale, Avonmore River,	—	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	
	90	Ferruginous Quartz Boulder, ..	Drift, ...	Wicklow,	Ballykillagear, Hagan's Farm, Gold Mines Valley,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	91	Ferruginous Quartz Boulder, ..	..	..	.. .. ..	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	92	Decomposed Dolerite, ..	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	

* Highest Assay.

ASSAY RESULTS—*continued*.

Date.	No. Sample	NATURE OF MATRIX.	FORMATION.	COUNTY.	LOCALITY.	Gold Assay Value.	Silver Assay Value.	REMARKS.
						oz. dwt. grs.	oz. dwt. grs.	
1899 May.	93	Highly Ferruginous Quartz, ..	..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	Assay Plan.
	94	Chloritic Quartz, ..	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	95	Ferruginous Quartz Boulder, ..	Drift, ...	..	Lord Wicklow's Estate, Shelton Abbey, Avonmore River,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	96	Ferruginous Vein Quartz,	Lower Silurian, ..	..	P. Byrne's Farm, Croghan Kinshelagh, Gold Mines Valley, Acheson's Working,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	Assay Plan.
	97	Iron-stained Quartz Boulder, ..	Drift, ...	..	Ballykillagear, Hagan's Farm, Gold Mines Valley,	Traces.	—	
		Duplicate, ..	..	..	.. .. ..	—	—	Assay Plan.
	98	Chloritic Quartz, ..	..	..	.. .. ..	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	99	Ferruginous Vein Quartz,	Lower Silurian, ..	..	Lord Wicklow's Estate, Shelton Abbey, Avonmore River,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
June.	100	Iron-stained Quartz Boulder, ..	Drift, ...	Wicklow,	Earl Fitzwilliam's Estate, Shillelagh,	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	101	Quartzite, ...	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	102	Chloritic Quartz, Quartz Boulder,	Drift, ...	..	Ballykillagear, Hagan's Farm, Gold Mines Valley,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	103	Quartzite, ...	Lower Silurian, ..	..	Colonel Tottenham's Estate, Ballycurry,	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	104	Eurite, ...	..	..	Glendalough, ...	—	—	Assay Plan B.
		Duplicate, ..	..	..	.. .. ..	—	—	

	Duplicate, ..	..	..	.. .. ..	—	—	
107	Brick Clay, ..	Drift, ...	..	Rathnew Brick Works, ..	—	—	
	Duplicate, ..	..	..	.. .. ..	—	—	
108	Quartz Boulder, ..	Drift, ...	Dublin,	Hell Fire Club, down stream near R. C. Institution (Mr. Pollok),	—	—	
	Duplicate, ..	..	..	.. .. ..	—	—	
109	Quartz, ...	..	Dublin,	.. .. ..	—	—	
	Duplicate, ..	..	..	.. .. ..	—	—	
110	Ferruginous Quartz Boulder, ..	Drift, ...	Wicklow,	Avondale, Avonmore River,	Traces,	—	Assay Plan A.
	Duplicate, ..	..	..	.. .. ..	—	—	

Two Assay tons taken for each sample.

Each sample assayed in duplicate.

Traces vary from one to three grains per 2240 lbs.

Highest Assay, No. 65, 4 dwts.

The fluxes were assayed and found to contain no gold.

The number of the sample corresponds to that on the Assay Plan.

EDWARD ST. JOHN LYBURN,
Mining Engineer.

June 21*st*, 1899.

ASSAY RESULTS—*continued.*

Date.	No. Sample	NATURE OF MATRIX.	FORMATION.	COUNTY.	LOCALITY.	Gold Assay Value.	Silver Assay Value.	REMARKS.
						oz. dwt. grs.	oz. dwt. grs.	
1899 May.	93	Highly Ferruginous Quartz, ..	..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	94	Chloritic Quartz, ..	..	..	.. .. ..	—	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	95	Ferruginous Quartz Boulder, ..	Drift, ...	..	Lord Wicklow's Estate, Shelton Abbey, Avonmore River,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	96	Ferruginous Vein Quartz,	Lower Silurian, ..	..	P. Byrne's Farm, Croghan Kinshelagh, Gold Mines Valley, Acheson's Working,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	97	Iron-stained Quartz Boulder, ..	Drift, ...	..	Ballykillagear, Hagan's Farm, Gold Mines Valley,	Traces.	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	98	Chloritic Quartz, ..	..	..	.. .. ..	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	99	Ferruginous Vein Quartz,	Lower Silurian, ..	..	Lord Wicklow's Estate, Shelton Abbey, Avonmore River,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
June.	100	Iron-stained Quartz Boulder, ..	Drift, ...	Wicklow,	Earl Fitzwilliam's Estate, Shillelagh,	Traces,	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	101	Quartzite, ...	..	..	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	102	Chloritic Quartz, Quartz Boulder,	Drift, ...	..	Ballykillagear, Hagan's Farm, Gold Mines Valley,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	103	Quartzite, ...	Lower Silurian, ..	..	Colonel Tottenham's Estate, Ballycurry,	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	104	Eurite, ...	..	..	Glendalough, ...	—	—	Assay Plan B.
		Duplicate, ..	..	..	.. .. ..	—	—	
	105	Dolerite, ...	..	..	Arklow Rock, ...	—	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	106	Ferruginous Quartz Vein,	Lower Silurian, ..	..	Lord Wicklow's Estate, Shelton Abbey, Avonmore River,	Traces,	—	Assay Plan.
		Duplicate, ..	..	..	.. .. ..	—	—	
	107	Brick Clay, ..	Drift, ...	..	Rathnew Brick Works, ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	108	Quartz Boulder, ..	Drift, ...	Dublin,	Hell Fire Club, down stream near R. C. Institution (Mr. Pollok),	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	109	Quartz, ...	..	Dublin,	.. .. ..	—	—	
		Duplicate, ..	..	..	.. .. ..	—	—	
	110	Ferruginous Quartz Boulder, ..	Drift, ...	Wicklow,	Avondale, Avonmore River,	Traces,	—	Assay Plan A.
		Duplicate, ..	..	..	.. .. ..	—	—	

Two Assay tons taken for each sample.
Each sample assayed in duplicate.
Traces vary from one to three grains per 2240 lbs.
Highest Assay, No. 65, 4 dwts.
The fluxes were assayed and found to contain no gold.
The number of the sample corresponds to that on the Assay Plan.

EDWARD ST. JOHN LYBURN,
Mining Engineer.

June 21*st*, 1899.

XXXII.

ON SOME PROBLEMS CONNECTED WITH ATMOSPHERIC CARBONIC ANHYDRIDE, AND ON A NEW AND ACCURATE METHOD FOR DETERMINING ITS AMOUNT SUITABLE FOR SCIENTIFIC EXPEDITIONS. By PROFESSOR E. A. LETTS, D.Sc., Ph.D., and R. F. BLAKE, F.I.C., F.C.S., Queen's College, Belfast.

[COMMUNICATED BY DR. W. E. ADENEY, F.I.C., F.C.S.]

[Read January 16; Received for Publication January 28; Published June 6, 1901.]

In a recent memoir on the subject of the "Carbonic Anhydride of the Atmosphere,"[1] we have directed attention to several problems which require investigation, especially the causes of the variations in its amount. On this point we express ourselves as follows:—

"These variations, if actually small, are *relatively* large, and correspond with fluctuations of at least 10 per cent. of the total quantity, and according to some observers to a much higher proportion.

"Thus the oscillations in the amount of atmospheric carbonic anhydride must be admitted, even by those who take the lowest estimate, to be comparable in extent with the variations which occur in atmospheric pressure, and they may have a significance quite as important as these latter.

"But in attempting to unravel the separate effects of those natural agencies which influence the proportion of atmospheric carbonic anhydride, very great difficulty is experienced, and indeed the task appears to be almost impossible in some cases with the material at present available for discussion.

"This is due in great measure to the fact that many of the natural agencies are antagonistic in their effect, and that several of them

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[1] These Proceedings (New Series), 9 [1900] Part 2, No. 15.

may be acting at the same time, thus giving a mixed result. Then, too, a difficulty arises as to the trustworthiness of the work of some of the observers—the fact that they have in many cases employed different methods of determination, and that very few of these have been tested as regards their degree of absolute accuracy ; and also that the observers have collected their air samples at different heights above the ground.

"In our opinion, the subject is an important one, and is worthy of a systematic re-investigation by a number of skilled observers, working in different localities and employing the same method of determination, which shall have been proved to give results which do not vary from the true amount by more than two or three parts per million of air."

Among the problems relating to atmospheric carbonic anhydride which we think are specially worth attention, the following may be mentioned :—

(1) *Is Schlœsing's Theory correct ?*—Do the oceans really act as regulators of the amount, owing to the presence in them of earthy bicarbonates and carbonates—the first (in solution) dissociating when a decrease below the normal occurs, the second (in suspension or on the ocean bed) dissolving when the reverse occurs?

As a consequence of this theory, latitude should influence the amount of atmospheric carbonic anhydride, which ought to be less in polar than in tropical regions.

The great ocean currents should also have an effect, absorbing carbonic anhydride from the air as they pass from warmer to colder regions. As a further consequence of the theory, the air of the northern hemisphere ought to contain more carbonic anhydride than that of the southern, the larger water surfaces of the latter being colder than those of the former where land predominates. And, according to Müntz and Aubin, this is actually the case, the figures which they give as the mean amounts for the two being 2·82 and 2·72 parts per 10,000 respectively—a variation of 4 per cent.

(2) *The influence of Day and Night.*—Nearly all the observers have found an increased amount of atmospheric carbonic anhydride at night over land surfaces, to account for which two theories have been advanced—(*a*) the cessation of plant activity in decomposing the gas, owing to the absence of light, and (*b*) the streaming out

of ground air (rich in carbonic anhydride) from the soil, owing to the lowering of temperature.

At sea no such influence can be exerted, but an absorption of atmospheric carbonic anhydride may occur at the surface of the water, owing to lowering of temperature, thus reversing the land effect. This question has received scarcely any attention.

(3) *The effects of Atmospheric Precipitates*, and especially of snow, which appears to increase the amount of atmospheric carbonic anhydride. No reasonable theory has been proposed to account for this curious phenomenon, and it would be interesting to ascertain whether it occurs at sea as well as on land, and the same remark would apply to fog and rain, both of which appear to affect the amount also.

Other supposed causes of variation are worth studying, such as the effects of the seasons, direction and force of the winds, the prevailing type of weather, height above the Earth's surface, &c., but those which we think most interesting are such as a scientific mission would be under peculiarly favourable conditions, to investigate, and especially the proposed Antarctic expeditions—English and German—whose work will be performed largely at sea.

It is the investigation of the carbonic anhydride over the ocean which, in our opinion, presents so many problems of interest, and which, up to the present time, has received so little attention.

. . . .

In the memoir we have referred to, we have also described a method for determining atmospheric carbonic anhydride—a modification of Pettenkofer's process—by means of which results of great accuracy may be obtained. Thus in the final set of test experiments with artificial mixtures of purified air and carbonic anhydride, a mean error (in six determinations) of about 1 per cent. of the gas was found corresponding with some 4 parts per million of the air taken.

For certain purposes—and especially for employment by a scientific expedition—it seemed to us, however, that a different process is required, in which the operations at the place of observation should be simple, and of such a nature as to permit the actual determinations to be made later when the resources of a properly equipped laboratory are available. The method employed by Müntz and Aubin during the French Transit of Venus Expedition to Central and Southern America in 1882 was of this kind, but had certain disadvantages, notably the large volume of air which had to be operated on (200–300 litres), and the time and trouble which had to be expended in preparing the long absorption tubes containing pumice moistened with caustic potash solution, to say nothing of the complicated apparatus and operations subsequently necessary for liberating and measuring the absorbed carbonic anhydride.

The process which we have devised is simple, and as we shall show is accurate also. On the one hand, it resembles Pettenkofer's in that a relatively small volume of air is examined; while on the other, Müntz and Aubin's principle is adopted of absorbing the carbonic anhydride by caustic potash solution, and afterwards liberating it by an acid and measuring its volume.

Details of the New Process.

Absorbing Solution.—The solution which we use for absorbing the carbonic anhydride from a given air sample consists of weak caustic potash, containing about 3 grams of ordinary stick potash dissolved in 2 litres of distilled water. Such a solution is roughly $\frac{N}{40}$, and is neutralized by about $\frac{1}{4}$ of its volume of carbonic anhydride.

As it is essential that no carbonic anhydride should gain access to this solution when once the amount which it always contains (as carbonate) has been ascertained, we keep it stored in a bottle A shown in the diagram (fig. 1).

The tube B contains soda lime, so that when drawing off a charge of the solution through the long tube C, the air entering the bottle to take its place is freed from carbonic anhydride. The ends of the tubes D and C are closed when this operation is not in progress by plugs consisting of short glass rods attached to pieces of india-rubber tubing, and the pinch-cock E is also closed to prevent evaporation of the liquid into the soda lime.

Measuring a Charge of Absorbent.—To measure off a charge of the absorbent, we employ an apparatus similar in some respects to a nitrometer, and accurately marked, as shown in the diagram, for containing or delivering charges of 40 and 50 c.c., respectively.

In measuring off a charge, the vessel is first filled with mercury, and the three-way stop-cock F closed. It is then connected by a piece of thick-walled india-rubber tube with the bottle containing the stock of potash solution, the mercury reservoir lowered, and the stop-cock F turned so that liquid is drawn over from the bottle into the measuring vessel. Any bubble of air which may also be drawn over is got rid of through G, and the charge measured off

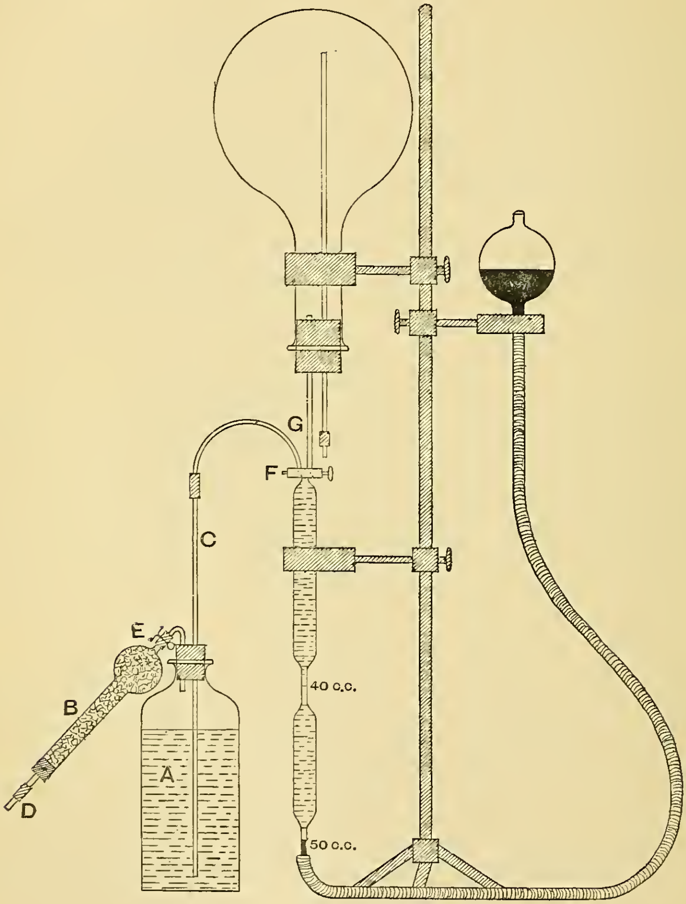

Fig. 1.

by raising or lowering the mercury reservoir to the proper level. When detaching the stock bottle of potash solution the rubber juncture of C is pinched between the finger and thumb, and then plugged with a piece of glass rod so that C remains full of liquid.

Collecting and Absorbing Vessels.—The vessels we employed for this purpose in our test experiments were ordinary 6-litre flasks, fitted either with ordinary corks, well soaked in hot paraffin wax, or india-rubber corks; but in either case a layer of paraffin wax, about $\frac{1}{8}$th inch in thickness, was melted on to their lower surface Two tubes passed through the cork attached to each receiver, a long one reaching about three-quarters of the way down the vessel, and a short one which terminated flush with the lower surface of the cork. The upper ends of these two tubes were plugged, when necessary, with short pieces of india-rubber tube attached to glass rods. But for use by a scientific expedition, we have had a different vessel constructed which we shall describe presently.

Apparatus for Liberating and Measuring the Absorbed Carbonic Anhydride.—For this purpose we employed the excellent and reliable apparatus described by Dr. W. E. Adeney in the Transactions of the Royal Dublin Society, Vol. 5 (series 2), Part 11 [1895], p. 548, and used by him in his important research on the dissolved gases in natural and polluted waters—slightly modified by ourselves. Constant experience of this apparatus extending over some years has proved to us that it is most serviceable for boiling out the dissolved gases from a liquid *in vacuo*, and yields very accurate results in their subsequent analysis. The error in the latter is probably less than 0·01 c.c.

The Process.—The absorbing vessel is first filled with the air-sample to be examined; and in order to do this, the method of exhaustion is preferable, the operator being at a sufficient distance from the collecting area to avoid the possibility of breath contamination. An exhausting syringe is attached to one end of an india-rubber tube about six feet long, while the other end of this tube is connected with either of the glass tubes passing through the cork of the receiver. The syringe is set in motion, and pumping continued until 20–30 litres of air have passed through the receiver. The india-rubber tube is then detached, and the receiver plugged, a note being taken of the readings of the barometer and of the wet and dry bulb thermometers.

The receiver is next clamped in an inverted position to a tall retort-stand: the measuring vessel charged with 50 c.c. of the absorbent brought beneath it as shown in fig. 1, and connexion made between the short tube of the receiving vessel and the vertical tube of the measuring apparatus, this latter tube being previously filled with mercury. In performing this operation, the india-rubber tube forming part of the plug attached to the receiver is pinched between the finger and thumb while the glass rod previously attached to it is removed, and the end of the india-rubber tube slipped over the tube of the measuring vessel.

The stop-cock of the measuring vessel is now turned, and the mercury reservoir raised so that the charge of absorbent flows slowly into the receiver. As soon as all has passed in and some mercury has risen above the india-rubber junction, the receiver is detached and plugged with the same precaution as before to prevent escape of air. The receiver is now detached, and rolled round so as to wet all parts of its inner surface with the absorbent solution. It is then allowed to remain undisturbed for a sufficient time for the absorption of the carbonic anhydride to occur. Three hours are probably sufficient for the purpose, but in order to be on the safe side in all our experiments, twenty-four were allowed.

The next operation consists in transferring the potash solution from the absorbing vessel back again into the measuring apparatus; but as it is obviously impossible that the whole can be transferred (as a portion clings to the receiver) only an aliquot part is removed. The operations for this transfer are precisely similar to those employed when running in the charge of absorbent, and need not therefore be described: the only difference being that the mercury reservoir is lowered instead of being raised, and that the measuring vessel is filled to the mark 40 c.c. instead of 50 c.c.

The receiver is now detached, well washed with distilled water, and dried, ready for another determination. The measuring vessel and its contents are removed to the Adeney apparatus—the 40 c.c. of absorbent transferred to the boiling-out flask containing acidulated gas-free water—and the operation completed by boiling out the gases which the absorbent contains (*in vacuo*), and determining the amount of carbonic anhydride they contain by measuring the pressure at constant volume before and after their treatment with caustic potash.

One other determination is necessary, namely, that of the carbonic anhydride which the absorbing solution contains before treatment with the air sample. This is done by measuring off 50 c.c. from the stock-bottle, and proceeding as just described. Duplicate analyses are advisable; but the amount having been once definitely ascertained for a given stock of the absorbent, it is obvious that no re-determinations are necessary until the stock is exhausted.

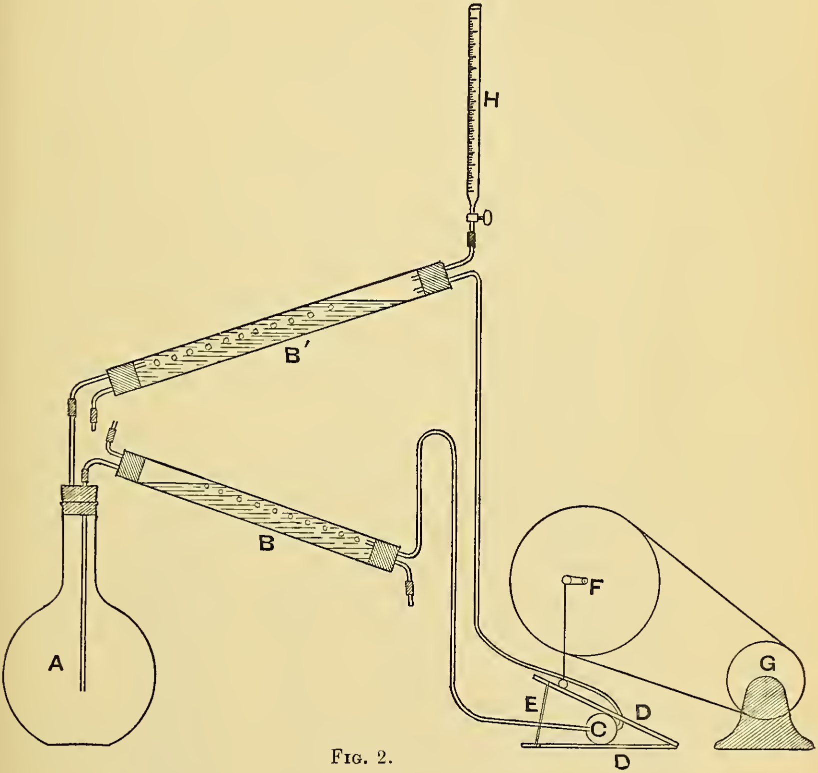

Fig. 2.

Testing the New Method.—In testing the new method, artificial mixtures were employed containing measured volumes of carbonic anhydride, and air previously freed from that gas, the mixture corresponding as far as possible in composition with ordinary air.

Some difficulty was experienced in devising a method for obtaining a supply of air freed from carbonic anhydride in a *dry* vessel. Eventually the arrangement shown in fig. 2 was employed and was found to work admirably. By means of a motor G connected by a strap to the cranked wheel F, the hinged boards DD (provided with an india-rubber band E to act as a spring) were made to move continuously like an ordinary bellows, the movement actuating an india-rubber "spray" apparatus C placed between the boards, thus causing the air in the receiver A to circulate through the two tubes B and B′ containing weak baryta solution coloured with phenol-phthaleïn. The upper of these tubes (through which the air passed out of the receiver) served also to indicate when all the carbonic anhydride had been removed from the air—weak baryta solution (1 c.c. = 0·1 c.c. CO_2 at N.T.P.) being added from the burette H from time to time until the solution remained of a faint pink colour for an hour or so. It was found that every trace of carbonic anhydride was removed from the air when the apparatus had been working for about six hours.

In order to obtain an artificial mixture of the air thus purified with a known volume of carbonic anhydride, the receiver was detached from the two absorbing tubes, plugged (with the precaution already mentioned for preventing access or egress of air) and transferred to an apparatus for introducing a measured volume of carbonic anhydride (fig. 3).

The tube A standing over mercury contained a supply of pure carbonic anhydride—obtained by heating sodium bicarbonate until a portion of the escaping gas was entirely absorbed by caustic potash solution—and dried by a layer of sulphuric acid in the tube itself. This tube was attached by an india-rubber junction at G, completely immersed in a mercury trap, to the measuring pipette B, accurately marked at its lower (capillary) part to contain a definite volume of gas.

Previous to attaching the receiver of purified air, this measuring pipette was filled with mercury by raising the mercury reservoir D, closing the stop-cock of the manometer tube C, and opening the three-way stop-cock E, so that F also was filled with mercury when the stop-cock was closed. The receiver of purified air clamped in an inverted position to a tall retort-stand (not shown in the figure) was next brought over F, and the latter attached to it by the rubber junction forming part of the plug of the short tube of the receiver. The stop-cock of the manometer tube was now opened, the mercury reservoir lowered, and the stop-cock of the measuring tube turned, so as to fill the latter accurately to the mark with carbonic anhydride at the existing temperature and pressure.

It only remained to transfer this measured volume of the gas to the receiver of purified air by precisely the same manipulation as was employed for filling the meauring pipette with mercury.

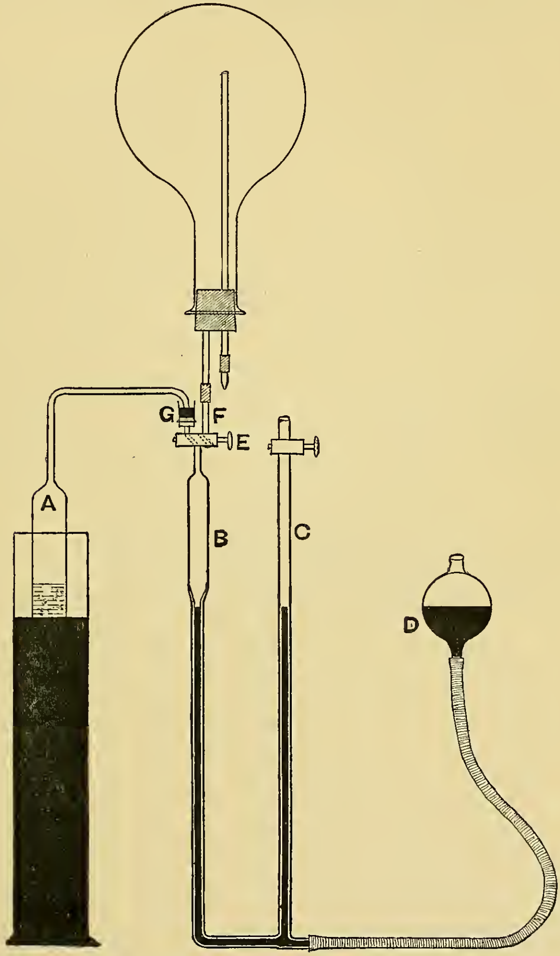

Fig. 3.

By this means, as the capacity of the receiver and its attached tubes had been previously ascertained, a mixture of pure air and carbonic anhydride in known proportions was obtained, ready for analysis by the new method. The following are the results obtained, first with artificial mixtures, and then with ordinary air in duplicate determinations:—

Blank Experiments.

Fifty c.c. of the potash solution boiled *in vacuo* with acidulated gas-free water yielded:—

——	Volume.	Pressure.	Temperature.
(I.) Total gases, ...	14·822 c.c.	68·5 m.m.	13·3° C.
After absorption by potash, . .	,, ,,	58·0 ,,	13·5 ,,
(II.) Total gases, ...	,, ,,	65·0 ,,	14·0 ,,
After absorption by potash, .	,, ,,	54·5 ,,	14·3 ,,

	I.	II.
Total gases at N.T.P., . . .	1·274 c.c.	1·206 c.c.
After absorption by potash, . . .	1·078 c.c.	1·010 c.c.
CO_2 in 50 c.c. of absorbent, . .	0·196 c.c.	0·196 c.c.

Determinations in Artificial Mixtures.

50 c.c. of the potash solution employed in each case as absorbent, and 40 c.c. subsequently taken for the determinations.

——	Volume.	Pressure.	Temperature.
(1.) Total gases, ...	14·822 c.c.	138 m.m.	12·7° C
(2.) ,, ,, ...	,, ,,	138·5 ,,	11·2 ,,
(3.) ,, ,, ...	,, ,,	136 ,,	14·3 ,,
(4.) ,, ,, ...	,, ,,	135 ,,	11·7 ,,
(5.) ,, ,, ...	,, ,,	133·5 ,,	12·2 ,,
(1.) After treating the gases with potash,	,, ,,	46·5 ,,	13·0 ,,
(2.) ,, ,, ,, ,,	,, ,,	46·5 ,,	11·5 ,,
(3.) ,, ,, ,, ,,	,, ,,	44·0 ,,	14·7 ,,
(4.) ,, ,, ,, ,,	,, ,,	47·5 ,,	12·2 ,,
(5.) ,, ,, ,, ,,	,, ,,	45·5 ,,	12·4 ,,

CO_2 FOUND AT N.T.P.

No.	Found in 40 c.c. of absorbent.	Calculated amount in 50 c.c. of absorbent.
1	1·706	2·132
2	1·724	2·155
3	1·706	2·132
4	1·638	2·047
5	1·643	2·054

No.	Total CO_2 found in 50 c.c. absorbent.	*Minus* amount in blank determination.	Equals CO_2 absorbed from artificial mixture.
1	2·132	0·196	1·936
2	2·155	0·196	1·959
3	2·132	0·196	1·936
4	2·047	0·196	1·851
5	2·054	0·196	1·858

Results of 5 *Determinations.*

No.	CO_2 taken at N.T.P.	CO_2 found at N.T.P.	Error.
1	1·938 c.c.	1·936 c.c.	– 0·002 c.c.
2	1·945 ,,	1·959 ,,	+ 0·014 ,,
3	1·968 ,,	1·936 ,,	– 0·032 ,,
4	1·911 ,,	1·851 ,,	– 0·060 ,,
5	1·906 ,,	1·858 ,,	– 0·048 ,,
Mean	1·933 ,,	1·908 ,,	– 0·025 ,,

As the receiver had a capacity of 6586 c.c. these results may be summed up as follows :—

	On the CO_2 taken.	Equivalent in parts per 10,000 of air to :—
Mean error, ...	1·3 per cent., . . .	0·04
Greatest error, . . .	3·1 ,, ,, . . .	0·09
Least, ...	0·0 ,, ,, . . .	0·00

They prove that the process sufficiently fulfils the conditions of accuracy, which we consider to be necessary for tracing the fluctuations in the amount of atmospheric carbonic anhydride.

It is also very probable that part at least of the errors arose, not from the process of determination, but in the preparation of the artificial mixtures of purified air and carbonic anhydride, the accurate measurement of the small volumes of the latter employed for the purpose being somewhat difficult.

As a final test of the new method we made duplicate determinations of carbonic anhydride in ordinary fresh air collected in two different receivers.

Determination of Carbonic Anhydride in Air taken from the Grounds of the Queen's College, Belfast.

Temperature, 16·94° C. (dry bulb), 13·61° C. (wet bulb).

Barometer, 757·5. Weather fine, with light S.W. breeze.

(1) Volume of air taken, 6584 c.c. = 6178·9 c.c. at N.T.P. without correction for moisture, or 6098·2 with correction for moisture.

CO_2 found at N.T.P. = 1·822 c.c.

(2) Volume of air taken, 6672 c.c. = 6261·5 c.c. at N.T.P. without correction for moisture, or 6179·7 with correction for moisture.

CO_2 found at N.T.P. = 1·872 c.c.

No.	CO_2 found in 10,000 of air without correction for moisture.	CO_2 found in 10,000 of air with correction for moisture.
(1.)	2·948	2·987
(2.)	2·989	3·028
Difference,	0·041	0·041

Modification of the process proposed for Field Work or for employment by a Scientific Expedition.

For these purposes we propose that a series of sealed tubes should be prepared in the laboratory, each tube containing a charge of exactly 50 c.c. of the weak potash solution.

The only operations to be performed at the place of observation will be the collection of the air sample in a suitable receiver, the transfer of the contents of one of the sealed tubes to the latter, and after absorption of the atmospheric carbonic anhydride, their retransfer, as far as possible, to the same tube, which will again be sealed.

The tubes can, of course, be kept for an indefinite period, both before and after their contents have been thus treated, and the determination of the absorbed carbonic anhydride made, when convenient, with an aliquot portion of their contents.

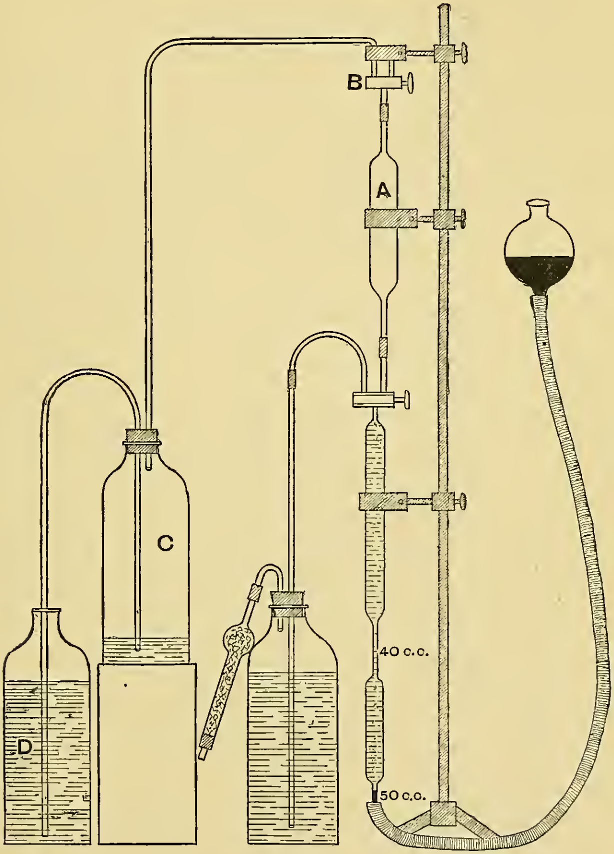

Fig. 4.

The necessary operations for the whole process will be as follows:—

Filling and sealing the Tubes (fig. 4).—A tube A of the form shown in figure 4 is attached at its lower extremity by a piece of thick-walled india-rubber tube to the measuring apparatus, which, in its turn, is connected with the stock-bottle of weak potash solution—(the carbonic anhydride content of which has been previously ascertained), and the upper extremity of the tube connected in a similar manner with the three-way stop-cock B attached as shown to a bottle C containing air which has been in contact with the solution of caustic potash (which latter the bottle also contains) for some hours, so that the air is freed from carbonic anhydride. This bottle is also connected by a siphon tube with a second bottle D filled with the potash solution.

The mercury reservoir attached to the measuring tube is then raised and the two stop-cocks opened, so that the air in the tube passes out into the atmosphere and the tube itself becomes filled with mercury. The upper stop-cock is then turned, so as to connect the tube with the air in the bottle C, and the mercury reservoir lowered when the tube again becomes filled with air, which now, however, contains no carbonic anhydride. The measuring tube is next filled to the mark 50 c.c. with the potash solution contained in the stock-bottle, and this charge slowly transferred to the tube by raising the mercury reservoir, turning the lower stop-cock in the proper direction, and the upper one, so that the displaced air again passes into the bottle, and mercury just shows above the lower rubber junction. The upper extremity of the tube is then sealed off, the tube itself inverted while still attached at its lower extremity to the measuring tube, then detached together with the india-rubber tube forming the junction. It only remains to draw off and seal the lower end (now the upper end), when the tube contains exactly 50 c.c. of the weak potash solution, together with some air, which, however, is free from carbonic anhydride.

New form of Receiver.—As an ordinary 6-litre flask is somewhat unwieldy and fragile, and a cork which has to be removed frequently is an unsatisfactory method of enclosing a definite volume of air within the flask, we propose to employ a bottle-shaped receiver of stout glass instead, provided with an accurately-ground hollow stopper and glass tubes blown into the latter as shown in the diagram (fig. 5, D.)—the extremities of these tubes to be plugged when necessary with pieces of thick-walled india-rubber tube and glass rods.

Transfer of the contents of one of the sealed Tubes to the Receiver containing the Air to be examined, and their re-transfer after absorption of the Carbonic Anhydride.—Method 1. A glass stop-cock A (fig. 5)

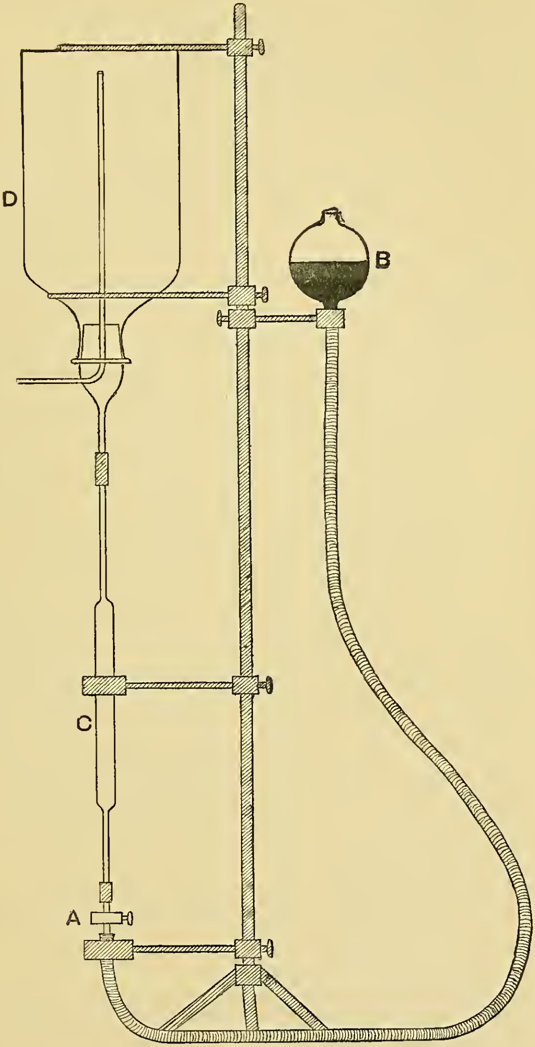

FIG. 5.

connected by thick-walled india-rubber tubing to the mercury reservoir B, is clamped as shown to a tall retort-stand. A short piece of thick-walled india-rubber tube is also attached to the open end of the stop-cock, and by turning the latter, is filled with mercury.

The end of one of the sealed tubes, C, is then pushed down into this tube until it is firmly attached, and the sealed tube clamped vertically to the retort-stand.

The receiver D containing the air sample is next clamped in an inverted position above the upper end of the sealed tube and attached to the latter as shown, care being taken when making the attachment that the india-rubber junction connected with the receiver is pinched between the finger and thumb, both when removing the glass rod plug and also when inserting the end of the sealed tube. Both ends of the latter are then broken off within the rubber junctions; and lastly by slowly turning the stop-cock, the contents of the sealed tube are gently driven into the receiver. The stop-cock is then closed, and the receiver detached and plugged (with the same precautions as before for preventing access or egress of air); then rolled round to spread the absorbent over its inner surface, and allowed to remain at rest during the period necessary for absorption. Meanwhile the tube previously containing the absorbent remains filled with mercury.

In order to make the re-transfer of the absorbent from the receiver to the tube, the receiver is clamped to the retort-stand in the same position as it occupied before, the same attachments made, and the solution withdrawn from the receiver by first lowering the mercury reservoir, and then slowly opening the stop-cock until a little air makes its way into the upper end of the sealed tube. The receiver is then removed, and the upper end of the tube sealed off. The tube is then inverted, its lower (now its upper end) detached, and also sealed off. We prefer this method, but another one may also be employed.

Method 2.—To the receiver containing the air sample two lengths of thick-walled india-rubber tube are attached, the longer to B and the shorter to A (fig. 6).

Both of these contain the air sample to be examined (the volume of which is added to the capacity of the receiver in the subsequent calculation); and previous to the absorbing process the ends of these two are plugged with short pieces of glass rod. They replace, in fact, the short plugs previously described.

To absorb the carbonic anhydride in the air of the receiver, one of the sealed tubes is attached to these tubes as shown, with the precautions already mentioned for preventing access or egress of air during the attachment, and its ends are then broken off inside the india-rubber tubes. By holding or supporting these latter as shown, the absorbing solution passes into the receiver. After the period necessary for the absorption has elapsed, the receiver is inverted as shown in fig. 7, and the sealed tube held or supported at such an angle that the bulk of the absorbent flows into it. The upper end is first detached and sealed off, and then the lower end after inverting the tube and allowing the narrow part to drain.

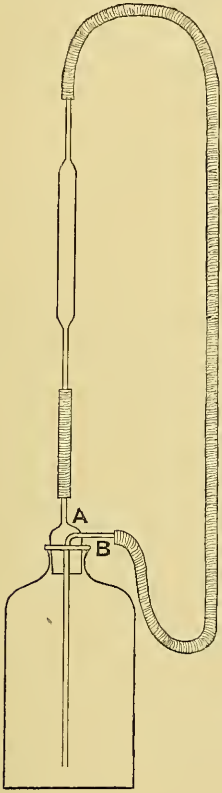

FIG. 6.

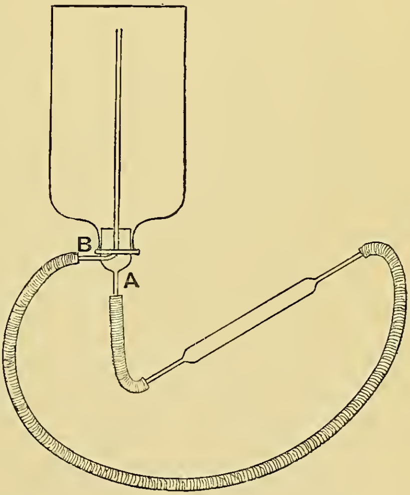

FIG. 7.

Before sealing off, it is advisable to repeat the process of transfer and retransfer, so as to thoroughly mix the solution.

XXXIII.

ON A SIMPLE AND ACCURATE METHOD FOR ESTIMATING THE DISSOLVED OXYGEN IN FRESH WATER, SEA WATER, SEWAGE EFFLUENTS, &c.

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[communicated by dr. w. e. adeney, f.i.c., f.c.s.]

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Several volumetric processes have been devised for determining the dissolved oxygen in fresh water, for which a considerable degree of accuracy has been claimed, and probably the best known are those of Schützenberger and Thresh. The first of these (originally described in the *Comptes Rendus*, 75, p. 879, and in Schützenberger's work on Fermentation) has received a considerable amount of attention from different observers,[1] and especially from Roscoe and Lunt,[2] who introduced an important modification into the process, and compared the results obtained by the method thus modified with those yielded by boiling out the dissolved gases *in vacuo*, and determining the oxygen by gasometric analysis. In all the determinations, more oxygen appears to have been found by them by the volumetric than by the gasometric method. In London tap-waters, the greatest difference between the two sets of determinations amounted to 0·44 c.c. per litre, and the least to 0·10, and they say:—"The oxygen values obtained by the two methods show close agreement, considering the possible experimental error in so complex a comparison. The mean

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[1] König und Mentschler, Berichte 10 [1877], p. 2017: König, Berichte 13 [1880], p. 154: Tiemann und Preusse, Berichte 12 [1879], p. 1768; Bernthsen, Berichte 13 [1880], p. 2277: Duprè, Analyst 10 [1885], p. 156: Ramsay and Williams, Chem. Soc. Journ. Trans. 49 [1886], p. 751.

[2] Chem. Soc. Journ. Trans. 55 [1889], p. 552.

difference being only 0·28 c.c. of oxygen per litre of water, showing that the method gives good results with ordinary drinking waters."

With Thames water at Richmond the greatest difference was 0·98 c.c. per litre, the least 0·07, and the mean 0·56, while with Thames water opposite the southern sewage out-fall, worse results were obtained, the mean difference being 0·63 c.c.

Thresh's method,[1] in the hands of its inventor, appears to have given exceedingly accurate results. The test experiments were chiefly made with distilled water saturated with air at 10°, 15°, 20°, and 25°C., respectively, and the results compared with the gasometric determinations made by Roscoe and Lunt at the same temperatures. The greatest mean difference between the two sets of figures amounted to 0·09 c.c. of oxygen per litre of water, and the least to 0·02. Thresh makes the following remark:—"The results, however, can be made to vary, the extreme limit being 0·5 mgs. (0·31 c.c.) of oxygen per litre of water, using 250 c.c. for the estimation."

One of the authors of this Paper has employed this method on several occasions, but although every care was taken, and all the precautions mentioned in Thresh's paper carefully observed, the results were not very satisfactory, and in the case of sea-water polluted with sewage they were definitely unsatisfactory. With distilled water, a variation of 0·4 c.c. of oxygen per litre from the true amount was found several times; while in the case of the polluted sea-water, some of the samples, when kept in stoppered bottles filled to the brim and immersed in water, actually showed a *gain* in dissolved oxygen when kept for twelve days, amounting in one of the samples to more than 0·6 c.c. per litre, although there cannot be the slightest doubt that a decrease had really occurred. As an important technical question was involved in these determinations, and interests of considerable magnitude were at stake, the determinations were practically valueless.

In the two volumetric processes mentioned above, and apparently indeed in all similar methods for determining dissolved oxygen, the titration is performed in a vessel through which a current of hydrogen or other inert gas is made to pass, which not

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[1] Chem. Soc. Journ. Trans. 57 [1890], p. 185.

only complicates the operation, but renders a special apparatus necessary, and unfits the process for "field" work.

. . . .

The amount of dissolved oxygen which a water contains either originally or which it loses on keeping—and especially the latter—is probably a more important criterion of what may be termed "active" pollution than any other;[1] and some simple and efficient method of determination which can be used by the ordinary analyst, and if necessary, at the place where the sample is collected, seemed to the authors to be a desideratum of importance.

In the process which they have devised for the purpose, the simplest apparatus is used, as well as the most ordinary reagents to be found in any chemical laboratory. No inactive gas is necessary, and the titration is performed in an open dish. The whole process, in fact, is one which a person of ordinary intelligence, and without any special chemical training, could be easily taught to perform. Its principle is simple, and consists in absorbing the dissolved oxygen in a measured volume of the water by ferrous sulphate and excess of ammonia in a vessel completely filled with the three, and closed both when mixing them and during the period necessary for the oxygen absorption. Sulphuric acid is then added in excess in such a way that no air gains admission during the process, after which the mixture is transferred to an open dish and there titrated either with permanganate or bichromate.[2] The details of the process are as follows:—

STANDARD SOLUTIONS.—(1) *Ferrous Sulphate.*—About 12 grammes of the crystallized salt are dissolved in 250 c.c. of distilled water. Theoretically, 12·444 grammes give a solution, each

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[1] See the highly important paper of Dr. W. E. Adeney on this subject, Roy. Dublin Soc. Trans. 5 (series 2), [1895], p. 539.

[2] The principle of absorbing the dissolved oxygen in water by ferrous sulphate and an alkali, with subsequent determination of the unoxidized ferrous salt in the acidulated mixture by permanganate, is an old one, and was first employed, we believe, by Mohr (Lehrbuch d. Titrirmethoden von Fr. Mohr, 4 Aufl., p. 239). The method as carried out according to his directions is, however, open to several sources of error, which we have sought to eliminate in the process here described.

This opportunity may be taken to refer to papers by Adams (Chem. Soc. Journ. Trans., 61 [1892], p. 310), Blarez (Journ. de Pharm. [5], 18, p. 55), and apparently Latieu also (Journ. Pharm. Anvers [1887], p. 570), on methods for the determination of the dissolved oxygen in water, in which the use of an inactive gas is avoided.

cubic centimetre of which is equivalent to 1 cubic centimetre of oxygen at N. T. P., but nothing is gained by preparing a solution of exactly this strength. The solution becomes turbid after some days, but it is easily cleared by filtration previous to a series of determinations, so that the same solution may be employed for months, and has been thus kept and used in the authors' experiments.

(2) *Standard Permanganate.*—The most convenient solution is of such strength that 1 cubic centimetre is equivalent to 1 cubic centimetre of oxygen at N. T. P.; and such a solution is obtained by dissolving 5·6538 grammes of the pure crystallized potassium salt in 1 litre of distilled water.[1]

For the estimation of the dissolved oxygen in distilled water itself, or in ordinary water, a solution of one-tenth this strength may be used; but for all practical purposes the stronger solution will be found to give sufficiently accurate results, especially if a narrow burette of 10 c.c. capacity is employed with which readings may be made accurately to 0·025 c.c. The stronger solution keeps well (in the dark), but the weaker one should be prepared freshly from the former for each series of experiments.

(3) *Standard Bichromate*, of a strength corresponding with that of the permanganate, may be employed instead of the latter; and in the case of sewage effluents and in that of sea water, is undoubtedly to be preferred, as will be shown by the results to be mentioned presently. Of course, in using bichromate, potassium ferricyanide must be employed as indicator; and as the ferrous sulphate solution is highly diluted by the water under examination, the strong bichromate can alone be employed with advantage. This is prepared by dissolving 8·7906 grammes of the pure crystallized potassium salt in 1 litre of distilled water, each cubic centimetre of such a solution corresponding with 1 cubic centimetre of oxygen at N. T. P.

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[1] This amount is calculated on the basis of (1) Ostwald's atomic weights, $O = 16$, and $KMnO_4 = 158·226$, and (2), the mean of the determination of the density of oxygen by Regnault, Leduc, Rayleigh, and Jolly (1 litre at N.T.P. = 1·4293914 grammes).

A decinormal solution of the permanganate (3·164 grammes per litre) is also of suitable strength for the titrations, 1 c.c. of this solution corresponding with 0·56 c.c. of oxygen at N.T.P.

(4) *Sulphuric Acid.*—A mixture of equal volumes of the strong acid and water is employed.

Absorbing Vessel.[1]—The vessel in which the water under examination is mixed with the ferrous sulphate and ammonia, and in which, too, the mixture is afterwards acidulated with sulphuric acid, is an ordinary separating vessel of the shape and capacity shown in the diagram (fig. 1). The exact dimensions, however, are of no consequence, provided that the vessel holds a sufficient volume of water and that the tube forming its lower extremity is wide enough to contain the quantity of sulphuric acid required to acidulate the ammoniacal mixture before titration.

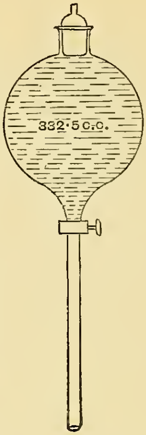

Fig. 1.

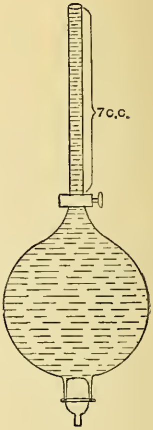

Fig. 2.

The Process.—The separating vessel is filled to the brim with the water under examination, and for this purpose the authors have always employed a glass siphon tube, one limb of which is dipped almost to the bottom of a Winchester quart bottle (filled originally to the brim and then stoppered) containing the sample of water, while the other and longer limb is connected with a piece of india-rubber tube clamped with a pinch-cock.

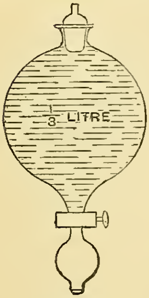

Fig. 3.

A little of the water is first drawn off and the separating vessel rinsed with it. The end of the rubber tube is then passed to the bottom of the separating vessel, the pinch-cock opened, and the water allowed to flow in until the vessel is not only full, but a fair quantity has overflowed. In this way the possibility of error

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[1] As an ordinary separating funnel is somewhat unwieldy for the purpose of these determinations, owing to the length of the tube, Messrs. Baird and Tatlock, of London, have constructed for us a special form of apparatus shown in the diagram (fig. 3), which is very handy and convenient, and contains exactly $\frac{1}{3}$ litre. The same firm also supplies the whole of the necessary apparatus and reagents for the determinations, packed in a box of portable form.

owing to absorption of atmospheric oxygen by the upper layer of the water as it flows into the wide part of the vessel is avoided.

The stopper is now inserted, and the excess of water drained off. The stopper is next removed and about 7 c.c. of the water taken out by a pipette and thrown away. 5 c.c.[1] of the (clear) ferrous sulphate solution are then carefully measured off in an accurately graduated pipette and allowed to flow into the separating vessel, the nozzle of the pipette being just dipped below the surface of the water, where the ferrous sulphate owing to its higher density flows in a stream to the bottom of the water. Strong ammonia solution is then cautiously poured on to the top layer of the water until the vessel is just full, when the stopper is inserted; but even if a drop or two of the ammonia is lost when inserting the stopper no harm is done, as the ammonia floats on the surface and does not appreciably mix with the contents of the vessel. A little dexterity is necessary in inserting the stopper so that no air bubble is enclosed. Within the separating vessel there is now a layer of ferrous sulphate below, next the water, and above all the ammonia. These are mixed together by inverting the vessel once or twice by a swinging motion, when a greenish turbid mixture results, containing ferrous hydrate partly in solution and partly in suspension, which rapidly darkens as it absorbs the dissolved oxygen. In all the authors' experiments an interval of fifteen minutes was allowed for the purpose. Experience has shown it to be sufficient, but it is possible that a shorter period would suffice. The next operation consists in inverting the vessel, still stoppered, and then filling or nearly filling its tube or lower extremity (now, however, its upper extremity) with the mixture of sulphuric acid and water (fig. 2). The stop-cock is then opened, when the acid flows downwards into the alkaline mixture, and in the course of a few minutes dissolves the iron hydrates to a clear solution.[2]

Should an air bubble remain in the boring of the stop-cock, it prevents this flow, but a few taps causes it to be displaced and to rise through the acid.

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[1] Of course these quantities would have to be be varied if a vessel were used either much smaller or much larger than the one described.

[2] In some of the test experiments with distilled water saturated with air this did not occur until the mixture was heated. But with all samples of natural waters, sewage effluents, &c., no heating was necessary.

The acidulated solution is finally run off into a porcelain dish, and titrated either with the permanganate or bichromate solution.

It remains to determine the value of the ferrous sulphate solution; and in the authors' experiments this was always done under similar conditions to those obtaining in the dissolved oxygen determination itself, that is to say, the separating vessel was filled with the water under examination, 7 c.c. removed, and the remainder poured into a porcelain dish, where it was mixed with the same volume of sulphuric acid and the same volume of ferrous sulphate solution as were employed in the dissolved oxygen determination, and then titrated. In this way the error arising from oxidizable substances in the water is eliminated even when their amount is considerable.

In practice it was found convenient to standardize the iron solution during the interval required for the absorption of the dissolved oxygen, and consequently as a preliminary to the latter process, to first of all fill the separating vessel with the water under examination and to transfer the latter (after removing 7 c.c.) to a porcelain dish ready for the addition of the ferrous sulphate and sulphuric acid.

Calculating the Results.—With the stronger solution of either the permanganate or bichromate, it is obvious that the amount of dissolved oxygen contained in the volume of water operated on is expressed in cubic centimetres at N.T.P. by the difference between the burette readings for the blank experiment and those of the actual determination—with a correction for the dissolved oxygen contained in the 5 c.c. of the ferrous sulphate solution and the 2 c.c. of ammonia. Such a correction is, however, small, and in all the authors' experiments, the assumption was made that the 7 c.c. of mixed reagents contained the same proportion of dissolved oxygen as the water under examination.[1]

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[1] Thus, in one of the determinations, the difference between the burette readings for the blank and dissolved oxygen determinations was 2·35 c.c.

Assuming that the 7 c.c. of reagent added contained the *same* amount of dissolved oxygen as the water under examination, then the latter contained per litre—

$$\frac{2350}{332\cdot 5} = 7\cdot 067 \text{ c.c. dissolved oxygen, per litre, at N.T.P.}$$

The following experiments show the extent of accuracy of the process, with different samples of natural waters, sewage effluents, and sewage itself:—

Distilled Water saturated with air at 15°*C.*—(Titrations by permanganate 1 c.c. = 1 c.c. oxygen at N. T. P.)

A.	Blank experiment required, . . .	3·83 c.c.
	Oxygen determination required, . . .	1·48 ,,
	Dissolved oxygen =	2·35 ,,
B.	Blank experiment required, . . .	3·83 c.c.
	Oxygen determination required, . . .	1·48 ,,
	Dissolved oxygen =	2·35 ,,

Dissolved oxygen per litre, .	7·06 c.c. found.	
,, ,, ,,	6·96 ,,	Roscoe & Lunt's result for distilled water at 15° C.
Difference,	0·10 ,,	

Distilled Water saturated with Air at 13·7°*C.*—(Titrations by permanganate 1 c.c. = 0·1 c.c. oxygen at N. T. P.)

A.	Blank experiment required, . . .	38·1 c.c.
	Oxygen determination required, . . .	13·9 ,,
	Difference, . .	24·2 ,,
	Dissolved oxygen =	2·420 c.c.
B.	Blank experiment required, . . .	38·05 c.c.
	Oxygen determination required, . . .	13·90 ,,
	Difference, . .	24·15 ,,
	Dissolved oxygen =	2·415 c.c.

Whereas assuming that the 7 c.c. of reagents contained *no* oxygen, the figures become—

$$\frac{2350}{325\cdot5} = 7\cdot219 \text{ c.c. dissolved oxygen, per litre, at N.T.P.}$$

The difference is 0·152 c.c. per litre, which, for most practical purposes, is unimportant, and the actual error would certainly be much less. The error, so far as the ferrous sulphate solution is concerned, could be eliminated by saturating it with air at the given temperature previous to a determination, while that from the small volume of ammonia added is too insignificant to need correction.

Dissolved oxygen per litre, .	7·27 c.c. found (A).	
,, ,, ,, .	7·26 ,, ,, (B).	
,, ,, ,, .	7·20 ,,	Roscoe & Lunt's results for distilled water at 13·5° C.
Mean difference,	0·065 ,,	

Distilled Water, with one per cent. of foul Sewage added; the mixture being then thoroughly aerated at 15° C.—(Titrations by permanganate 1 c.c. = 0·1 c.c. oxygen at N. T. P.)

Blank experiment required, . . .	38·1 c.c.
Oxygen determination required, . . .	14·4 ,,
Difference, . .	23·7 ,,

Dissolved oxygen = 2·37 c.c.

Dissolved oxygen per litre,	7·13 c.c. found.	
,, ,, ,,	6·96 ,,	Roscoe & Lunt's results for distilled water at 15° C.
Difference, .	0·17 ,,	

The next determinations were made with the view of testing the results of the new process against those obtained by gasometric analysis. For the latter purpose the excellent and reliable apparatus devised by Dr. W. E. Adeney was employed,[1] slightly modified by the authors. In this apparatus a measured volume of the water is boiled *in vacuo* with dilute sulphuric acid, and the evolved gases analysed at constant volume.

Belfast Water supply from Main.—Titrations by permanganate 1 c.c. = 0·1 c.c. oxygen at N. T. P.)

A.	Blank experiment required, . . .	37·8 c.c.[2]
	Oxygen determination required, . . .	18·5 ,,
		19·3 ,,
B.	Blank experiment required, . . .	37·8 c.c.
	Oxygen determination required, . . .	18·5 ,,
		19·3 ,,

Dissolved oxygen = 1·93 c.c.

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[1] Adeney, Roy. Dublin Soc. Trans., 5 (series 2), 1895, p. 547.

[2] The same ferrous sulphate solution was employed as in experiments 1 and 2, but a period of three weeks had elapsed since those determinations.

Gasometric Analysis.

200 c.c. of the water gave—		Equivalent to, per litre—
CO_2	7·05 c.c.	35·25 c.c.
O_2	1·15 ,,	5·75 ,,
N_2	2·71 ,,	13·55 ,,
Total,	10·91 ,,	54·55 ,,

Dissolved oxygen, per litre, by new process,	5·80 c.c.
,, ,, ,, by gasometric analysis,	5·75 ,,
Difference,	0·05 ,,

Sewage Effluent from Belfast experimental "Bacteria Beds" after double contact, and subsequent exposure in pond for one hour.—(Titrations by permanganate 1 c.c. = 1 c.c. oxygen at N. T. P.)[1]

A.	Blank experiment required,	4·05 c.c.
	Oxygen determination required,	3·15 ,,
		0·90 ,,
B.	Blank experiment required,	4·05 c.c.
	Oxygen determination required,	3·15 ,,
		0·90 ,,

Dissolved oxygen = 0·90 c.c.

Gasometric Analysis.

200 c.c. of the effluent gave—		Equivalent to, per litre—
CO_2	25·04 c.c.	125·20 c.c.
O_2	0·63 ,,	3·15 ,,
N_2	2·87 ,,	14·35 ,,
Total,	28·54 ,,	142·70 ,,

Dissolved oxygen, per litre, by new process,	2·71 c.c.
,, ,, ,, by gasometric analysis,	3·15 ,,
Difference,	0·44 ,,

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[1] The weaker solution was also tried but did not work well, the end coloration fading too rapidly for accurate observation.

Sea Water from Belfast Lough. (Titrations by permanganate 1 c.c. = 1 c.c. oxygen at N. T. P.)

A.	Blank experiment required, . . .	4·23 c.c.
	Oxygen determination required, . . .	2·55 ,,
		1·68 ,,
B.	Blank experiment required, . . .	4·74 c.c.[1]
	Oxygen determination required, . . .	3·03 ,,
		1·71 ,,

Dissolved oxygen = 1·695 c.c. (mean of above).

Gasometric Analysis.

200 c.c. of the water gave—		Equivalent to, per litre—
CO_2	9·14 c.c.	45·70 c.c.
O_2	0·90 ,,	4·50 ,,
N_2	2·10 ,,	10·50 ,,
Total,	12·14 ,,	60·70 ,,

Dissolved oxygen, per litre, by new process, . .	5·09 c.c.
,, ,, ,, by gasometric analysis,	4·50 ,,
Difference, . .	0·59 ,,

The two preceding results show that the method fails, to some extent, in the cases of sewage effluents and sea water, when permanganate is used for the titrations. It was therefore decided to try bichromate instead, and to contrast the results obtained with it with those yielded by permanganate and by gasometric analysis respectively.

Sea Water from Belfast Lough—filtered and saturated with air at 19·5°C. (Titrations by permanganate 1 c.c. = 1 c.c. oxygen at N. T. P.)

Blank experiment required, . . .	4·29 c.c.
Oxygen determination required, . . .	2·51 ,,
	1·78 ,,

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[1] A new solution of ferrous sulphate was employed.

(Titrations by bichromate 1 c.c. = 1 c.c. oxygen at N. T. P.)

Blank experiment required,	3·90 c.c.
Oxygen determination required,	2·10 ,,
	1·80 ,,

Dissolved oxygen, per litre, found by Permanganate,	5·35 c.c.
,, ,, ,, ,, by Bichromate,	5·41 ,,
,, ,, ,, Dittmar's result at 20° C.,	5·31 ,,

Sea Water from Belfast Lough, filtered and saturated with air at 20·8°*C.*—(Titrations by permanganate 1 c.c. = 1 c.c. oxygen at N. T. P.)

Blank experiment required,	4·39 c.c.
Oxygen determination required,	2·55 ,,
	1·84 ,,

(Titrations by bichromate 1 c.c. = 1 c.c. oxygen at N. T. P.)

Blank experiment required,	3·90 c.c.
Oxygen determination required,	2·20 ,,
	1·70 ,,

Gasometric Analysis.

200 c.c. of the water gave—		Equivalent to, per litre—
CO_2	9·03 c.c.	45·15 c.c.
O_2	1·02 ,,	5·10 ,,
N_2	1·99 ,,	9·95 ,,
Total,	12·04 ,,	60·20 ,,

Dissolved oxygen, per litre, by new process (permanganate),	5·53 c.c.
,, ,, ,, ,, ,, (bichromate),	5·11 ,,
,, ,, ,, by gasometric analysis,	5·10 ,,

Sewage Effluent from Belfast experimental "Bacteria Beds" after double contact.—(Titrations by permanganate 1 c.c. = 1 c.c. oxygen at N. T. P.)

Blank experiment required,	4·42 c.c.
Oxygen determination required,	4·20 ,,
	0·22 ,,

(Titrations by bichromate 1 c.c. = 1 c.c. oxygen at N. T. P.)

Blank experiment required,	3·91 c.c.
Oxygen determination required,	3·77 ,,
	0·14 ,,

Gasometric Analysis.

200 c.c. of effluent gave—		Equivalent to, per litre—
CO_2	24·42 c.c.	122·10 c.c.
O_2	0·07 ,,	0·35 ,,
N_2	3·10 ,,	15·50 ,,
Total,	27·59 ,,	137·95 ,,

Dissolved oxygen, per litre, by new process (permanganate),	0·66 c.c.
,, ,, ,, ,, ,, (bichromate),	0·42 ,,
,, ,, ,, by gasometric analysis,	0·35 ,,

Sewage (Belfast) from tank previous to filtration through experimental "Bacteria Beds."—(Titrations by permanganate 1 c.c. = 1 c.c. oxygen at N. T. P.)

Blank experiment required,	6·52 c.c.
Oxygen determination required,	6·65 ,,
	0·13 ,,

Titrations by bichromate, 1 c.c. = 1 c.c. oxygen at N. T. P.)

Blank experiment required,	4·25 c.c.
Oxygen determination required,	4·25 ,,
	0·00 ,,

Gasometric Analysis.

200 c.c. of the sewage gave—		Equivalent to, per litre—
CO_2	23·78 c.c.	118·92 c.c.
O_2	none.	none.
N_2	2·95 ,,	14·76 ,,
Total,	26·73 ,,	133·68 ,,

The following experiments were made in order to ascertain whether the presence of nitrates or nitrites would interfere with the accuracy of the process :—

Effect of Nitrates.—A quantity of tap water was thoroughly aerated, and after remaining at rest for a quarter of an hour was divided into two portions. To one of these a standard solution of potassium nitrate was added in such quantity that the resulting mixture contained 0·7 grains per gallon of nitric nitrogen (or 1 part in 100,000). The dissolved oxygen was then determined in both portions, the titrations being made with strong permanganate (1 c.c. = 1 c.c. of oxygen at N.T.P.).

Series 1.—*Aerated Tap Water alone.*

(1)	Oxygen determination required, . .	1·53 c.c. $KMnO_4$
(2)	,, ,, ,, . .	1·53 ,, ,,

Aerated Tap Water with added Nitrate.

(1)	Oxygen determination required, . .	1·53 c.c. $KMnO_4$
(2)	,, ,, ,, . .	1·56 ,, ,,
(3)	,, ,, ,, . .	1·53 ,, ,,
	Mean, .	1·54 ,, ,,

For the above determinations a very old solution of ferrous sulphate was used, and by an oversight a blank determination was made with the aerated tap water only and not with the nitrated water in addition as had been intended. Taking this one determination as the basis of calculation, the amount of dissolved oxygen was as follows:—

Aerated Tap Water alone.

Blank experiment required, . .	3·98 c.c. $KMnO_4$
Oxygen determination (mean) required,	1·53 ,, ,,
Dissolved oxygen, .	2·45 c.c.
Dissolved oxygen, per litre, . .	7·37 c.c.

Aerated Tap Water with added Nitrate.

Blank experiment required, . .	3·98 c.c. $KMnO_4$
Oxygen determination (mean) required,	1·54 ,, ,,
Dissolved oxygen, .	2·44 c.c.
Dissolved oxygen, per litre, . .	7·34 c.c.

SERIES 2.[1]—The determinations were made in the same way as before, but a stronger solution of nitrate was added to the aerated tap water, so that the resulting mixture contained 10 grains per gallon of nitric nitrogen. Blank experiments were made both with the nitrated and non-nitrated water, and a freshly prepared solution of ferrous sulphate was employed.

Aerated Tap Water alone.

Blank experiment required, . .	4·89 c.c. $KMnO_4$
Oxygen determination required, . .	2·38 ,, ,,
Dissolved oxygen, .	2·51 c.c.
Dissolved oxygen, per litre, . .	7·55 c.c.

Aerated Tap Water with added Nitrate.

Blank experiment required, . .	4·88 c.c. $KMnO_4$
(1) Oxygen determination required, . .	2·39 ,, ,,
(2) ,, ,, ,, . .	2·39 ,, ,,
Dissolved oxygen, .	2·49 c.c.
Dissolved oxygen, per litre, . .	7·49 c.c.

From both series of experiments it is evident that the presence of nitrates in a water even in considerable quantities scarcely, if at all, affects the dissolved oxygen determination by the new process.

Effect of Nitrites.—As nitrites are not only reducing agents, but also, when mixed with an acid, absorb atmospheric oxygen, we anticipated that their presence in a water might interfere with the new process in two ways. First, by reducing a larger volume of the permanganate or bichromate solution than might be suitable for the titrations; and second, by the absorption of atmospheric oxygen which would occur during the titration, the amount of which would, no doubt, vary with the time required for the latter, so that if the titration were performed rapidly, more of the bichromate or permanganate would be required than if it were performed slowly.

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[1] Each of the series of experiments, both with nitrates and nitrites, was made on different days, when no doubt the temperature at which the water was saturated with air was not quite the same: hence the variations in the amount of dissolved oxygen found in the water.

But the amount of nitrites which may be found in water or sewage effluents is usually minute, and the question therefore which we had to decide was whether such quantities would appreciably interfere with the accuracy of the process.

The experiments were made in the same way as with the nitrates, with the following results:—

Series 1.—*Aerated Tap Water, with added Sodium Nitrite, equivalent to 1 grain of Nitrous Nitrogen per gallon.*

Blank experiment required, . . 7·51 c.c. $KMnO_4$
Oxygen determination required, . . 4·20 ,, ,,
Dissolved oxygen = 3·31 c.c.
Dissolved oxygen, per litre, . = 9·96 c.c.

Aerated Tap Water alone.

Blank experiment required, . . 4·70 c.c. $KMnO_4$
Oxygen determination required, . . 2·22 ,, ,,
Dissolved oxygen = 2·48 c.c.
Dissolved oxygen, per litre, . = 7·46 c.c.

Series 2.—*Aerated Tap Water, with added Sodium Nitrite, equivalent to 0·1 grain Nitrous Nitrogen per gallon.*

(1) Blank experiment required, . 5·14
(2) ,, ,, ,, . 5·13
} mean = 5·135 c.c. $KMnO_4$
(1) Oxygen determination required, 2·53
(2) ,, ,, ,, 2·54
} mean = 2·535 ,, ,,
Dissolved oxygen = 2·600 c.c.
Dissolved oxygen, per litre, = 7·82 c.c.

Aerated Tap Water alone.

(1) Blank experiment required, . 4·70
(2) ,, ,, ,, . 4·69
} mean = 4·695 c.c. $KMnO_4$
(1) Oxygen determination required, 2·21
(2) ,, ,, ,, 2·21
} mean = 2·210 ,, ,,
Dissolved oxygen = 2·485 c.c.
Dissolved oxygen, per litre, = 7·47

SERIES 3.—*Aerated Tap Water, with added Sodium Nitrite, equivalent to* 0·0084 *grains per gallon* (*or* 0·012 *parts per* 100,000) *of Nitrous Nitrogen.*

Blank determination required, . . . 4·900 c.c. $KMnO_4$
(1) Oxygen ,, ,, 2·34 } mean = 2·345 ,, ,,
(2) ,, ,, ,, 2·35 }

Dissolved oxygen = 2·555 c.c.

Dissolved oxygen, per litre, = 7·68 c.c.

Aerated Tap Water alone.

Blank determination required, . . . 4·890 c.c. $KMnO_4$
(1) Oxygen ,, ,, 2·31 } mean = 2·325 ,, ,,
(2) ,, ,, ,, 2·34 }

Dissolved oxygen = 2·565 c.c.

Dissolved oxygen, per litre, = 7·71 c.c.

From the above experiments, it appears that the process ceases to give accurate results when the quantity of nitrite corresponds with 0·1 grain per gallon of nitrous nitrogen (or about 0·14 parts per 100,000), but that when the quantity is only about one-tenth as much, no perceptible error is introduced. In all probability, the process would give sufficiently accurate results for all practical purposes in waters containing nitrous nitrogen up to 0·05 grains per gallon.

In conclusion, we desire to express our thanks to Mr. John Hawthorne, B.A., for the valuable assistance he has rendered us in carrying out the above experiments on the effects of nitrites and nitrates.

XXXIV.

THE APPLICATION OF THE KITSON LIGHT TO LIGHTHOUSES AND OTHER PLACES WHERE AN EXTREMELY POWERFUL LIGHT IS REQUIRED. By JOHN R. WIGHAM, M.R.I.A.

[Read November 21, 1900; Received for Publication April 26; Published June 7, 1901.]

Recent experience has shown that the electric light is not the best light as a lighthouse illuminant, sea captains and others competent to judge having testified that it is misleading in clear weather, and absolutely useless in foggy weather. The Trinity House appear to have concurred in this view, for they have not established any electric light since the date of their Report on the South Foreland Experiments. On the contrary, when they recently established the great Lundy Island Lights the old oil lamp was adopted as the illuminant, and the controversy seems to have been conclusively settled by the statement of Mr. Ritchie, President of the Board of Trade (who is also the mouthpiece of the Trinity House in Parliament), in reply to a question in the House, that it was true that electric lights had been found inferior, under certain circumstances, to oil.

The claims of the electric light as a lighthouse illuminant having thus been disposed of, the question arises: Can we find a light with the intensity of the electric light without its defects for lighthouse purposes? The new light which I am about to describe is one which seems to possess that desideratum; it is also rich in the red and yellow rays, in which the electric light is deficient, and it has besides the necessary volume which contributes to the power of making itself visible in foggy weather, and has also a uniform steadiness not attainable by the electric arc light. This light is an American invention, and is called, after the name of its inventor, the "Kitson" Light. It is really a gas light, though made from cold petroleum, and possesses those valuable properties which originally commended the gas system to Professor Tyndall and the Irish Lights Commissioners. Under the Kitson system the petroleum is placed in a steel receiver capable of containing the quantity required for a light for a lighthouse or other place for the time for which the light is to be shown. Over the oil in the receiver, atmospheric air is compressed by an ordinary air pump to a pressure of say 50 lb. per square inch. This pressure remains practically constant; a very few strokes of the piston of the pump on the occasion of each new charge of petroleum being sufficient to renew the necessary pressure. The petroleum under this pressure is forced through a soft brass tube, of very small bore, by which it is conveyed to the position in which the light is placed. Being heated at that point it is converted into combustible vapour or gas, and discharged through a needle-hole orifice. The quantity of petroleum thus heated is so exceedingly small that there is no possible danger of fire or explosion. The tube in which this heating takes place is only about 8 inches in length and $\frac{1}{4}$ inch in diameter.

To start the lamp the flame of a little methylated spirit is applied for two or three minutes to the heating tube, after which the heat is maintained by the light itself. The gas issuing from the needle-hole enters a wider tube of peculiar shape and dimensions, and in that tube it is mixed with air, forming a powerful Bunsen burner, which heats to splendid incandescence a mantle provided for the purpose. This mantle may be similar to the ordinary mantle with which we are so familiar, or may be one of stronger character and larger size. The intensity of the light is not produced by the heat alone, as in the case of the ordinary incandescent burner, but also by the high pressure at which the petroleum gas is burned, coupled with the high illuminating power of that gas.

The Kitson light, as first shown in this country, was not well adapted for lighthouse purposes, inasmuch as the apparatus connected with the conversion of the petroleum into a gaseous condition obstructed to a certain extent the passage of the light to the horizon. It was necessary to devise a means of placing this in a different position with respect to the burner, so that the light might be applicable to the ordinary dioptric apparatus of lighthouses. This alteration I have made, thus rendering the Kitson light suitable for general use in lighthouses.

The little apparatus by which the light is produced consists of a cylindrical receiver and pump, the connecting tube, the heating tube, and the burner, and is well adapted for lighthouse purposes, and also for general illumination, not only of large rooms, but of streets, wharves, open spaces, courtyards, public buildings, &c. It is also capable of fulfilling a function which many shipmasters have anxiously desired that lighthouses should perform, namely, the illumination of clouds by what is termed "sky-flashing." The best examples of this kind of illumination are afforded by the search-lights used in the Navy. They are of vastly greater power than any ordinary lighthouse lights, having powerful reflectors projecting the beams in any direction in which the lights may be turned; but if this light, with its great intensity, were placed in the focus of revolving annular lenses there might be a constant upward and downward illumination without depriving the mariner of any of the light transmitted horizontally by the lighthouse. The dioptric apparatus in which the rays of the illuminant are only parallelized vertically, has but a feeble beam compared with that shown through the annular lenses by which the light is parallelized not only vertically but horizontally.

Some years ago I had the honour of reading a paper to this Society on a method of increasing the efficiency of the lighthouse service, by giving to the sailor a perfectly new continuous light of great power and distinctive individuality.[1] This method of lighthouse illumination was tested by Sir Robert Ball, F.R.S., the eminent scientific adviser to the Commissioners of Irish Lights, in the presence of Sir Howard Grubb, F.R.S., and others. Sir Robert reported very favourably concerning it, saying, in effect, that it was a powerful lighthouse light, a novelty in lighthouse illumination of great promise, which provided a means of adding much variety to the existing system of lights.

Since that time I have made much improvement in that system of continuous light, and have applied to it the burner which I have described in this paper. Not only is the general effect better and the light more powerful and more lightning-like in its appearance, but the cost is much less than the cost of the

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[1] Scient. Proc. Roy. Dublin Soc., vol. viii., p. 347.

light which Sir Robert examined and commended, and I hope to show him this new improvement.

The great economy which attends the use of this light—a matter of great importance in the eyes of lighthouse authorities—may be seen from the fact that it is produced at the cost of half a pint of petroleum per hour, say about one halfpenny per hour, very much less than any other light of similar power yet introduced.

The light shown is of 1000 candle power. I am having a burner made which I believe will give four times that power, and so small is its cost that this great power may be applied constantly, and not only as the state of the weather requires it, as in the present gas and oil system, thus making the sailor independent of the lightkeeper's observation of the weather. Of course these high candle powers to which I refer are those of the light only, and are quite independent of the great assistance which the lenticular apparatus gives to it in its transmission to the horizon.

It is one of the advantages of this system that it can be applied in districts and places where it is almost, if not altogether, impossible to obtain gas light or electric light. Its portability is another of its peculiarities. Although it is, as has been said, essentially a gas light, yet the gas-making apparatus which is necessary to produce it is truly portable and vastly simpler and smaller in compass than any ordinary gas-making apparatus. It is the small space which it requires which renders this kind of light peculiarly suitable for isolated positions, such as rock lighthouses, beacons, and lightships.

The paper was illustrated by an exhibition of the new light as a lighthouse light in the focus of a first order dioptric apparatus, and also as a sky-flashing light. Afterwards the light was allowed to illuminate the Lecture Theatre.

XXXV.

ON THE PSEUDO-OPACITY OF ANATASE.

By J. JOLY, Sc.D., F.R.S.,
Honorary Secretary, Royal Dublin Society.

[Read February 20; Received for Publication February 22; Published June 11, 1901.]

The mineral species octahedrite exhibits remarkable variations in crystalline habit, colour, and transparency. The variety *anatase*, found in many of the Swiss metamorphic rocks (as in the Maderanerthal and the valley of Binn) occurs in black and generally highly lustrous octahedra, exhibiting often not the smallest trace of transparency, and resembling, save for the obvious dimetric nature of the octahedron and a higher lustre, the mineral magnetite. On the other hand, the variety *wiserine* (which is more especially abundant in the Binn locality) possesses a rich yellow-brown colour, high adamantine lustre, and is transparent. Again, found often side-by-side with the anatase, the orthorhombic species Brookite occurs in plates having the same transparency as the wiserine, but generally with more or less symmetrically arranged inclusions of dark and nearly opaque matter within.

It is remarkable that the first-named species, anatase, owes its opacity almost entirely to its crystalline form and its high refractive index. The opacity is, in fact, only apparent, the substance of the mineral being most generally transparent or highly translucent, and of a pale, very delicate blue colour. In some individuals, the transparency is diminished by irregularities and inclusions, and in some few specimens, the crystals are truly opaque, or nearly so. These last are wanting in the splendid lustre of the transparent specimens. Others, again—but these seem rare—are *visibly* transparent; but this seems due largely to the scattering of light by cracks and inclusions within the crystals, or to absence of the smooth and lustrous surface. In longest dimension anatase crystals from the Swiss localities seldom exceed 3 to 4 millimetres.

Some few years ago I had occasion, when exhibiting to an audience the trimorphism of titanium oxide, to imbed a couple of the lustrous black anatase crystals in Canada balsam. Bright flashes of blue, red, and greenish light then showed themselves, emitted near the acute extremities of the octahedron, the slide being held considerably below the level of the eye, with the crystals in a vertical position, and the light coming from above and behind the slide. I put the matter aside till recently, ascribing, without much consideration, the brilliant appearance to diffraction colours arising from striations on the octahedral faces and internal reflections within the slide. Only recently I have found that the light is transmitted, being refracted and dispersed by passage through the acute pyramids of the octahedron. Holding the slide at the proper angle against the light so as to produce the brilliant silvery blue light over the lower octahedral face, it was found possible, using a lens, to *see* objects held above and behind the slide in close contact with the glass: the meshes of wire gauze, for instance. The wires of the mesh are then seen to be bordered with spectrum colours, just as large objects appear when examined through a glass prism held close to the eye. Placed on the stage of the microscope, and an image of a mantle-burner formed beneath the crystal by the substage condenser, every detail of the luminous meshes could be seen through the greater part of the crystal. In this experiment, it could be plainly observed that the true colour of the anatase was a pale blue.

Other specimens were examined with the same results, in balsam and in melted sulphur (refractive index about 2). In the last material (even if it be let grow solid around the anatase), the clear transparency and pale blue colour of the crystals may often be seen to extend through the entire mass of the crystal.

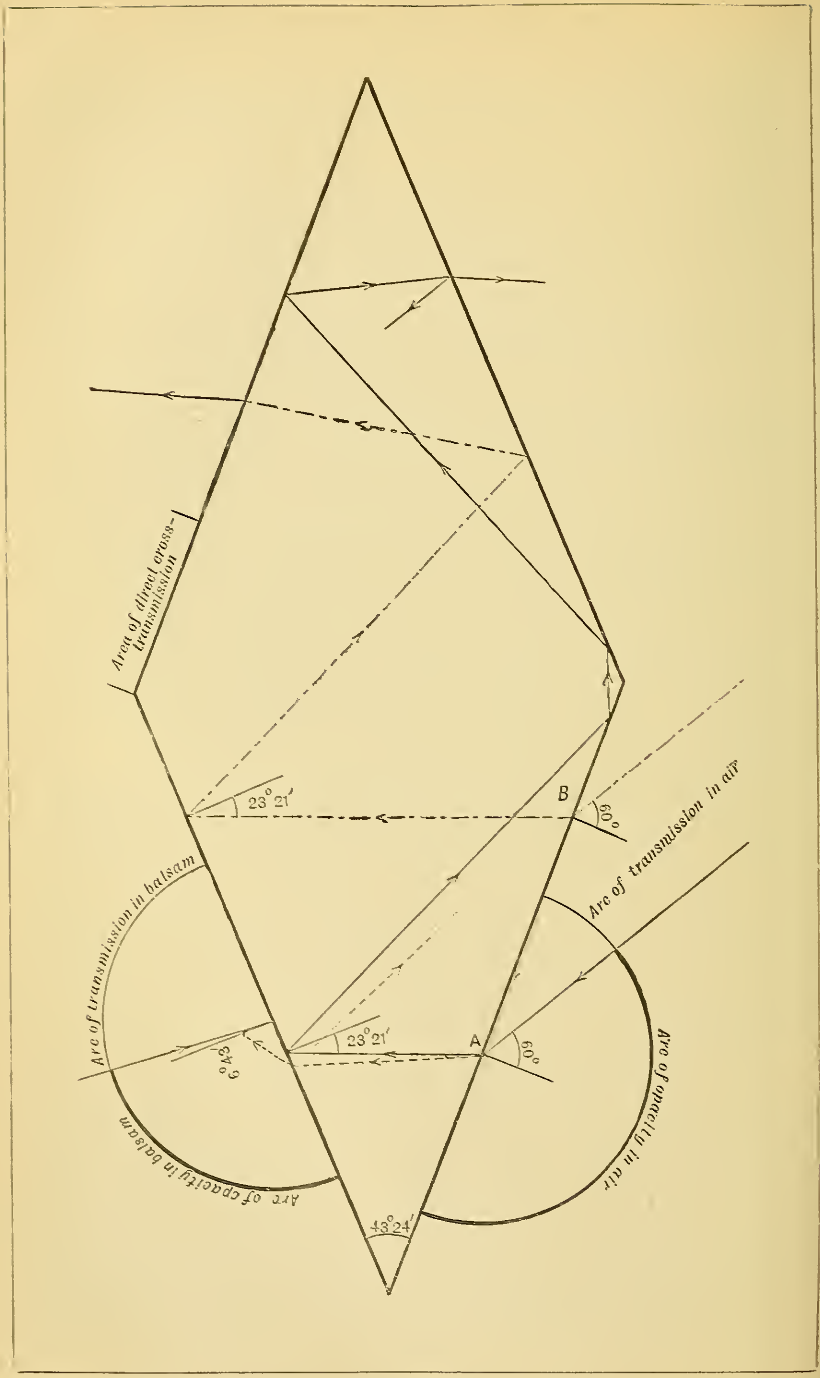
To what, then, is the apparent opacity of the lustrous black anatase due? An explanation is readily found.

The refractive indices of anatase are, for D wave-lengths, $\omega = 2{\cdot}53536$, $\epsilon = 2{\cdot}49588$ (Schrauf), the mean index being given as 2·524. The corresponding critical angle in air (ϕ) is 23° 20′. A ray of light, therefore, entering the octahedron, and meeting the opposite face at any angle of incidence greater than this, is totally reflected, and retained within the crystal. If it meets it at an angle of incidence *very* nearly as great as this, some may escape, but the greater part is retained. It will then return to the illuminated side, and either escape or be again reflected wholly or in part.

It is easy to show that, if a prism of any material be cut to such a refracting angle, that this is equal to 2ϕ for the particular substance and wave-length, then no light of this wave-length can pass through the prism, or, what is practically the same thing, only that ray can pass which enters and emerges at grazing incidence. In fact, a ray in such a prism enters at grazing incidence with a refracting angle ϕ, and preserves the symmetrical position of minimum deviation, emerging at the grazing angle. Now the critical angle for the mean refractive index of anatase is, as we have seen, 23° 20′, and the opposite faces of the octahedron meet at the apex of the octahedron at the angle 43° 24′. This is so nearly the value of 2ϕ (46° 40′), that rays refracted according to the mean index, even if entering at grazing incidence (90°), are to a great extent returned by internal reflection, and those arriving at an incidence of less than 60° are totally reflected within the crystal, and that not only at the first reflection, but are repeatedly retained from escape by internal reflection, total or partial; finally for the most part escaping on the side of entry.

Only near the basal edge of the octahedron are the phenomena different. Here rays can pass through the opposite parallel faces of the octrahedron, and accordingly a transparent belt should here be detected. Unmounted crystals examined for this belt sometimes exhibit it in the form of a chink of blue light: its visibility is, however, often greatly reduced by deep-cut striations near the basal edge, which divide and scatter the light both at entrance, at exit, and within.

The accompanying figure shows the path (dotted) of a ray entering a vertical section of the octahedron (at the point 'A') at grazing incidence (90°); also one entering at an angle of incidence (60°) such that it is totally reflected at the opposite face of the crystal. The course of the last is then traced (full line) till it finally is, for the most part, returned (if not previously absorbed) at the side of entry. A second ray entering at an incidence of 60°, but so near the base (point B) as to meet on second reflection the adjoining face above the base, is also traced (dot and dash line).


Area of direct cross-transmission
23° 21′
B
60°
Arc of transmission in air
Arc of transmission in balsam
23° 21′
A
60°
6° 43′
Arc of opacity in air
Arc of opacity in balsam
43° 24′

It is thus seen that transmission, save near the basal edge of the pyramid, is very limited, almost nil. It will be evident that the transmission of the ordinary ray (anatase being optically negative, and the ordinary index the greater) will be more restrained than the extraordinary.

The difficulty of passing a ray through these crystals vanishes when they are immersed in a substance of high refractive index, such as Canada balsam (1·593). The index from balsam to anatase is 1·584, and the critical angle 39° 9′. Rays entering from balsam at an incidence less than 6° 43′ are totally reflected and returned. There is thus a wide arc of transmission from grazing incidence (90°) to 6° 43′, an arc of 82° 17′. This arc is set out in the figure. In consequence, light entering from the air, refracted by the glass and balsam of the cell in which the crystal is mounted, reaching the crystal incident within this arc, passing through and again bent both on emergence from the anatase and the containing balsam and glass, finally reaches the eye, deviated some 43° from its original path. This angle was observed by a refractometer.

The light coming through the crystal, imbedded in Canada balsam, exhibits spectrum colours which, however, appear to be pure only at either end of the visible spectrum. That is, when the crystal is held at the suitable angle, and illuminated by a small and bright source of white light, the red, first brought into view, is seen to have the richness and purity of the lower red of a pure spectrum. The orange, yellow, and green which succeed are evidently whitish and impure, but the blue and violet are rich and brilliant. This is explained as follows :—

The ray of white light entering the crystal is resolved into two plane polarized rays. One, the ordinary, executes vibrations, the refractive indices of which are, for the B wave-lengths, 2·51118, for the H wave-lengths, 2·64967. These indices are constant, *i.e.* are independent of the inclination of the rays traversing the crystal. The second, the extraordinary ray, vibrating in the plane of incidence and of the optic axis, has indices which vary with the inclination of the rays within the crystal; that is, with their direction in the ellipsoid of elasticity. When the rays are transmitted at right angles to the optic axis, the B vibrations have the index 2·47596, the H 2·58062.[1] The substance is, in fact, optically

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[1] Schrauf, Wien. Ak. Ber. 42, 1860, p. 107.

negative, and for the same wave-lengths the ordinary index is greater than the extraordinary. It follows at once that the polarized rays are dispersed into spectra which are considerably different in deviation. Each wave-length, according as this has been polarized within the crystal in the ordinary or extraordinary direction, seeks its own focus.

The ordinary vibrations will, for each wave-length, show a greater deviation than the corresponding wave-lengths of the extraordinary vibrations. Thus two overlapping spectra are formed. The violet and part of the blue are solely formed of polarized ordinary vibrations, and are therefore pure; the green, orange, and red of the ordinary are mingled with the violet, blue, and green of the extraordinary, and are thereby rendered impure; while finally, at the end of the spectrum nearest the refracting angle, the red of the extraordinary spectrum exists unadulterated with shorter wave-lengths.

The relative positions of the two spectra may be roughly compared by a Haidinger's dichroscope, which simultaneously shows two images of the crystal, the one of ordinary rays only, the other of extraordinary. The light refracted through the lower faces of these images is seen to be differently coloured: a violet ordinary image being accompanied by a dark extraordinary; a green ordinary by a violet extraordinary, and so on.

These spectra may be more accurately observed and compared on a refractometer—or a goniometer used as such—the collimator being fitted with a nicol over the lens. When the nicol is placed with its plane of polarization in the horizontal position, the optical axis of the crystal being also horizontal, we observe the extraordinary spectrum only, and when the nicol is now turned through a right angle, the ordinary spectrum only. The phenomena observed are very striking and beautiful, the dispersion being considerable; the refracting pyramid of the octahedron lighting up with brilliant flashes as the nicol is rotated. Accurate measurements are complicated by the effects of the balsam, and were only attempted so far as was requisite to obtain assurance as to the nature of the effects observed. The colours appearing in anatase when rays refracted through the pyramids are examined by a nicol, present, in short, a polychroism, due neither to absorption nor to interference, but to refraction only.

The readiest mode of exhibiting the very perfect transparency of many of these black and seemingly opaque crystals is to imbed them in melted sulphur or fused silver nitrate. The first mentioned substance is excellent, as formerly observed. The results may be examined either when the mountant is melted or solidified. Through the yellow translucent sulphur we see, in the latter case, the sky-blue anatase, like certain clear, pale sapphires; every enclosure and flaw within being clearly visible. Some of them have large cavities; others enclosures having the form of spirally arranged plates (Brookite ?), or quite irregular cloudy enclosures. Nevertheless, examined by the naked eye in the air, no trace of transparency may be revealed.

A similar phenomenon is, in a less degree, exhibited by other substances of high refractive indices. A cleavage fragment of blende will present a perfect opacity on edges which, when more carefully examined, are found to be transparent. It is remarkable that anatase crystallises with such an apical, interfacial angle as to exhibit the phenomenon nearly at its greatest degree of perfection. Even if rigorously possessing 2ϕ as the value of the refracting angle, but little would be gained in opacity, while the capabilities of direct cross-transmission from diagonally opposite and parallel faces of the octahedron would be increased. The nearly complete transparency of wiserine is a consequence of the subordination of the acute octahedral faces in its case.

It will be gathered from the foregoing explanation of the behaviour of anatase that the high lustre and smooth surface play an essential part in bringing about its pseudo-opacity. Any dullness or roughness permits light both to enter and leave the crystal irregularly, and the phenomenon described does not occur.

XXXVI.

INCANDESCENT ELECTRIC FURNACES.

By J. JOLY, M.A., Sc.D., F.R.S., Hon. Sec. R.D.S., Professor of Geology and Mineralogy in the University of Dublin.

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It is now more than a year ago since I made, for a special purpose, a minute electric furnace consisting of a platinum wire imbedded in refractory clay. It was obvious that the construction admitted of many applications to experimental purposes. In my own case I desired to obtain an intense local temperature undisturbed by chemical effects, and which might be prolonged for many hours, or even days, without risk of serious variation in temperature; as the matter being investigated was the viscous yielding of silicates at high temperatures. Postponing for the present an account of the special apparatus I then constructed, I proceed to describe the principles and mode of construction of the incandescent electric furnace which originated in these experiments.[1]

Any form suitable to requirements may be given to the furnace. If required for fusions, chemical operations, roasting, etc., the crucible pattern is most convenient. The conducting wire of platinum or manganese steel may be imbedded in the wall of the crucible itself, or in the wall of a furnace within which the crucible is placed. The latter form is of the most general use (see figure). Here an outer vessel of fireclay, lined with a reflector, encloses the crucible-shaped vessel in which the wire is imbedded, and which may be maintained at a white heat by a current. Within this vessel the crucible containing the substances being operated on is placed. The inner crucible may obviously be of any refractory material, platinum, Berlin porcelain, etc.

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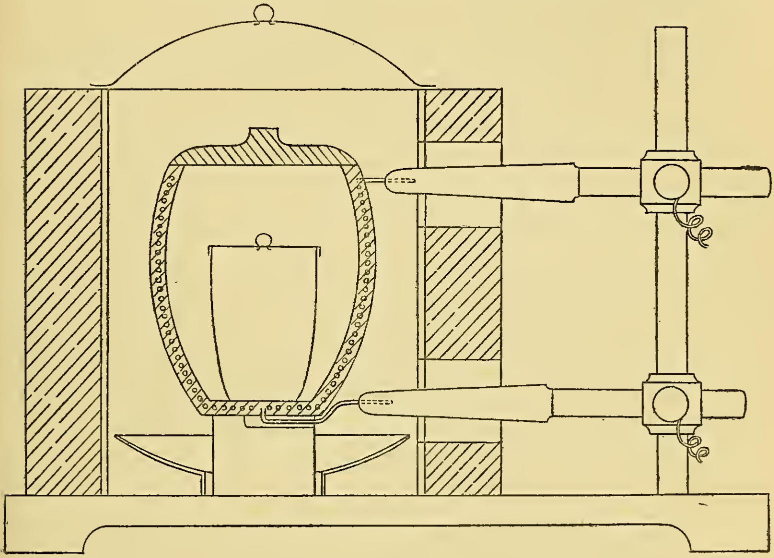
[1] Described in a provisional protection (since abandoned), dated March 15, 1900 (No. 4892).

In these furnaces the fireclay plays the part of a conductor of heat, but not sensibly, of electricity—distributing the heat produced on the wire evenly over the area of the vessel. It will probably be found that under prolonged usage—unless the clay is a nearly pure silica—the electrical resistance of the clay will diminish. But the change is a slow one, even in impure clays.



A refractory clay, rendered coherent by silicate of soda (as supplied by Messrs. Fletcher, of Warrington), has successfully served many purposes to which I have applied these furnaces. A certain amount of cracking ensues with this clay after repeated heating; but the wire binding the parts together maintains the integrity of the crucible with but little loss of usefulness.

The wire is best of platinum, and as it may be used over again on the wearing of the crucible, it is not a source of running expense. A diameter of about two-thirds of a millimetre is not too heavy. The temperature obtained must be found by melting substances of known fusibilities in the inner vessel. A chart of current and temperature may then be plotted, and will hold good for a considerable amount of use, but should be checked by occasional observations. The regulation of the temperature is an easy matter, as any current regulator will accomplish it:

nor would it be difficult to cause the crucible to regulate its own temperature by the changes of resistance which a platinum thermometer placed within the heated muffle would experience.

It is apparent that for experimental petrology this method of utilizing electric energy in maintaining constant temperatures for long periods and local in application should prove of value.

Where platinum wire is not used, the life of the crucible is briefer, owing to the largely unequal expansion of the wire and the fire-clay. This difficulty might be obviated by imbedding the wire, in the first instance, not naked, but covered by a substance which, on the baking of the crucible, would be removed; *e.g.* a non-conducting fusible material (as paraffin wax), or a cotton covering which would be practically removed by combustion. In this way space would be left in which the wire might expand.

The particular manner in which the wire is coiled is not of importance, provided it is distributed with approximate uniformity throughout the fire-clay; a flat spiral for the bottom, rising in an expanding helix in the walls, is the form I have found most useful. For some purposes it may be advisable not to imbed the wire, but to insert it between an inner and an outer refractory vessel.

XXXVII.

ON AN IMPROVED METHOD OF IDENTIFYING CRYSTALS IN ROCK SECTIONS BY THE USE OF BIREFRINGENCE.

By J. JOLY, M.A., ScD., F.R.S., Hon. Sec. R.D.S., Professor of Geology and Mineralogy in the Univsrsity of Dublin.

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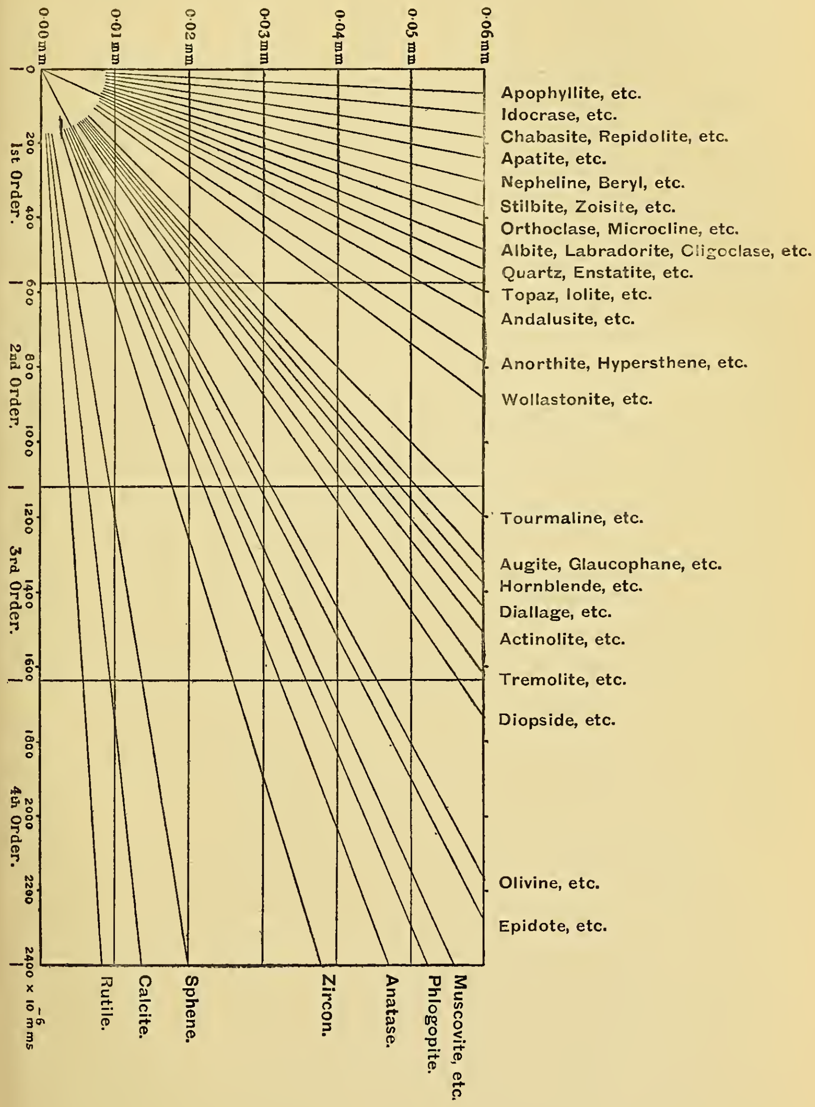
Optically uniaxial minerals when compared in sections of equal thickness give the highest interference colours in sections parallel to the optic axis and biaxial substances in sections taken at right angles to the optical normal; in other words, in sections containing the greatest and least axes of elasticity, and, therefore, containing the optic axes.

From these principles is derived one of the most valuable means of diagnosis at the disposal of the petrologist; for not only are many substances sharply differentiated from others by the brightness and colour of their interference tints, but this character is generally ascertained after a brief examination.

A section of the substance under investigation is sought which shows the highest interference tint according to Newton's scale of colours. This tint will appear in greatest intensity when the principal section of the plate is at 45° with the planes of vibration of polarizer and analyser. If the crystals of the substance are at all numerous in the rock slice, the sections exhibiting the highest tint will almost certainly approximate to the maximum interference tint proper to the specific mineral and the thickness conferred upon it in the rock slice. We may now, by the use of M. Michel Lévy's *Comparateur*, estimate the retardation giving rise to the observed tint, and, dividing by the thickness of the rock slice (expressed in the same units of length as are used to measure the retardation), determine the birefringence; or we may, in many cases, proceed still more directly to find this important constant by reference to the valuable chart which MM. Lévy and Lacroix have provided in their work: "Les Minereux des Roches." It will facilitate the understanding of the simple apparatus to be described in this paper if the nature of this chart is first briefly referred to (fig. 1).

From left to right, over the rectangular area of the chart, are reproduced the successive colours, according to Newton's scale, as derived from interference produced by increasing retardations in a crystalline plate of differing elasticities. The chart is thus, in the original, traversed by vertical bands of colour, which begin at black, and, passing through grays, white-grays, white, yellowish-white, yellow, orange-yellow, etc., etc., reproduce the first four orders of Newton's scales—beyond which the tints become so diluted with white as to be useless. The scale, according to which these colours are distributed horizontally, is to a unit of 1×10^6 mms., or millionths of millimetres retardation.

The amount of retardation being made up of the product of two quantities—the thickness of the plate and its birefringence—we can assign to its place on this scale any suitably oriented section of known thickness and birefringence; *i.e.*, we can determine the interference colour to which it will give rise. Let the entire vertical height of the chart represent to scale a mineral section of the thickness 0·06 mms. We can now assign to any substance of known birefringence a place along the upper boundary of the chart, scaling from the left (according to the scale of millionths of millimetres used to distribute the colours) the retardation proper to a plate of the substance possessing the thickness of 0·06 mms. Thus if, for example, the substance be quartz, which has a birefringence of 0·009, we place it on this upper line, at a distance measured to the right of 54×10^6 mms.; this being the product of the thickness and birefringence. The colour at this point will be that produced by a quartz plate of the thickness 0·06 mms. But as the retardation is proportional to the thickness, we can, by joining this point on the upper boundary to the lower left-hand corner (the origin) of the diagram, obtain at once an indication of the tint which any thickness of quartz less than 0·06 mms. will occasion. We simply ascend this uniformly inclined line proper to quartz till we have risen in the diagram to a height corresponding to the thickness of our section, and at this point find the tint to be expected. Accordingly the diagram is divided, as shown by horizontal lines drawn at heights representing to scale thicknesses of


0·00 mm
0·01 mm
0·02 mm
0·03 mm
0·04 mm
0·05 mm
0·06 mm
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400 × 10⁻⁶ mms
1st Order.
2nd Order.
3rd Order.
4th Order.
Apophyllite, etc.
Idocrase, etc.
Chabasite, Repidolite, etc.
Apatite, etc.
Nepheline, Beryl, etc.
Stilbite, Zoisite, etc.
Orthoclase, Microcline, etc.
Albite, Labradorite, Oligoclase, etc.
Quartz, Enstatite, etc.
Topaz, Iolite, etc.
Andalusite, etc.
Anorthite, Hypersthene, etc.
Wollastonite, etc.
Tourmaline, etc.
Augite, Glaucophane, etc.
Hornblende, etc.
Diallage, etc.
Actinolite, etc.
Tremolite, etc.
Diopside, etc.
Olivine, etc.
Epidote, etc.
Rutile.
Calcite.
Sphene.
Zircon.
Anatase.
Phlogopite.
Muscovite, etc.

0·01, 0·02, &c., mms. Plotting in this manner the lines of the principal anisotropic transparent minerals, MM. Lévy and Lacroix have provided a chart from which by inspection the interference colour of crystal sections of known mineral species and thickness can be ascertained.

Ordinary good rock-sections are about of the thickness 0·015 to 0·02 mms. It follows that we find in such sections many of the most abundant of the rock-forming minerals showing but little differences in their maximum interference tints. Thus quartz, orthoclase, many of the plagioclase felspars, and even nepheline and topaz, may, so far as the colour diagnostic is concerned, be confounded in the more thinly cut sections. In order to evade this difficulty, a quartz plate may be used to raise the interference tint of the crystal and transfer it to the orange, reds, or blues, of the first or second orders, which then may be determined by a *comparateur*. A glance at the chart (fig. 1) will, however, show that this cannot be expected to give distinctive results in all cases. We find, for example, that the sloping lines proper to quartz, plagioclase (for the most part), and orthoclase, are so closely approximated by their convergence at the small thickness obtaining in good sections, that merely adding equally to the retardation produced by each substance, and thus shifting the whole series upward in the scale of colours, that is to the right on the chart, cannot produce discriminative differences. MM. Lévy and Lecroix recommend that the auxiliary quartz plate of known retardation be, for the sake of greater sensitiveness, cut to the thickness proper to the *teinte sensible*. It would appear, however, better in such cases to use a wedge of quartz, graduated on the edge, and in each case adjust it over the section till the tint of passage is found.

A method which I have found of great use in increasing the discriminative value of birefringence can now be intelligibly described. It will at once appear that could we transmit the polarized ray *twice* through the section under investigation an interference effect is obtained equivalent to that of a section of twice the thickness. We would, in such a case, without having recourse to sections of a thickness unsuitable to observations with high powers, obtain the more distinctive interference effects of crystal plates 0·03 to 0·04 mms. thick. At this thickness the lines proper to the several substances have attained double their former divergencies and corresponding colour changes. In other words, their effects are distributed over twice the range of colour-variation. The nepheline line exchanges its dull gray for white of the first order; the microline, anorthoclase, and orthoclase line enters on the yellow, sections assuming a straw yellow tint; the albite, oligoclase, and labradorite line rises into a distinct pale yellow; the quartz-enstatite line rises to a bright yellow, while topaz and iolite enter the orange-yellow. Referring to the more strongly birefringent substances, we find anorthite rising from the palest straw yellow to a full orange-red; hypersthene will closely follow the same colour change. Tourmaline exhibits a conspicuous change of tint, from yellow of first order to green and bluish green of the second order. Augite rises from shades of orange-yellow of first order to corresponding shades of the second order, the colour-change being in amount just the one order. In a word, we find that a large number of the most important minerals—such as augite, tourmaline, hornblende, diallage, actinolite, which in the thickness of the normal rock-section show interference colours restricted to the yellows and oranges of the first order, in sections of doubled thickness—possess tints distributed over the much more varied hues of the second order, and with differences of retardation increased two-fold. Again, minerals which in normal rock-sections appear in the vivid colours of the second order become displaced into the pale and milky tints of the third and fourth orders.

The optical arrangements whereby the polarized ray may be passed twice through the section are very simple. An "opaque illuminator" of the Zeiss, Leitz, or Nachet pattern may be used. Fig. 2 explains its construction. It will be seen that light entering through the opening in front of the prism is reflected downwards through the objective and so on the object being examined, the ray being again returned by reflection from the object into the microscope and to the eye of the observer. In the figure the illuminator (which strictly consists of the collar and prism only, seen above the objective) is shown furnished with a nicol prism placed over the aperture. The illuminator thus reflects downwards on the object a polarized beam. This addition is necessitated by the present method. The only other apparatus required is a small mirror to be placed immediately beneath the rock-section upon the stage of the microscope or laid on the upper surface of the Abbe condenser, when it may be lowered till flush with the surface of the stage. The polarized ray after passing downwards through the crystal under examination is reflected upwards by this mirror and passes a second time through the section before reaching the eye of the observer. If the crystal plate is placed with its principal axis at 45° with the plane of polarization of the ray incident from the illuminator, and, if higher, in the microscope, or above the eye-piece, is placed a second nicol set to extinction with the beam from the uncovered mirror, the interference tint received from the crystal is the maximum one proper to a plate of twice the actual thickness of the section.

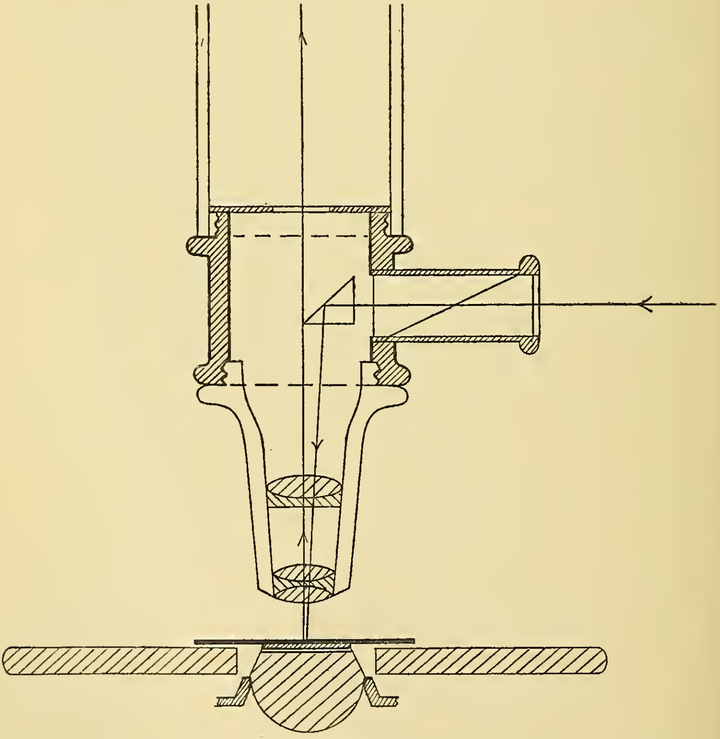


Fig. 2.

For the mirror a disc of polished speculum metal, or silver (about one centimetre in diameter or less), gives the best results, and in the case of small crystals it is well to place the section cover-glass downwards upon the mirror, so that the reflecting surface is as close as possible to the crystal plate. A small galvanometer mirror of long focus also serves the purpose, but not so well. With diffused daylight, and without aid of condenser, the use of a No. 3 Leitz gives ample illumination. Considerably higher powers may be used with concentrated rays, solar or artificial. The application of this mode of examination to crystals of very small dimensions is, with the foregoing arrangements, not satisfactory owing to a certain amount of paralactic displacement of the ray returning from the mirror: the illumination not being quite vertical.

The change of phase, introduced by reflection at the surface of the metal, of the component vibrations into which the crystal plate resolves the rays from the illuminator, appears to be sufficiently small to be negligible. It can be shown that the change of phase produced by metallic reflection of a polarized ray at normal incidence is zero, and will be small at the higher angles. In the present case the ray is nearly normal. The loss of phase arising on the total reflection of the beam within the prism of the illuminator, and before the rays reach the rock-section, might be expected to create a more marked effect. However, when elliptic polarization is sought for by a double image prism of Iceland spar replacing the eye-piece of the microscope, the extinction of the one image is found to be very perfect; as complete, nearly or quite, as when the normally polarized beam of the sub-stage nicol is examined in the same manner. The disposition in which the ray reflected in the illuminator is polarized at right angles to the angle of incidences should be the best.

A simple experiment further serves to show that for thin sections at least, this method of examining a crystal plate truly affords an interference colour proper to a section of double the thickness. A thin cleavage flake is taken from a limpid crystal of selenite, and of such a thinness as to show a vivid interference colour in transmitted light, and uniformly over a sufficient area. The plate is then cut across the area of uniform illumination and the two halves attached upon a glass slip, the cut ends being overlapped by a millimetre or thereabouts. Examined now, first in light once transmitted through the plate, the doubled thickness where the plates overlap should present the same interference tint as the single thickness will reveal when examined in polarized light twice transmitted through the crystal. It is found to prove so. The same experiment may be made with cleavage plates of mica.

It will be evident that in this method of examination colour effects due to rotary polarization, as in the case of quartz, are eliminated, for the rays evidently traverse the plate on their second passage, in the opposite direction as regards right and left to that which obtained on their first passage. However, as in thin sections these effects are in any case inconspicuous or inappreciable, this fact appears to be of no value in diagnosis.

Colour effects due to absorption are increased in intensity by the double transmission of the rays through the plate.

The mode of procedure in the examination of a rock-section by the arrangement I have described is very simple. The illuminator, with its attached nicol, is first inserted above the objective, and the reflecting prism of the illuminator turned till white light, received from the clouds or from an artificial source of white light, entering the nicol of the illuminator, appears reflected to the eye from the little mirror which is laid upon the upper surface of the Abbe condenser. This adjustment is easily made. The analyser or upper nicol of the microscope is now placed in the position which it occupies when its plane of polarization is at 90° with the sub-stage nicol, and the nicol attached to the illuminator turned till the light reflected from the mirror is extinguished. The sub-stage polarizer and the nicol of the illuminator are now similarly oriented with regard to the analyser, and neither need be disturbed during subsequent operations.

Removing the mirror and placing the rock-section on the microscope stage, examination for a maximum extinction tint is made by trial of several sections of the mineral being investigated in the usual manner. One of the brightest being selected and placed at 45° with its position of extinction and its tint then carefully observed, the Abbe condenser is lowered and the little mirror placed on its upper surface by means of a forceps, and the Abbe again raised till the mirror is in contact with the slide, which, if the crystal is small, should be face downwards on the stage. [The smallest crystals should be examined in this position without a cover-glass.] The light transmitted from beneath is now cut off from the section, and that entering from the illuminator caught by the mirror and returned through the crystal to the eye. The crystal originally showed a white, suppose; it now exhibits a clear and pronounced yellow. If the question was between orthoclase and quartz, the decision is that the mineral is quartz. Measurement of the thickness of the section is, in such a case, hardly required, for a section of orthoclase giving a distinct yellow must possess a thickness of over 0·05 mms., and half of this thickness is more than is usually conferred upon good rock-sections. Generally, too, undoubted felspars or other minerals will be present, observation of which in the same manner will settle the question. A more accurate mode of using this method is to measure the retardation in each case with the *comparateur.*

The illuminator may be left permanently in position upon the microscope if provision is made for the withdrawal of the reflecting prism when its use is not required. The mirror, which need not be more than 5 or 6 millimetres in diameter, might conveniently be carried in a sliding piece fitted in the stage of the telescope. Or a half mirror only is used (or one perforated centrally), so that part of the field is illuminated by once-transmitted, part by twice-transmitted light. This may be left in position during most examinations, the tints due to double thickness being compared with those of single thickness by a small movement of the slide; or even when obtaining simultaneously in the one crystal, one half of the crystal being brought over the mirror, while the other half is illuminated by light transmitted from beneath.

Alternative dispositions of the polarized illuminator of course also suggest themselves. Thus the small loss of phase due to elliptic polarization upon reflection of the beam may be obviated by placing the reflector above or in advance of the polarizer, locating both in the wider body of the microscope above the objective. This, however, is hardly required. A construction which would confer more perfect verticality upon the incident ray would, however, be advantageous as enabling examination by this method to be extended to more minute crystals. Perfect verticality would be obtained by the use of a semi-transparent mirror placed in the axis of the microscope and at 45° with this axis; this mirror reflecting the polarized beam, and transmitting the ascending beam. However, a disposition which secures a degree of verticality sufficient for the examination of very fine-grained rocks consists in applying a construction similar to that figured in the text at a point higher up in the body of the microscope. This may be conveniently done by utilising the aperture provided in many microscopes for an analyser between objective and eye-piece. Into this aperture a nicol, carrying at its inner extremity a totally reflecting prism, is pushed. The horizontal ray is received either from a mirror or lens, enters the nicol, and after traversing it is reflected downwards, nearly in the axis of the microscope. The disposition is in fact essentially similar to that figured, but its location higher in the microscope reduces the angle between the incident and reflected rays. For most purposes the use of the ordinary opaque illuminator, fitted with a nicol, is quite adequate.

XXXVIII.

A NEW THERMO-CHEMICAL NOTATION. By JAMES HOLMS POLLOK, B.Sc.

[Read April 17 ; Received for Publication April 19 ; Published July 6, 1901.]

In the study of Thermo-chemical Equations a good deal of difficulty is experienced in clearly and briefly expressing the various quantities under consideration, so as to retain a view of the actual chemical and physical changes taking place, and likewise of the quantity of heat evolved or absorbed thereby. No doubt, in print, one can readily state in the preamble the particular states of the various reagents and products, and tabulate the thermal quantities in a clear and intelligible manner ; but, in the actual calculations necessary to arrive at these tabulated results, the tendency to confusion is very great indeed, and though the methods of Thomsen or Berthelot have been found to work well in the past they are scarcely now sufficient. Thomsen's method of statement is logical and correct from a purely thermal point of view, but is exceedingly confusing from a chemical point of view. Berthelot's method, on the other hand, is clear, because the chemical equation is retained almost without alteration, but as it is not an algebraic equation, it is only a statement of results, and gives no facility for further calculation. What is required is a correct algebraic equation which will at once indicate clearly the chemical and physical changes under consideration, together with the heat evolved in the reaction. Each definite quantity of matter or energy being indicated by a definite symbol, so that the sum of the system before and after the reaction will be clearly set forth. Such an equation would obviously be capable of all the processes of algebra for the determination of unknown terms. In the thermal expression of any ordinary chemical reaction it is necessary to take account not only of the state of combination of all the reacting elements, both before and after the reaction, but also of the precise physical state of each reagent and product. Now the heat due to distinctly physical change is divisible into five quantities; viz., the heat capacity or specific heat of the body in the solid, the liquid, and the gaseous states, and the latent heat of fusion and of vaporization. The heat due to distinctly chemical change is divisible into two quantities, the heat of formation from the elements, and the heat of allotropic or molecular modification. To these must be added the heat of hydration, solution, and dilution, in aqueous and other solvents, changes of a partly physical and partly chemical character. That is for each individual substance taking part in a reaction, we have no less than ten distinct quantities to keep a record of, so that with a very simple chemical equation, involving no more than two reagents and two products, we might have no less than forty magnitudes to deal with. It is therefore highly desirable that we should be able to briefly and clearly indicate them, without burden to the memory, without confusion in the calculation, and without destroying the purely chemical interpretation of the equation.

Inasmuch as matter and force are indestructible, if we start with any given quantity of matter and force, and go through any number of operations, we must still have the same quantity of matter and force, and to keep a clear and intelligible record all that is necessary is to express precisely the total matter and energy at the initial and final stages of our reaction, and see that those balance. The energy that invariably falls to be measured is that evolved by our operation. If we were able to state exactly the total energy associated with each particular element or compound in any reaction, and coupled such with the symbol expressing the matter thereof, then the energy evolved in a reaction would simply be added to the equation as one of the products of the reaction, after the manner of an ordinary chemical equation, and the equation would then balance both in matter and energy; but there is no hope that we will ever be able to ascertain the total absolute quantity of energy associated with any substance, for no matter what processes we subject it to, we can never be certain that we have depleted it of all its energy. The only energy of which we have any real knowledge is that evolved in the transition of any system of atoms or molecules from one state to another. It is therefore necessary to select arbitrarily a particular state as our standard of reference and then indicate the heat evolved, be it positive or negative, in the transition from this state to any other. The particular state that I believe to be the most convenient for the standard of reference is that of the elements in their normal condition at 0° C., but by common consent 15° C. has already been chosen. The heat of formation of a gram molecule of any particular compound is therefore the energy evolved, and measured as heat in its formation from the elements in their normal condition at 15° C. This evolved energy I indicate by affixing to the formula the letter ξ with the numerical value of the heat evolved, represented in kilogram or gram degrees per gram molecule, and indicated by the letters $K°$ and $k°$ as suggested by Mr. J. Y. Buchanan, thus $\xi H_2O = 69K° = 69000k°$ represents that the heat evolved in the formation of water is equal to 69 kilogram degrees or 69,000 gram degrees per gram molecule. Where a substance undergoes change of state, and it is desired to indicate the heat evolved in this change, without reference to that of the formation of the molecule from its elements, this is done by enclosing the formula in brackets and indicating the initial and final states, at the bottom and top of the evolved energy sign. For example, if x be the heat evolved in the transition of water from the state "*a*" to the state "*b*," this would be indicated thus:—

$$\xi_a^b(H_2O) = xK°.$$

All quantities must be so dealt with that

$$\xi_a^b(H_2O) + \xi_b^c(H_2O) + \xi_c^d(H_2O) = \xi_a^d(H_2O),$$

and

$$\xi_a^b(H_2O) = -\,\xi_b^a(H_2O).$$

If, on the other hand, we wish to indicate the heat evolved when a system undergoes chemical change, the state of all the substances reacting is represented by the ordinary chemical notation, the initial state of the system being indicated at the lower part of the evolved energy sign, and the products of the reaction, or of the final state, at the upper part. Thus the formation of water from its elements might be represented by $\xi^{H_2O}_{H_2+O}$, but in all simple cases the lower part is understood and the symbol contracted to the form already shown ξH_2O and the complicated cases will be dealt with later under equations. To indicate the physical state of each substance the signs · – ⊤ or ° are placed under its formula or symbol to indicate the solid, liquid, gaseous, or dissolved states, after the manner of the vowel points in Hebrew. If the solution be other than a dilute aqueous one, an asterisk or other sign is used with a footnote to this effect, and if the solution be saturated the sign ⊙ is used, thus:—$\xi\underset{\cdot}{H_2O}$, $\xi\underset{-}{H_2O}$, $\xi\underset{\top}{H_2O}$ indicate the heat of formation of water in the solid, liquid, and gaseous states, respectively.[1]

In all cases where the energy under consideration is that of the formation of the substance in its normal condition at 15° C. from its elements in their normal condition at 15° C., it is indicated simply by affixing the evolved energy sign to the ordinary chemical formula of the substance, which is understood to be present in its molecular proportion in grams, and the signs for the solid liquid and gaseous states are omitted.

If the final state be other than the normal condition at 15° C., the proper sign must be used, and the temperature will be understood to be that of the transition from this state to the one nearest the normal. Thus

$$\xi\underset{\cdot}{CO_2} = 100{\cdot}1K^\circ$$

indicates the heats of formation of solid CO_2 at its melting point from its elements in their normal condition at 15° C.

If the initial state be other than the elements in their normal condition at 15° C., it is necessary to write the expression in full, thus:—

$$\xi^{\underset{-}{ICl}}_{\underset{\top}{Cl}+\underset{\top}{I}} = 9{\cdot}8K^\circ.$$

Or preferably expand it in the equation form as will be shown later. If the temperature be other than 15° C., or the melting or boiling point as above explained, or if the pressure be other than the normal, this should be indicated at the beginning or by placing an asterisk under the formula referring to a footnote, but this is very seldom required.

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[1] These signs may be conveniently remembered as follows:—

. *Solid*, the most coherent form of matter.
– *Liquid*, indicated by its horizontal surface.
⊤ *Gas*, tends to expand in three directions.
° *Solution*, substance in a surrounding medium.
⊙ *Saturated solution*, maximum solid present.

In any ordinary chemical equation it is obvious that the left hand indicates the initial, and the right hand the final states of the reacting substances; it is therefore unnecessary to place them one above the other, but we may enclose in brackets and place the evolved energy sign at the beginning, and the actual thermal quantity at the end, and if necessary the physical states beneath, thus:—

$$\xi\,[\mathrm{C_2\underset{-}{H}_6O} + 6\underset{\mathrm{T}}{\mathrm{O}} = 2\underset{\mathrm{T}}{\mathrm{C}}\mathrm{O_2} + 3\underset{-}{\mathrm{H}}_2\mathrm{O}] = 325{\cdot}7\mathrm{K}^\circ$$

expressing at once the chemical and physical changes, and their accompanying evolution of energy, in the combustion of 46 grams of alcohol. Now if it is remembered that the left hand is the initial and the right hand the final states, we need only affix the negative sign to every substance in its initial condition, and the positive sign to every substance in its final condition, abolish the equality sign within the brackets, and we get a true thermal and algebraical equation representing the evolution of energy in the transition from one state to the other, so that we may subject it to any number of transformations or changes, combine it with other equations, or subtract them from it, without any fear of error or confusion, thus:—

$$\begin{aligned}
&\xi\,[\mathrm{C_2H_6O} + 6\mathrm{O} = 2\mathrm{CO_2} + 3\mathrm{H_2O}] = 325{\cdot}7\mathrm{K}^\circ \\
&-\xi\mathrm{C_2H_6O} - \xi 6\mathrm{O} + \xi 2\mathrm{CO_2} + \xi 3\mathrm{H_2O} = 325{\cdot}7\mathrm{K}^\circ \\
&+\xi\mathrm{C_2H_6O} = -\,0 + 188{\cdot}5 + 207 \quad - 325{\cdot}7\mathrm{K}^\circ \\
&\qquad\qquad = 69{\cdot}9K^\circ.
\end{aligned}$$

The foregoing rule is a direct consequence of the general proposition that if we proceed from any one state of combination or condition to any other state of combination or condition the energy evolved or absorbed will be dependent solely on the initial and final states, and altogether independent of the particular stages by which they are reached. As we agree to select as our point of origin the normal condition of the elements at 15° C., we know that if $\xi_n^a(xyz)$ represent the energy evolved by any substances X, Y, Z in their transition from their normal elementary state "n" to a particular state "a," and likewise if $\xi_n^b(xyz)$ represent the energy they evolve in their transition to any other state "b," then the energy evolved or absorbed in the transition from the state "*a*" to the state "*b*" will be that obtained by subtracting the first quantity from the second which we express in our notation as :—

$$\begin{aligned} \xi^{a}_{n}(xyz) + \xi^{b}_{a}(xyz) &= \xi^{b}_{n}(xyz) \\ \xi^{b}_{a}(xyz) &= \xi^{b}_{n}(xyz) - \xi^{a}_{n}(xyz). \end{aligned}$$

If in a reaction we desire the thermal value after any change of state in either the reagents or products, all we need do is to *add* to each the thermal values of the particular changes of state, be these values positive or negative, and retain the sign proper to the position of each in the equation, or we might put the rule thus, add to every positive quantity and subtract from every negative quantity the thermal value of the particular change be it positive or negative. For example, if gaseous hydrochloric acid combines with gaseous ammonia to form solid chloride of ammonia we have the equation

$$\xi[\underset{\text{T}}{NH_3} + \underset{\text{T}}{HCl} = \underset{\cdot}{NH_4Cl}] = 42{\cdot}5\text{K}^\circ.$$

Find the thermal value of the reaction with the reagents and product in solution, given the heat of solution of ammonia, hydrochloric acid, and ammonium chloride, respectively, as :—

$$\xi^{\circ}_{\text{T}}(NH_3) = +8{\cdot}435\text{K}^\circ \;.\; \xi^{\circ}_{\text{T}}(HCl) = 17{\cdot}314\text{K}^\circ \;.\; \xi^{\circ}_{\cdot}(NH_4Cl) = -4{\cdot}00\text{K}^\circ.$$

$$\begin{array}{lllll} \xi[\underset{\text{T}}{NH_3} & + \underset{\text{T}}{HCl} & = \underset{\cdot}{NH_4Cl}] & = 42{\cdot}5\text{K}^\circ. & \\ -\,\xi\underset{\text{T}}{NH_3} & -\,\xi\underset{\text{T}}{HCl} & +\,\xi\underset{\cdot}{NH_4Cl} & = 42{\cdot}5\text{K}^\circ. & \\ -\,\xi^{\circ}_{\text{T}}(NH_3) & -\,\xi^{\circ}_{\text{T}}(HCl) & +\,\xi^{\circ}_{\cdot}(NH_4Cl) & = & -8{\cdot}435\text{K}^\circ - 17{\cdot}314\text{K}^\circ - 4{\cdot}00\text{K}^\circ. \\ -\,\xi\underset{\circ}{NH_3} & -\,\xi\underset{\circ}{HCl} & +\,\xi\underset{\circ}{NH_4Cl} & = 42{\cdot}5 - 8{\cdot}435 & -17{\cdot}314 \quad -4{\cdot}00. \\ \xi[\underset{\circ}{NH_3} & + \underset{\circ}{HCl} & = \underset{\circ}{NH_4Cl}] & = 12{\cdot}751\text{K}^\circ. & \end{array}$$

When the reagents and products are in their normal state at 15° C., or in dilute solution, there is as a rule no need to make mention of this, or it can be conveniently mentioned in the opening statement, and we may write at once our reagents with negative signs, our products with positive signs, and the evolved energy of the reaction in kilogram degrees, and then combine with any other equation similarly stated to eliminate common terms of the equations, and evolve the value of any unknown term; thus in dilute solution, we have

$$\xi[\mathrm{Zn} \quad + 2\mathrm{HCl} = \mathrm{ZnCl_2} + 2\mathrm{H}] \ = 34{\cdot}2\mathrm{K}^\circ,$$

and

$$\xi[\mathrm{ZnO} + 2\mathrm{HCl} = \mathrm{ZnCl_2} + \mathrm{H_2O}] = 17{\cdot}8\mathrm{K}^\circ.$$

Expand these in true thermal equations by lifting the brackets, affixing the energy sign to every quantity within them, placing a negative sign before each substance in its initial condition, a positive sign before each in its final condition, and removing the sign of equality within the brackets, and we have

$$- \xi\mathrm{Zn} \quad - \xi 2\mathrm{HCl} + \xi\mathrm{ZnCl_2} + \xi\mathrm{H_2} \quad = 34{\cdot}2\mathrm{K}^\circ,$$

$$- \xi\mathrm{ZnO} - \xi 2\mathrm{HCl} + \xi\mathrm{ZnCl_2} + \xi\mathrm{H_2O} = 17{\cdot}8\mathrm{K}^\circ.$$

Subtracting, transposing, and omitting zero quantities, we have at once

$$\begin{aligned} \xi\mathrm{Z\underset{\cdot}{n}O} &= 34{\cdot}2 - 17{\cdot}8 + \xi\mathrm{H_{\underline{2}}O}, \\ &= 34{\cdot}2 - 17{\cdot}8 + 69, \\ &= 85{\cdot}4\mathrm{K}^\circ. \end{aligned}$$

Possibly in a simple case like the above there is no necessity to go through this form of demonstration, or even use the energy signs, but the process of reasoning would be precisely that actually expressed above, and, if we take a complicated case, we find that the clearness of expression is a very real help in calculation, and avoids risk of confusion. If elements are capable of existing in allotropic forms, the best known, or most defined, is taken as the standard of reference and termed the *a* state, and all others indicated by Greek letters added at the right-hand upper corner of the symbol S^β, S^γ, S^δ.

We have now a full and clear expression of every quantity likely to occur in thermal equations, and for use, all that is necessary is to tabulate the heat of formation of all ordinary compounds in their normal condition at 15° C., from their elements in their normal condition at a like temperature, and also the molecular specific heats in the solid, liquid, and gaseous states, the molecular heats of fusion and vaporization, and the molecular heat of solution, of formation in solution, and of neutralization; and, for convenience in calculation, the total molecular heat of fusion and vaporization should also be tabulated, that is, the heat necessary to raise the substance from 15° C. to the temperature of fusion or vaporization and then fuse or vaporize it. Many of the physical data are wanting, but anything that clearly brings out what is wanting is one step in the direction of securing it.

I will now give some thermo-chemical Exercises in illustration of the proposed notation:—

1. Given that 12 grams of carbon in the state of diamond (α) gives on combustion to carbon dioxide 94·3 kilogram degrees of heat. State this in the notation

$$\xi CO_2 = 94{\cdot}3K^\circ.$$

2. Given the above, and the fact that the heat evolved on the solidification of 44 grams of carbonic acid is 5·8 kilogram degrees. Express in proper form the calculation for the heat of formation of carbonic acid in the solid state.

$$\begin{aligned} \xi C\underset{\tau}{O}_2 &= 94{\cdot}3K^\circ. \\ \dot{\xi}_{\tau}(CO_2) &= 5{\cdot}8K^\circ. \\ \xi C\underset{\cdot}{O}_2 &= 100{\cdot}1K^\circ. \end{aligned}$$

3. The heat of formation of a gram molecule of CS_2 in the liquid state is − 12·7K°, that of CO_2 is 94·3K°, and that of SO_2 is 69·2K°: find the heat of combustion of CS_2.

$$\begin{array}{ll} \text{Let} & \xi[CS_2 + 6O = CO_2 + 2SO_2] = xK^\circ. \\ \text{Then} & -\xi CS_2 - 6\xi O + \xi CO_2 + 2\xi SO_2 = x. \\ \text{Therefore} & +12{\cdot}7 - 0 + 94{\cdot}3 + 138{\cdot}4 = x. \\ & 245{\cdot}4 = x. \end{array}$$

4. Given the heat of formation of oxide of copper and nitric acid, and the heat of neutralization of nitric acid by the oxide: find the heat of formation of the salt in solution.

Let $\xi\underset{\cdot}{\mathrm{Cu}}\mathrm{O} = 37{\cdot}2\mathrm{K}^\circ$, $\xi\mathrm{H}\underset{\circ}{\mathrm{N}}\mathrm{O}_3 = 27{\cdot}1\mathrm{K}^\circ$.

and $\xi[\underset{\cdot}{\mathrm{Cu}}\mathrm{O} + 2\mathrm{H}\underset{\circ}{\mathrm{N}}\mathrm{O}_3 = \mathrm{Cu}(\underset{\circ}{\mathrm{N}}\mathrm{O}_3)_2 + \underset{-}{\mathrm{H}_2}\mathrm{O}] = 15\mathrm{K}^\circ$.

$$-\zeta\mathrm{CuO} - 2\xi\mathrm{HNO}_3 + \xi\mathrm{Cu(NO_3)_2} + \xi\mathrm{H_2O} = 15\mathrm{K}^\circ.$$

$$\begin{aligned}\xi\mathrm{Cu}(\underset{\circ}{\mathrm{N}}\mathrm{O}_3)_2 &= 15 + \xi\underset{\cdot}{\mathrm{Cu}}\mathrm{O} + 2\xi\mathrm{H}\underset{\circ}{\mathrm{N}}\mathrm{O}_3 - \xi\underset{-}{\mathrm{H}_2}\mathrm{O},\\ &= 15 + 37{\cdot}2 + 54{\cdot}2 - 69,\\ &= 37{\cdot}4\mathrm{K}^\circ.\end{aligned}$$

5. Given the thermal quantities

$$\xi\underset{T}{\mathrm{HI}} = -\,6{\cdot}2\mathrm{K}^\circ, \qquad \xi\underset{\circ}{\mathrm{HI}} = +\,13{\cdot}2\mathrm{K}^\circ,$$

$$\xi\underset{T}{\mathrm{H}_2}\mathrm{S} = +\,4{\cdot}6\mathrm{K}^\circ, \qquad \xi\underset{\circ}{\mathrm{H}_2}\mathrm{S} = +\,9{\cdot}2\mathrm{K}^\circ,$$

prove that the reaction

$$2\mathrm{HI} + \mathrm{S} \underset{\circ}{\overset{T}{\rightleftarrows}} \mathrm{H_2S} + \mathrm{I_2}$$

is thermally reversible, according to whether the substances be dry or in solution.

$$\begin{aligned}\xi[\underset{\circ}{\mathrm{H}_2}\mathrm{S} + 2\underset{\cdot}{\mathrm{I}} = 2\underset{\circ}{\mathrm{HI}} + \underset{\cdot}{\mathrm{S}}] &= x,\\ -\,\xi\underset{\circ}{\mathrm{H}_2}\mathrm{S} - \xi 2\underset{\cdot}{\mathrm{I}} + 2\xi\underset{\circ}{\mathrm{HI}} + \xi\underset{\cdot}{\mathrm{S}} &= x,\\ -\,9{\cdot}2 - 0 + 26{\cdot}4 + 0 &= x,\\ +\,17{\cdot}2 &= x.\end{aligned}$$

A positive quantity, the reaction is therefore thermally probable. If we reverse the equation and change the states, we have

$$\begin{aligned}\xi[2\underset{T}{\mathrm{HI}} + \underset{\cdot}{\mathrm{S}} = \underset{T}{\mathrm{H}_2}\mathrm{S} + \underset{\cdot}{\mathrm{I}_2}] &= x,\\ -\,\xi 2\underset{T}{\mathrm{HI}} - \xi\underset{\cdot}{\mathrm{S}} + \xi\underset{T}{\mathrm{H}_2}\mathrm{S} + \xi\underset{\cdot}{\mathrm{I}_2} &= x,\\ +\,12{\cdot}4 - 0 + 4{\cdot}6 + 0 &= x,\\ +\,17{\cdot}0 &= x.\end{aligned}$$

An almost equal evolution of heat in the opposite direction, consequent upon the change of state. We may therefore anticipate that the reaction will be reversible according as the substances are dry or in solution.

6. Find the heat of formation of hydrocyanic acid from its heat of combustion

$$\xi[2\underset{\mathrm{T}}{\mathrm{HCN}} + 5\underset{\mathrm{T}}{\mathrm{O}} = \underset{-}{\mathrm{H_2O}} + 2\underset{\mathrm{T}}{\mathrm{CO_2}} + \underset{\mathrm{T}}{\mathrm{N_2}}] = 316\mathrm{K}^\circ.$$

$$-2\xi\mathrm{HCN} - 5\xi\mathrm{O} + \xi\mathrm{H_2O} + 2\xi\mathrm{CO_2} + \xi\mathrm{N_2} = 316\mathrm{K}^\circ.$$

$$-316 + 69 + 188{\cdot}6 + 0 = 2\xi\underset{\mathrm{T}}{\mathrm{HCN}}.$$

$$\therefore\ \xi\underset{\mathrm{T}}{\mathrm{HCN}} = 29{\cdot}2\mathrm{K}^\circ.$$

7. Find the heat of formation of dilute sulphuric acid from the following data :—

$$\xi\underset{\mathrm{o}}{\mathrm{SO_2}} = 76{\cdot}8, \quad \xi\underset{\mathrm{o}}{\mathrm{HCl}} = 39{\cdot}3, \quad \xi\mathrm{H_2O} = 69.$$

$$\xi[\underset{\mathrm{o}}{\mathrm{SO_2}} + \underset{\mathrm{T}}{\mathrm{Cl_2}} + 2\underset{-}{\mathrm{H_2O}} = \underset{\mathrm{o}}{\mathrm{H_2SO_4}} + 2\underset{\mathrm{o}}{\mathrm{HCl}}] = 73{\cdot}9.$$

$$-\xi\underset{\mathrm{o}}{\mathrm{SO_2}} - \xi\underset{\mathrm{T}}{\mathrm{Cl_2}} - 2\xi\underset{-}{\mathrm{H_2O}} + \xi\underset{\mathrm{o}}{\mathrm{H_2SO_4}} + 2\xi\underset{\mathrm{o}}{\mathrm{HCl}} = 73{\cdot}9.$$

$$\therefore\ \xi\underset{\mathrm{o}}{\mathrm{H_2SO_4}} = +\xi\mathrm{SO_2} + \xi\mathrm{Cl_2} + 2\xi\mathrm{H_2O} - 2\xi\mathrm{HCl} + 73{\cdot}9$$

$$= 76{\cdot}8 + 0 + 138 - 78{\cdot}6 + 73{\cdot}9$$

$$= 210{\cdot}1.$$

For the heat of formation of pure sulphuric acid we have

$$\bar{\xi}_{\mathrm{o}}(\mathrm{H_2SO_4}) = -17\mathrm{K}^\circ.$$

$$\therefore\ \xi\underset{-}{\mathrm{H_2SO_4}} = \xi\underset{\mathrm{o}}{\mathrm{H_2SO_4}} + \bar{\xi}_{\mathrm{o}}(\mathrm{H_2SO_4})$$

$$= 210{\cdot}1 - 17$$

$$= 193{\cdot}1.$$

8. Given the heat of formation of hydrochloric acid, the heat of solution of chlorine, the heat of neutralization of hydrochloric acid and hydriodic acid by caustic potash, and the heat of substitution of iodine by chlorine in iodide of potassium: find the heat of formation of hydriodic acid in solution

$$\xi\underset{\mathrm{o}}{\mathrm{HCl}} = 39{\cdot}3, \quad \xi\underset{\mathrm{o}}{\mathrm{Cl}} = 1{\cdot}5.$$

1st. $$\xi[\underset{\circ}{\mathrm{HI}} + \underset{\circ}{\mathrm{KHO}} = \underset{\circ}{\mathrm{KI}} + \underset{-}{\mathrm{H_2O}}] = a \doteqdot 19{\cdot}1.$$

$$-\xi\underset{\circ}{\mathrm{HI}} - \xi\underset{\circ}{\mathrm{KHO}} + \xi\underset{\circ}{\mathrm{KI}} + \xi\underset{-}{\mathrm{H_2O}} = a.$$

$$\therefore \quad \xi\underset{\circ}{\mathrm{HI}} = -\xi\underset{\circ}{\mathrm{KHO}} + \xi\underset{\circ}{\mathrm{KI}} + \xi\underset{-}{\mathrm{H_2O}} - a.$$

2nd. $$\xi[\underset{\circ}{\mathrm{KI}} + \underset{\circ}{\mathrm{Cl}} = \underset{\circ}{\mathrm{KCl}} + \underset{\bullet}{\mathrm{I}}] = b \doteqdot 19{\cdot}2.$$

$$\therefore \quad \xi\underset{\circ}{\mathrm{KI}} = -\xi\underset{\circ}{\mathrm{Cl}} + \xi\underset{\circ}{\mathrm{KCl}} + \xi\underset{\cdot}{\mathrm{I}} - b.$$

3rd. $$\xi[\underset{\circ}{\mathrm{KHO}} + \underset{\circ}{\mathrm{HCl}} = \underset{\circ}{\mathrm{KCl}} + \underset{-}{\mathrm{H_2O}}] = c \doteqdot 13{\cdot}7.$$

$$\therefore \quad \xi\underset{\circ}{\mathrm{KCl}} = +\xi\mathrm{KHO} + \xi\mathrm{HCl} - \xi\mathrm{H_2O} + c.$$

Substituting this value for ξKCl in the second equation and the value thus obtained for ξKI in the first equation, we get

$$\begin{aligned}\xi\underset{\circ}{\mathrm{HI}} &= -\xi\underset{\circ}{\mathrm{KHO}} - \xi\underset{\circ}{\mathrm{Cl}} + c \quad + \xi\underset{\circ}{\mathrm{KHO}} + \xi\underset{\circ}{\mathrm{HCl}} - \xi\underset{-}{\mathrm{H_2O}} \\ &\quad + \xi\underset{\cdot}{\mathrm{I}} \quad - b \quad + \xi\underset{-}{\mathrm{H_2O}} - a \\ &= \xi\,\underset{\circ}{\mathrm{HCl}} \quad - \xi\underset{\circ}{\mathrm{Cl}} - a - b + c \\ &= 39{\cdot}3 \quad - 1{\cdot}5 - 19{\cdot}1 \quad - 19{\cdot}2 + 13{\cdot}7 \\ &= 13{\cdot}2\mathrm{K}^\circ.\end{aligned}$$

In this last example a free use has been made of all the ordinary processes of algebra, and the result obtained by the proper statement of the correlation of the various quantities, and the subsequent development of the unknown quantity in terms of the known quantities. It is at least doubtful if such an example could be worked out by any of the notations previously in use, and it shows the benefit of giving a clear expression to the whole material system under consideration together with the energy evolved or absorbed in its various transformations. In conclusion, I have to thank Professor Hartley for his kind revision of this Paper, and for suggesting some of the illustrations of the use of the notation.

XXXIX.

ON THE SYNTHESIS OF GALACTOSIDES.

By PROFESSOR HUGH RYAN, M.A., D. Sc., F.R.U.I., and W. SLOAN MILLS, M.A., University College, Dublin.

[PRELIMINARY COMMUNICATION.]

[Read April 17; Received for Publication April 19; Published July 20, 1901].

It has been found by one of us that acetyl-chloride reacts with galactose[1] in a manner analogous with its action on glucose.[2] The compound formed by the interaction was obtained as a colourless syrup, which contained chlorine, and was converted into a galactoside, resembling somewhat the phenol-glucoside obtained by Michael from acetochloroglucose.[3]

As the study of the acetochlorogalactose mentioned in the above paper has been since taken up by Emil Fischer and Armstrong,[4] we find it necessary to communicate the results which we have already obtained, although our experiments with the substance are not yet completed.

Preparation of Acetochlorogalactose.—Twenty-four grams of galactose, dried at 105–110° and finely-powdered, were mixed with cooling in a freezing-mixture with fifty-one grams of acetyl chloride in a well-dried tube, and shaken at the ordinary temperature until the sugar was dissolved. The tube was cooled in a freezing-mixture of ice and salt before opening it. During the latter process the presence of a great internal pressure, due to the evolution of hydrochoric acid, was manifest. The contents of the tube were extracted with chloroform, and the solution washed first with powdered ice and water, then with an ice-cold solution of sodium carbonate until free from acid. The chloroform solution was dried with calcium chloride filtered and evaporated *in vacuo*.

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[1] Trans. Chem. Soc. 1899, p. 1057.

[2] Colley, Ann. Chem. Phys., 1870 [iv.]. 21. p. 363.

[3] Comptes Rendus, 1879. 89. p. 355.

[4] Sitz. der k. Akad. der Wissensch. zu Berlin, 1901. vii. p. 123.

The residue was a faint yellow semi-solid syrup, slowly soluble in cold alcohol, containing 6·1 per cent. chlorine, showing that it was impure acetochlorogalactose (Calc. Cl. 9·68).

Acetochlorogalactose is insoluble in cold ligroïn, dissolves in hot ligroïn or ether, and is readily soluble in chloroform. The yield was forty-eight grams.

a Naphthylgalactoside, $C_6H_{11}O_5 \cdot O \cdot C_{10}H_7$.—18·2 grams of acetochlorogalactose were dissolved in cold absolute alcohol, and mixed with strong cooling with a solution of 7·2 grams *a* naphthol and 2·8 grams potassium hydroxide in about 100 c.c. absolute alcohol. After remaining in the freezing-mixture for twelve hours, it was allowed to stay at the temperature of the laboratory for three days, by which time the colour of the solution was brown, and a considerable quantity of potassium chloride had separated. The mixture, which smelt of acetic ester, was boiled for two hours under a reflux condenser, and filtered, while hot, from a residue which was readily soluble in cold water, and consisted of potassium chloride.

The filtrate, evaporated on the water-bath, gave a syrupy residue which, after being left for five days, crystallized. The substance was washed free from *a* naphthol by ether, and recrystallized from alcohol.

It was dried in the air at 105°, and melted at 202 – 203°.

0·1078 gave 0·2571 CO_2 and 0·0572H_2O · C 62·51, H 5·9.
$C_{16}H_{18}O_6$ requires C 62·74, H 5·88 %

a Naphthylgalactoside crystallizes in rectangular plates, soluble in hot alcohol and hot water, slightly soluble in cold water, insoluble in ether, chloroform, benzene, and ethylic acetate. It has scarcely any action on Fehling's solution, but reduces it readily after hydrolysis by dilute sulphuric acid. Unlike carvacrylglucoside and *β* naphthylgalactoside it is not more soluble in dilute potash than in water. It does not, therefore, contain an unchanged phenolic hydroxyl group, and has a similar constitution to that of 3*β* naphthylglucoside.

XL.

ON THE SYNTHESIS OF GLUCOSIDES.

By PROFESSOR HUGH RYAN, M.A., D.Sc., F.R.U.I.,
University College, Dublin.

[Read April 17; Received for Publication, April 19; Published July 20, 1901.]

Of the many glucosides which occur in the vegetable kingdom very few have been obtained synthetically in the laboratory. Although the decomposition of a glucoside into its components is a comparatively simple operation, the reversal of the process is, in the vast majority of cases, very difficult. Two of the three methods hitherto used for synthesis of glucosides are indeed reversible. It has been shown by Hill,[1] Emmerling,[2] and Emil Fischer and Armstrong[3] that zymohydrolysis is a reversible operation. In this way Emmerling obtained isomaltose from glucose by the action of maltase, and Fischer galactasidoglucose from galactose, and glucose by the action of kephyr lactase. The method has, however, given successful results only in the above two cases. The second process for hydrolysing glucosides, the action of hot dilute acids, is also, as has been shown by Emil Fischer, reversible. Many hexosides were got in this way from the various hexoses. By the action of strong, cold, or diluted hot hydrochloric acid on glucose and methyl alcohol, two methylglucosides were got thus:—

$$C_5H_{11}O_5 \cdot CHO + HOCH_3 = C_5H_{10}O_5 \cdot CHOCH_3 + H_2O.$$

The one, α methylglucoside, is not acted on by emulsin, and is readily hydrolysed by yeast; the other is unacted on by yeast, and readily hydrolysed by emulsin, and was named by Fischer β methylglucoside. Similarly ethyl, propyl, isopropyl, amyl, and benzyl alcohols gave corresponding glucosides. The method was found applicable to the diatomic and triatomic alcohols as glycol and glycerol as well as ethyl, amyl, and benzyl mercaptans.[4]

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[1] Trans. Chem. Soc. 73, p. 634 [1898].

[2] Ber. 34 (1901), p. 600.

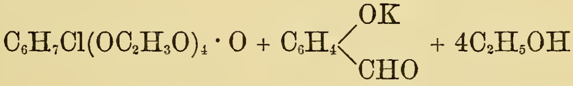
[3] Sitz. der k. Akad. der Wissensch. zu Berlin, 1901. vii. p. 123.

[4] Ber. 26 (1893), p. 2400, 27 (1894) pp. 674, 2483, 2985.

From the monatomic phenols, glucosides could not be obtained in this way,[1] but again, in the case of the diatomic and triatomic phenols, complex condensation products were got which resembled somewhat the glucosides. Thus glucose combines with one or two molecules of resorcinol to form amorphous condensation products, hydrolysable by boiling dilute acids. Similar substances have been obtained from pyrogallol and orcinol[2] and from phloroglucinol.[3]

Not only is the method useful in the case of the hexoses glucose, mannose, galactose, fructose, and sorbinose, but also for the pentoses arabinose and xylose. In the case of the dodecoses, methyl and ethyl lactosides appear to have been formed, but never satisfactorily isolated.[4] Isomaltose was synthesised in this way by Emil Fischer.[5]

The naturally occurring glucosides helicin and methylarbutin were obtained synthetically by Michael[6] by the third method of forming glucosides. By utilizing the acetochloroglucose of Colley as parent-substance, Michael obtained from it, by the action of the potassium compound of salicylic aldehyde in alcoholic solution, the well crystallized glucoside helicin. The reaction had proceeded thus:—



$$C_6H_7Cl(OC_2H_3O)_4 \cdot O + C_6H_4\left\langle\begin{matrix} OK \\ CHO \end{matrix}\right. + 4C_2H_5OH$$
$$= C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CHO + 4CH_3COOC_2H_5 + KCl.$$

Similar reactions were carried out by Michael with phenol, guaiacol and eugenol,[7] and by Drouin with thymol and α napthtol.[8] I have obtained the three cresylglucosides, β naphthyl and carvacrylglucosides from acetochloroglucose and the corresponding phenolic compounds in alkaline alcoholic solution. The method is very troublesome and the yield of glucoside poor. The latter fact is possibly due to the nature of the acetochloroglucose used, which was not crystalline, and probably a mixture of the isomerides α and β chloroacetoglucose, which would give a mixture of α and β glucosides, the latter of which only was isolated. This is confirmed

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[1] Emil Fischer and Jennings, Ber. 27 (1894), p. 1358.

[2] *Ibid.*

[3] Councler, Ber. 28 (1895), p. 27.

[4] Emil Fischer, Neue Zeitsch. f. Rübenzucker-industrie, 31. p. 67.

[5] Ber. 23 (1890), p. 3687.

[6] Comptes Rendus, 89. p. 355.

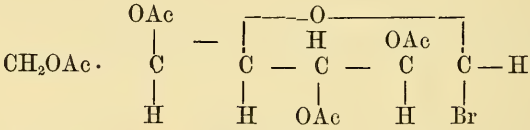
[7] Amer. Chem. Jour. 6. p. 336.

[8] Bull. Soc. Chim. III. 13. p. 5.

by the fact that the well-crystallized acetobromoglucose of Königs[1] gives a much more satisfactory yield of carvacrylglucoside than the corresponding syrupy chlorine compound, possibly due to the crystalline acetobromoglucose being a pure β compound.

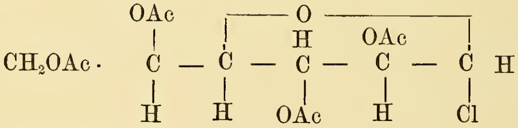
Michael's method has been found generally applicable to the monatomic phenols, but not for the alcohols or polyatomic phenols. Fischer's method, on the other hand, is generally applicable to the alcohols and polyatomic phenols, but unsuccessful in exactly those cases where Michael's method succeeds. Acetobromoglucose can, however, as Königs has shown, be converted in the presence of silver carbonate into tetracetylmethylglucoside, and, as I have found into carvacrylglucoside, thus uniting the two series of glucosides by formation from a single parent substance by simple operations.

It also follows from these facts that the bromine atom in acetobromoglucose is attached to the end carbon atom and its formula is :—



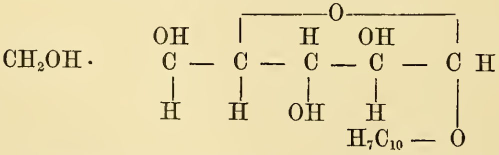
$$CH_2OAc\cdot\underset{H}{\overset{OAc}{C}} - \overbrace{\underset{H}{C} - \underset{OAc}{\overset{H}{C}} - \underset{H}{\overset{OAc}{C}}\quad \underset{Br}{C}}^{O} - H$$

and that of acetochloroglucose formed from it by the action of silver chloride is—



$$CH_2OAc\cdot\underset{H}{\overset{OAc}{C}} - \overbrace{\underset{H}{C} - \underset{OAc}{\overset{H}{C}} - \underset{H}{\overset{OAc}{C}} - \underset{Cl}{C}}^{O}\ H$$

$\beta\ \beta$ napthyl-glucoside has the formula



$$CH_2OH\cdot\underset{H}{\overset{OH}{C}} - \overbrace{\underset{H}{C} - \underset{OH}{\overset{H}{C}} - \underset{H}{\overset{OH}{C}} - \underset{H_7C_{10} - O}{C}}^{O}\ H$$

and similar formulæ are good for the cresylglucosides, but carvacrylglucoside does not belong to the same series. It was obtained from carvacrol and potash by the action of acetochloroglucose, and

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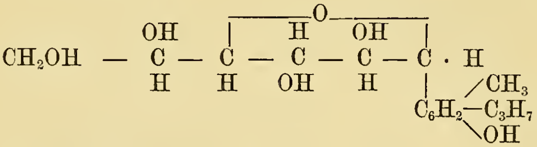
[1] Sitz. der k. Bayr. Akad. der Wissensch., 1900. p. 103.

differs from the other glucosides of the series by its being more difficultly hydrolysable, by its great solubility in dilute alkali and reprecipitation by dilute acids or ammonium carbonate. Hence carvacrylglucoside contains an unchanged phenolic hydroxyl group, and has the formula:—



$$CH_2OH - \underset{H}{\overset{OH}{C}} - \overbrace{\underset{H}{C} - \underset{OH}{\overset{H}{C}} - \underset{H}{\overset{OH}{C}} - \underset{C_6H_2\begin{cases}CH_3\\C_3H_7\\OH\end{cases}}{C}}^{O} \cdot H$$

The acetochloroglucose has reacted with carvacrol with separation of hydrochloric acid and formation of *a substance for which there is no analogue in the whole range of organic chemistry.* Although the generic formula of the new class of substances $X \cdot Y \cdot OH$ is no longer included in that of the glucosides $X \cdot O\,X_1$, where X is a carbohydrate radicle, I have preferred to retain the name carvacryl glucoside for the body owing to its similarity in appearance, and its hydrolysis by dilute acids or emulsin to glucose and carvacrol.

Preparation of Acetochloroglucose—The acetochloroglucose was prepared by Colley's method[1] with some slight alterations which render the substance more easily accessible. Pure, crystallized, anhydrous glucose (18 grams), after passage through a fine sieve, was mixed with acetylchloride (39 grams) in a well-dried Volhard tube. The tube was cooled in a freezing mixture, sealed off at once, and shaken on a machine during 24–30 hours at the ordinary temperature. The colourless solution was dissolved in chloroform, washed first with iced water, then with ice-cold sodium carbonate solution until freed from acid. The chloroform solution was separated, filtered, dried with calcium chloride, and, after evaporation in a vacuum, gave a colourless semi-solid mass of acetochloroglucose. It contained 9 per cent. chlorine (Calc. 9·68 Cl). The yield was about 36 grams.

It may be mentioned that attempts to prepare acetochloroglucose in an open vessel protected from atmospheric moisture by a calcium chloride tube, were unsuccessful. When 20 mols. of acetylchloride were employed with 1 mol. of glucose, the prin-

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[1] Ann. Chim. Phys., 1870, [iv], 21, p. 363.

cipal product was the dextrorotatory pentacetylglucose previously made by Erwig and Königs by the action of acetic anhydride and zinc chloride on grape-sugar.[1] It melted at 110° C., and gave on analysis the following result:—

0·1389 g. gave 0·2490 g. CO_2 and 0·0717 g. H_2O.
C = 48·9, H = 5·7.
$C_{16}H_{22}O_{11}$ requires C = 49·2, H = 5·6 per cent.

It would thus seem that the formation of the chlorine compound is due to the pressure of the hydrochloric acid in the sealed tube.

ββ Naphthylglucoside, $C_6H_{11}O_5 \cdot O \cdot C_{10}H_7$.—A solution of acetochloroglucose (70 grams) in absolute alcohol (150 c.c.) was added to β naphthol (23 grams) and potassium hydroxide (11 grams) dissolved in absolute alcohol, the total volume of the well-cooled mixture being about 300 c.c. After a few minutes, the solution became turbid, owing to the separation of potassium chloride. After remaining for three days at the ordinary temperature, the yellowish-brown solution, which smelt strongly of ethylic acetate, was heated to boiling for 45 minutes under a reflux condenser, cooled and filtered. After removal of the alcohol and ethylic acetate on the water-bath, a little water was added, and the solution on cooling solidified. The product (46 grams), which contained some unchanged naphthol, was recrystallized from boiling water, and finally from absolute alcohol. It separated in groups of long needles melting at 184–186° C., and was dried at 105° before analysis.

0·1806 gave 0·4150 CO_2, and 0·0944 H_2O, C = 62·67, H = 5·81.
$C_{16}H_{18}O_6$ requires C = 62·74, H = 5·88.

ββ Naphthylglucoside is soluble in alcohol or hot water, sparingly so in acetone, and almost insoluble in light petroleum, benzene, cold water, or ether. It is readily hydrolysed by dilute acids or emulsin, does not reduce Fehling's solution before, but readily after, hydrolysis, and is stable towards dilute alkali, in which it is almost insoluble. The taste is disagreeable.

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[1] Ber. 22 (1889), p. 1464.

Tetracetyl-ββ-naphthylglucoside.—A mixture of 0·7 g. ββ naphthylglucoside and 0·7 g. anhydrous powdered sodium acetate was heated to incipient ebullition in a porcelain dish with 4 c.c. acetic anhydride. The flame was removed, and the reaction which was violent was allowed to go on until the solid had dissolved. On pouring the contents of the dish into a large quantity of cold water a yellow oily mass, which quickly solidified, separated out. It was recrystallized from hot alcohol, from which it separated in the cold as long branching needles. It was dried at 105° C., and melted at 134–136° C.

0·1284 gave 0·2873 CO_2 and 0·0628 H_2O.
$C_{24}H_{26}O_{10}$ requires C 60·8, H 5·48,
Found C 61·0, H 5·43.

Tetracetyl-ββ-naphthylglucoside is scarcely soluble in cold water, soluble in cold alcohol, readily soluble in benzene, ethylic acetate, chloroform, ether, and hot alcohol. The crystals viewed with a polarising microscope are scarcely visible when the Nicols are crossed. It is hydrolysed with great difficulty by the successive actions of potash and sulphuric acid. Emulsin has no action on it. It would thus seem that the conversion of the hydroxy groups of a β glucoside into the corresponding acetoxy groups, without any other change in the configuration of the molecule, destroys its capability of being hydrolysed by emulsin.

An unsuccessful attempt to synthesise arbutin from acetochloroglucose hydroquinone and potash seemed to indicate that a substituting radicle in the paraposition to the ᴵOH group interfered with the reaction. To test this I tried to obtain by a similar experiment the glucosides of p.-nitrophenol, and again with a negative result. In order to find whether the failure of the reaction was due to the nature or position of the group, I examined the behaviour of the three cresols towards acetochloroglucose, with results which show that the position of the radicle does not explain the failure in the synthesis of arbutin. It is rather to be attributed to the negative nature of the second radicle which is confirmed by Michael's success with methylhydroquinone, in which the negative nature of the second group is removed by its conversion into the methoxy group.

Paracresylglucoside, $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH_3$.—Acetochloroglucose (36 grams), dissolved in absolute alcohol, was added to a solution of paracresol (11 grams) and potassium hydroxide (6 grams) in alcohol. The mixture, which became yellow, was left for 14 hours in ice-water, and then at the ordinary temperature for a day. The resulting crystalline magma of potassium chloride and the glucoside was diluted with alcohol to 500 c.c., left for two days, and then boiled gently for 1½ hrs. The filtrate, which smelt of acetic ester, left in an evaporating dish at the ordinary temperature for a few days, gave a separation of the glucoside in needles which, after recrystallization and drying at 100° C., melted at 175–177°. Yield 40 per cent.

0·1737 gave 0·3652 CO_2, and 0·1045 H_2O,
C = 57·34, H = 6·74
$C_{13}H_{18}O_6$ requires C = 57·77, H = 6·66 per cent.

β. p.-cresylglucoside is soluble in alcohol or water, sparingly so in acetone, and scarcely soluble in ether, benzene, light petroleum, or chloroform. It did not reduce Fehling's solution before, but readily after, hydrolysis, with emulsin or dilute acids.

Tetracetyl-β-p.-cresylglucoside, $C_6H_7(C_2H_3O)_4O_5 \cdot O \cdot C_6H_4CH$, was obtained by heating a mixture of 1 gram paracresylglucoside, 1 gram sodium acetate, and 4 c.c. acetic anhydride. It was recrystallized from absolute alcohol, and, when dried at 105°, melted at 119–120° C.

0·1560 gave 0·3289 CO_2 and 0·082 H_2O, C 57·5, H 5·84.
$C_{21}H_{26}O_{10}$ requires C 57·5, H 5·8.

It separates from alcohol as long glittering prisms, almost insoluble in water, soluble in benzene, ethylic acetate, ether, and hot alcohol. It is visible and multi-coloured between crossed Nicols.

β *Orthocresylglucoside*, $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH_3$, was obtained from a solution of 36·7 grams acetochloroglucose, 5·6 grams potassium hydroxide, and 10·8 grams orthocresol in about 250 c.c. absolute alcohol. The mixture was allowed to stand three days at the temperature of the laboratory, and the yellow solution then heated for 1½ hours on the water-bath. After filtering off the potassium chloride, the alcohol and acetic ester were allowed to evaporate spontaneously at the laboratory temperature. The glucoside was recrystallized from water, dried at 105–110°, and melted at 163–165°.

0·1406 gave 0·2966 CO_2 and 0·0894 H_2O · C 57·53, H 7·06.
$C_{13}H_{18}O_6$ requires C 57·77, H 6·66.

β Orthocresylglucoside crystallizes from water in beautiful needles, scarcely soluble in ether, but easily so in water or alcohol, and does not reduce Fehling's solutions before, but readily after, hydrolysis by dilute acids or emulsin. It has an intensely bitter taste. The yield of the orthoglucoside was similar in amount to that obtained from the para-derivative.

Tetracetylorthocresylglucoside, $C_6H_7(C_2H_3O_2)_4O \cdot O \cdot C_6H_4CH_3$, was obtained in the form of beautiful needles by heating a mixture of 1 gram orthocresylglucoside, 1 gram sodium acetate, and 4 c.c. acetic anhydride. The substance was isolated as in the case of the tetracetylnaphthylglucoside mentioned above. It was recrystallized from alcohol and dried at 105°; it melted at 143°.

0·1752 gave 0·3687 CO_2 and 0·0945H_2O, C 57·4, H 6.
$C_{21}H_{26}O_{10}$ requires C 57·5, H 5·8 per cent.

It is soluble in ether, benzene, ethylic acetate, and chloroform, scarcely soluble in cold alcohol or water. Between crossed Nicols it is visible, and multi-coloured. Like tetracetyl ββ naphthyl and β p.-cresylglucoside, it is not acted on by emulsin.

β *Metacresylglucoside*, $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH_3$, was prepared from metacresol in a similar manner to that described for the ortho-compound. The yield was poorer than in the cases of ortho- and para-cresols. It crystallizes from 60 per cent. alcohol in fine branching needles, scarcely soluble in benzene, chloroform, ethylic acetate, or carbon bisulphide, soluble in cold water or alcohol, and readily soluble in hot water or alcohol. It reduces Fehling's solution only after hydrolysis by dilute acids. It was dried at 105° and melted at 167·5–168·5°.

0·2004 gave 0·4239 CO_2 and 0·1181 H_2O · C 57·63, H 6·55.
$C_{13}H_{18}O_6$ requires C 57·77, H 6·66.

From the above it would seem that the monosubstituted alkyl phenols react even more readily with acetochloroglucose than does phenol itself.

As the preparation of acetochloroglucose is very troublesome and dangerous when working with large quantities, I sought to improve the process by using inactive pentacetylglucose instead of it as starting substance. From the brownish-red syrupy residue, from the action of pentacetyl glucose on an alcoholic solution of potassium phenolate, I was not, however, able to isolate any crystalline product after following the method successfully employed in the above-mentioned glucosides.

In the interval, however, it has been found by Königs and Knorr[1] that the Bromine compound analogous to acetochloroglucose is easily obtained crystalline by the action of acetylbromide on glucose. Königs has shown that it reacts with methyl alcohol to give β methylglucoside; and I have found that it may with advantage replace acetochloroglucose in the preparation of carvacrylglucoside. The method of preparing the acetobromoglucose used, which has not been described by Königs in his preliminary communication on this most interesting substance, was similar to that described above in the case of acetochloroglucose.

β *Carvacrylglucoside*, $C_6H_{11}O_5 \cdot C_6H_2 \cdot CH_3 \cdot C_3H_7 \cdot OH + \frac{1}{2} H_2O$, was prepared from two grams of acetobromoglucose, 0·7 gram carvacrol and 0·3 gram potassium hydroxide in a small quantity of absolute alcohol, the mixture being well cooled in a freezing mixture. A solid, which was afterwards found to be potassium bromide, separated very slowly. The mixture was boiled under a reflux condenser and filtered. On the spontaneous evaporation of the filtrate, a yellow oil remained, which, after being left a few days, crystallized. It was recrystallized from hot water, and agreed in properties with the carvacrylglucoside obtained in an analogous manner from acetochloroglucose. It crystallizes in groups of beautiful needles, and, when anhydrous, softens at 118° and melts not quite sharply at 135°. The glucoside after drying over calcium chloride, but not in a vacuum, was analysed.

0·1806 gave 0·3964 CO_2 and 0·1279 H_2O. C 59·8. H 7·9.

0·2384 lost 0·0064 H_2O at 90° in a vacuum over phosphorus pentoxide. H_2O = 2·7.

$C_{16}H_{24}O_6 + \frac{1}{2}H_2O$ requires C 59·8, H 7·8, H_2O 2·8 per cent.

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[1] Sitz. der k. Bayr. Akad. der Wissensch., 1900. p. 103.

The anhydrous compound gave the following numbers:—

0·1512 gave 0·3392 CO_2 and 0·1086 H_2O, C 61·2, H 7·9.

$C_{16}H_{24}O_6$ requires C 61·5, H 7·7 per cent.

Carvacrylglucoside is easily soluble in alcohol or acetone, but less readily so in cold water or ether, and is almost insoluble in benzene, chloroform, or light petroleum. It does not reduce Fehling's solution before, but readily after, hydrolysis by heating with dilute acids or emulsin.

The behaviour of carvacrylglucoside towards dilute alkali is characteristic. It dissolves slowly, but completely in the alkali, and is reprecipitated *unchanged* by the addition of dilute acids or ammonium carbonate. Hence carvacrylglucoside contains an unchanged phenolic hydroxyl group.

In conclusion, I must express my indebtedness to Mr. W. S. Mills, M.A., for his assistance in the above investigation, and to Professor Emil Fischer, in whose laboratory in the University of Berlin a portion of the work was carried out.

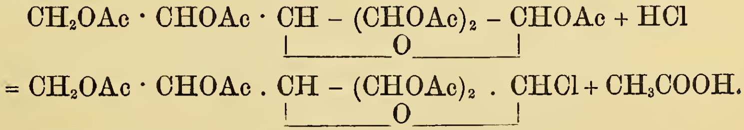
NOTE ADDED IN THE PRESS.

On the Constitution of Carvacrylglucoside.

Since the above paper was read before this Society two important papers by Emil Fischer and Armstrong, and by Koenigs and Knorr, have appeared in the Chemisches Centralblatt, which support my formula for carvacrylglucoside.

The constitution of the substance obviously depends entirely, so far as the glucose rest is concerned, on the constitution of acetochloroglucose or acetobromoglucose, since it has been obtained from both those substances by the replacement of Cl or Br atoms respectively by the carvacrol rest with simultaneous saponification of the acetyl groups.

Emil Fischer and Armstrong have shown that β pentacetylglucose reacts with liquid hydrochloric acid to form β acetochloroglucose:—



$$\mathrm{CH_2OAc \cdot CHOAc \cdot \underbrace{CH - (CHOAc)_2 - CHOAc}_{O} + HCl}$$

$$= \mathrm{CH_2OAc \cdot CHOAc\ .\ \underbrace{CH - (CHOAc)_2\ .\ CHCl}_{O} + CH_3COOH.}$$

Similarly β acetobromoglucose was obtained from β pentacetylglucose.[1]

The same formula for β acetobromoglucose was independently arrived at by Koenigs and Knorr.[2]

They converted the body into tetracetyl-β-methylglucoside, and thus proved that the bromine atom was at the end of the carbon chain.

Again I have converted acetobromoglucose into carvacrylglucoside, and it therefore follows that the glucose rest in the latter substance must have the formula

$$CH_2OH\cdot CHOH\cdot \underbrace{CH\ (CHOH)_2\cdot CH}_{O}.$$

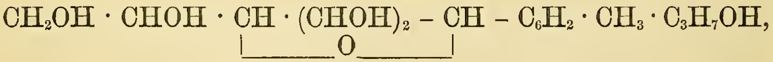
Carvacrylglucoside, as mentioned above, is soluble in dilute alkali, and reprecipitated by addition of dilute acids or ammonium carbonate.

The reprecipitated glucoside was found to be unchanged carvacrylglucoside, and its great solubility in dilute alkali was therefore not due to the decomposition of the glucoside by the action of the alkali, which fact was further confirmed by the non-reduction of Fehling's solution even on continued boiling.

It follows from the above facts that carvacrylglucoside contains a phenolic hydroxyl group, and that the carvacrol rest must have the formula:—

$$-\ C_6H_2\cdot CH_3\cdot C_3H_7\cdot OH.$$

The formula for the glucoside must therefore be:—



$$CH_2OH\cdot CHOH\cdot \underbrace{CH\cdot (CHOH)_2 - CH}_{O} - C_6H_2\cdot CH_3\cdot C_3H_7OH,$$

no other formula agreeing with all the facts mentioned in this paper.

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[1] Comptes Rendus, 1901. I. p. 884.

[2] Ber. 34 (1901). p. 957.

XLI.

ON THE PREPARATION OF AMIDOKETONES.

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[Read January 16 ; Received for Publication March 1 ;
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I.—Theoretical Part.

By the reduction of isonitrosoketones with tin and hydrochloric acid, a series of new and interesting bases were discovered by Victor Meyer and his pupils.

The compounds, then termed ketines, were in all cases liberated by the addition of solid caustic potash to a concentrated solution of the hydrochloride of the base and distilled over in a current of steam. On analysis of the base derived from isonitrosoacetone, it appeared to have the formula $C_6H_{10}N_2O$, but after being left some time in a vacuum dessicator over sulphuric acid, it gave off one molecule of water yielding a base $C_6H_8N_2$, which was afterwards identified as dimethylpyrazine.

The reaction had proceeded in the following manner :—

$$(a)\ 2CH_3\cdot CO\cdot CH:N\cdot OH + 4H_2 + 2HCl \\ = 2CH_3\,CO\,CH_2\,NH_2\,HCl + 2H_2O.$$

$$(b)\ 2CH_3\cdot CO\cdot CH_2\cdot NH_2\cdot HCl + 2KOH \\ = 2CH_3\cdot CO\cdot CH_2\cdot NH_2 + 2KCl + 2H_2O.$$

$$(c)\ 2CH_3\cdot CO\cdot CH_2 = NH_2\,C_6H_8N_2\cdot H_2O.$$

Various other methods of preparing amidoketones by the reduction of isonitrosoketones were proposed and unsuccessfully attempted. Amongst others it was sought to reduce them by the action of 2½ and 5 per cent. sodium amalgam on a dilute acid solution of the isonitrosoketone. Under these circumstances it was found by Gabriel and his pupils that the chief product is the corresponding amidoalcohol.[1]

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[1] Ber. 32 (1899), p. 1095.

It was supposed by Gabriel that the amidoketones, although unstable in the free state, could exist in the form of stable salts, such as the hydrochloride. This was confirmed by his experiments and those of his pupils.[1]

I have prepared two new members of the series, and examined some of their properties and reactions.

In doing so I have used two distinct methods with the object of finding by what procedure this very interesting but difficultly accessible group of bodies may be most readily obtained for synthetical purposes.

First Method of Preparing Amidoketones.—Xylyl bromide, treated with acetoacetic ester and sodium alcoholate, was converted into xylylacetoacetic ester. By the action of nitrous acid on substituted acetoacetic esters of the fatty series, Victor Meyer and his pupils[2] obtained, with yields of from 30–50 per cent., the simpler members of the isonitrosoketone series. For the higher fatty members, the yield was considerably poorer. In the aromatic series, Ceresole made isonitrosobenzyl acetone from the barium salt of benzylaceto-acetic acid by the action of nitrous acid, but the yield was poor.

With no better result I have prepared m-xylyl-isonitroso-acetone by the method used by Victor Meyer for the fatty series.

The low yield is mainly due to the slowness with which xylylacetoacetic ester dissolves in dilute potassium hydrate and the consequent decomposition of some of the already dissolved ester due to the prolonged standing of the alkaline solution. Moreover, oily by-products diminish the return of the pure product, which in the most favourable cases was only about 25 per cent.

The use of a shaking machine for producing the solution did not materially improve the yield.

The reduction of the i-nitrosoketone to the amido compound gave a yield of about 50 per cent. of the theoretically expected amount of the hydrochloride of the amidoketone.

Still the many operations necessary for the production of metaxylyl amidoacetone from metaxylene render the final yield very poor, which was only about 4 per cent. of the theoretical.

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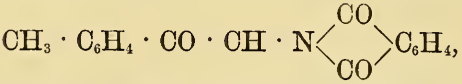
[1] Ber. 26 (1893), p. 2199; 27 (1894), pp. 1037, 1141; 28 (1895), pp. 1513, 2036; 29 (1896), p. 2603; 30 (1897), p. 1515.

[2] Ber. 11 323, etc.

Moreover, the time necessary for the several reactions, about eleven days, renders the method very tedious in practice.

Second Method of Preparing Amidoketones.—By the well-known method of Gabriel[1] for preparing primary amines, I have found that p-methyl-chlor-acetyl-benzene reacted with potassium phtalimide to give p-methyl-α-phtalimidoaceto-phenone.



$$CH_3 \cdot C_6H_4 \cdot CO \cdot CH \cdot N \langle \begin{matrix} CO \\ CO \end{matrix} \rangle C_6H_4,$$

which was hydrolysed with alcoholic potash to the corresponding phtalaminic acid :—

$$CH_3\ C_6H_4 \cdot CO\ CH \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH.$$

On boiling the latter with concentrated hydrochloric acid under the reflux condenser, it returned partly to the original compound, and decomposed partly into phtallic acid and the hydrochloride of p-methyl-α-amidoacetophenone :—

$$CH_3 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot NH_2 \cdot HCl.$$

The yield of amidoketone was about 23 per cent. of the amount theoretically obtainable from the quantity of ω-chloracetyl toluene used, and the time required for its preparation is less than two days.

Thus, both for convenience, saving of time, and yield, the method of Gabriel is to be preferred for aromatic amidoketones.

II.—Experimental Part.

A. *First Method of Preparation.*—Preparation of m-xylyl bromide $\underset{1}{CH_3} \cdot \underset{1}{C_6H_4} \cdot \underset{3}{CH_2}\ Br.$

The parent substance for the following experiments was prepared by the method of Radsziszewski and Wispek.[2]

310 gs. of bromine were allowed to drop slowly into 200 gs. of metaxylene heated to boiling in a glycerine bath. The hydrobromic acid escaped by a long vertical tube which served to condense the xylene. The product, which was dark coloured, was

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[1] See Richter's "Organic Chemistry," vol. i.

[2] Ber. (1882), 15, p. 1745. *Ibid.* (1885), 18, p. 1282.

distilled at 754 mm. pressure, and afforded a heavy liquid whose vapour attacks the eyes and skin violently. The fraction boiling between 208–222° was collected apart and weighed 244 grams. Yield 70 per cent.

The residue in the retorts crystallized on cooling.

By the action of sodium aceto-acetic ester on xylyl bromide it was converted into

2. *M-Xylyl-aceto-acetic Ester*, $CH_3CO\cdot CH(CH_2C_6H_4CH_3)CO_2C_2H_5$.—To a solution of 17 gs. sodium in 260 c.c. absolute alcohol, 100 gs. of aceto-acetic ester were added, and followed immediately by 120 gs. m-xylyl bromide. The mixture became hot, and a lively reaction ensued with the separation of sodium bromide. The mixture became neutral after two hours' boiling on the water-bath under a reflux condenser. After boiling off the alcohol, water was added to dissolve the sodium bromide. The layer of ester was separated, dried over potassium carbonate and distilled. At 36 mm. pressure it boiled at 195° C., condensing as a nearly colourless oil, which is scarcely soluble in water, easily in alcohol, very slowly in dilute alkali, and, shaken with a strong solution of caustic soda, gives a crystalline sodium salt. Yield, 67 per cent. theory.

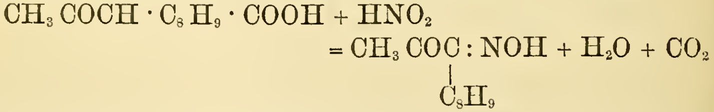
Analysis :—

0·3676 g. Sbst : 0·2616 g. H_20, 0·9716 g. CO_2.

$C_{14}H_{18}O_3$. Calc C 71·8, H 7·7.

Found C 72·1, H 7·9.

The action of nitrous acid on xylylacetoacetic acid can proceed in different directions according to the conditions of the experiment. In an aqueous solution, it gave i-nitrosoxylylacetone, thus :—



$$CH_3\,COCH\cdot C_8H_9\cdot COOH + HNO_2 = CH_3\,CO\underset{\overset{|}{C_8H_9}}{C}:NOH + H_2O + CO_2$$

On the other hand, in an alcoholic solution, the principal product of the reaction is isonitrosoxylylacetic acid, whose formation may be represented by the following equation :—

$$CH_3\,COCH\cdot C_8H_9\cdot COOH + HNO_2 = C_8H_9\cdot C:NOH\cdot COOH + CH_3\,COOH.$$

3. *Isonitrosoxylylacetic acid*, $CH_3\cdot C_6H_4\cdot CH_2\cdot C:NOH\cdot COOH$.—15 gs. of xylylacetoacetic ester were mixed with a

solution of 4 gs. potassium hydrate, and about 400 c.c. alcohol, 4 gs. of sodium nitrite were added to the well-cooled mixture, and acidified with good shaking by addition of 50 p. c. sulphuric acid. The solution was made alkaline, extracted with ether, and the alkaline residue let stand three days. It was acidified and extracted with ether. On evaporation of the solvent, an oil was obtained which gave colourless needles melting at 139° C. on standing in a vacuum desiccator over sulphuric acid. Owing to the method of isolation used the yield was poor.

Analysis:—

0·1550 g. Sbst : 0·0864 H_2O, 0·3528 CO_2.

$C_{10}H_{11}NO_3$. Calc C 62·2, H 5·7 p.c.

Found C 62·1, H 6·2 p.c.

The acid dissolves easily in alcohol, scarcely in ligroïn, does not give Liebermann's reaction, contrary to the i-nitrosoketone gives a colourless alkaline solution, and a silver salt which darkens on standing:—

$C_{10}H_{10}Ag \cdot NO_3$ · Calc Ag · 36·0. Found 36·0 p.c.

4. *Isonitrosometaxylyl acetone*, $CH_3CO \cdot C\ (C_8H_9) : NOH$ is got in the following manner:—Mix 28·6 gs. m-xylylacetoacetic ester with 20·5 gs. potash in about ½ a litre of water, and let the misture stand three days, with frequent shaking on the machine. Add 9 gs. sodium nitrite, and acidify under cooling and shaking. The mixture is made alkaline, and after extracting the unchanged ester with ether, the residue is let stand four days. Re-acidify under cooling, and extract the ketone with ether. On distilling off the solvent, the residual oil, after some days' standing in a vacuum over sulphuric acid, solidifies to bushy needles, which are readily soluble in alcohol, ether, and benzene. It dissolves in alkali with a *yellow* colour, and recrystallized from hot ligroïn melted at 54–55°. Yield 4·2 gs.

Analysis :—

0·1900 g. Sbst : 0·1212 g. H_2O, 0·4772 g. CO_2,

0·1293 g. Sbst : 0·0840 g. H_2O, 0·3258 CO_2,

0·1313 g. Sbst 8·1 c.c. N (19°, 767 m.m.),

$C_{11}H_{13}NO_2$ Calc C 69·1, H 6·8, N 7·3 p.c.

Found C 68·7, H 7·2, N 7·2,

C 68·5, H 7·1 p.c.

5. *Amido-m-xylylacetone*, $CH_3CO \cdot CH(C_8H_9)NH_2$, is obtained as hydrochloride by adding slowly 4·2 gs. i-nitroso-m-xylylacetone to a solution of 10 gs. crystallized stannous chloride in 15 c.c. fuming hydrochloric acid, with vigorous shaking and good cooling. During the experiment, the tin double salt separates out, and is dissolved in 200 c.c. water, which is heated on the water-bath for 15 minutes with granulated tin to convert the stannic into the stannous salt. The tin is precipitated with sulphuretted hydrogen, and filtered. On evaporating the filtrate at first over the free flame, and finally in a vacuum at 45° C., the residue crystallizes on cooling. It was dried in a desiccator over sulphuric acid, dissolved in a small quantity of hot absolute alcohol, and filtered from traces of sal-ammoniac. On cooling, the hydrochloride of the amidoketone was precipitated by addition of absolute ether in crystals melting at 150–151°.

Analysis :—

0·2082 g. Sbst; 0·1411 g. AgCl.
0·1998 g. Sbst; 12·3 c.c. N (26°; 757 m.m.)
$C_{11}H_{16}NOCl$. Calc Cl 16·6, N 6·6.
Found Cl 16·8, N 6·8.

It dissolves easily in alcohol or water, is scarcely soluble in ether, and reduces hot Fehling's solution, giving the characteristic odour of pyrazine. In later preparations, it was found more convenient to filter off the tin double salt, to dissolve in a little hot water, precipitate the tin as disulphide and evaporate directly on water-bath. The yield was about 50 p. c. theory.

The *tin double salt*, $(C_{11}H_{15}NO)_2 H_2SnCl_6$, is colourless, turns brown easily on exposure to air, melts at 177–178° C.

0·3110 g. Sbst: 0·0690 g. SnO_2.
$C_{22}H_{32}N_2O_2SnCl_6$ requires Sn 17·1 p.c.
Found 17·4 p.c.

The *platinum double salt*, $(C_{11}H_{15}NO)_2H_2PtCl_6$, is precipitated from its concentrated solution as yellow crystals melting at 187° C., and was dried at 100°C. for analysis.

0·1200 g. Sbst: 0·0305 g. Pt.
$C_{22}H_{32}N_2O_2PtCl_6$. Calculated Pt 25·5. Found 25·4.

The *picrate* crystallizes from a small quantity of water, and melts at 87° C.

0·1811 g. Sbst 22·2 c.c. N (23° C., 759 m.m.).
$C_{17}H_{18}N_4O_8$ requires 13·8 p. c. nitrogen.
Found 13·9 p. c.

B. *Second Method of Preparation.*—Para-methyl-ω-chloracetyl benzene ($CH_3C_6H_4COCH_2Cl$) was prepared by the method of Collet,[1] by adding in small quantities, with frequent shaking, a mixture of chloracetyl chloride and toluene (dried over sodium) to aluminium chloride covered with a layer of carbon disulphide in a flask. The mixture was finally kept at a temperature of about 40° C. until hydrochloric acid ceased to be evolved. It was poured into ice-cold water, acidified, separated, washed with a little water, dried over calcium chloride and fractionated.

The portion boiling between 260–265° C. solidifies on cooling, and consists of nearly pure p.-methyl-chloracetyl benzene.

P.-methyl-ω-phtalimidoacetophenone,

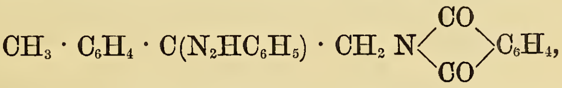
$$CH_3C_6H_4COCH_2N{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_4,$$

is got by 1 hour's heating of an intimate mixture of 16·8 grams p.-methyl-α-chloracetophenone, prepared by the method of Collet described above, and 18·5 gs. potassium phtalimide at 160°. A solid brown mass results on cooling, which, boiled out with water and alcohol, was recrystallized from glacial acetic acid and gave octahedra-like crystals, melting at 175°–176°. The yield of 20 gs. is 72 per cent. of the theoretical.

0·1956 g. Sbst : 9·3 c.c. N (25·5°, 756 m.m.).
$C_{17}H_{13}NO_3$ Calc N 5·0. Found 5·3.

The body is scarcely soluble in water, slightly in alcohol and ether, easily in hot glacial acetic acid.

P.-methyl-a-phtalimidoacetophenone-phenyl-hydrazone,



$$CH_3 \cdot C_6H_4 \cdot C(N_2HC_6H_5) \cdot CH_2\,N{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_4,$$

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[1] Bull. Soc. Chim. [3] 17. p. 506.

is formed from its components dissolved in glacial acetic acid, giving yellow needles melting at 154°.

0·1166 g. Sbst: 0·3172 CO_2, 0·0602 H_2O.
$C_{23}H_{19}N_3O_2$. Calc C 74·7, H 5·2.
Found C 74·2, H 5·7.

P.-methylacetophenone-ω-phtalaminic acid,

$CH_3C_6H_4CO\ CH_2NH\ CO\ C_6H_4\ COOH$,

is obtained by dissolving the phtalimidoketone in warm alcoholic potash, diluting the solution with water, precipitating with hydrochloric acid, and recrystallizing from alcohol. M. P. 165°.

Analysis:—

0·1826 g. Sbst: 7·9 c.c. N (22°, 756 m.m.).
$C_{17}H_{15}NO_4$. Calc N 4·7 p.c.
Found N 4·9 p.c.

It gives a blue copper and white silver salt.

$C_{17}H_{14}NO_4Ag$. Calc Ag 26·7.
Found Ag 26·8.

The aminic acid is decomposed on boiling under the reflux condenser for an hour with four parts of strong hydrochloric acid into phtallic acid, which separates on cooling, and the *hydrochloride of p.-methyl-ω-amidoacetophenone,* which remains in solution and gives colourless needles on evaporation. Recrystallized from alcohol, it melts at 206° to a red fluid.

Yield 3 gs.—32 per cent. theoretical.

0·1920 g. Sbst: 0·1512 g. AgCl.
0·1573 g. — 10·1 c.c. N (21°, 755 m.m.)
$C_9H_{12}NOCl$. Calc N 7·5, Cl 19·2.
Found N 7·3, Cl 19·4.

The solution of the salt reduces Fehling's solution, giving odour of pyrazine. With fixed alkali, it gives the free base which at once decomposes with production of a red-coloured compound.

Gold salt is precipitated from its concentrated solution in long needles. M.P. 167°.

$C_9H_{12}NOAuCl_4$ Calc Au 40·2.
Found Au 40·4.

The *platinum salt* $(C_9H_{11}NO)_2H_2PtCl_6$ crystallizes from hot water in long prisms melting at 206° C.

$C_{18}H_{24}N_2O_2PtCl_6$ Calc Pt 27·6 p.c.
Found Pt 27·8 p.c.

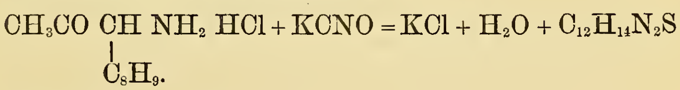
The *picrate* ($C_9H_{11}NO \cdot C_6H_3N_3O_7$ is precipitated by means of a $\frac{1}{10}$ normal sodium picrate solution, and crystallizes from alcohol in yellow needles melting at 176° C.

0·1007 g. Sbst : 12·8 c.c. N (22·5° C., 758 m.m.).
$C_{15}H_{14}N_4O_8$. Calc N 14·8 p.c.
Found N 14·4 p.c.

C. *Reactions of amidoketones.*—By evaporating an aqueous solution of equimolecular quantities of the hydrochloride of amidoxylylacetone and potassium thiocyanate on the water-bath, xylylmethylimidazolyl mercaptan separates out. The solid was washed with water and recrystallized from 50 p.c. alcohol. It crystallizes in prisms soluble in chloroform, benzene, and alcohol, and scarcely soluble in water. It does not dissolve easily in dilute alkali or acid. M.P. 267° C.

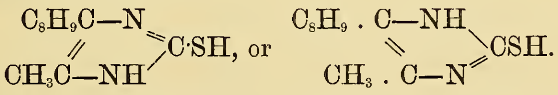
0·1327 g. Sbst : 0·3222 g. CO_2, 0·077 g. H_2O.
$C_{12}H_{14}N_2S$. Calc C 66·1, H 6·4
Found C 66·2, H 6·4.

The reaction had proceeded thus :—

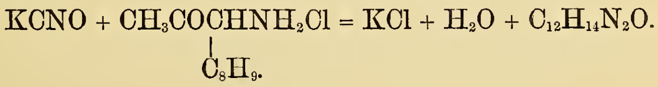


$$CH_3CO\,\underset{\displaystyle C_8H_9.}{\underset{|}{CH}}\,NH_2\,HCl + KCNO = KCl + H_2O + C_{12}H_{14}N_2S$$

Its formula may be :—

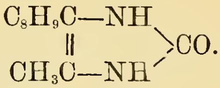


Similarly by evaporating equimolecular quantities of potassium cyanate and amidoxylyl acetone HCl xylylmethylimidazolone was obtained.



$$KCNO + CH_3CO\underset{\displaystyle C_8H_9.}{\underset{|}{C}}HNH_2Cl = KCl + H_2O + C_{12}H_{14}N_2O.$$

The formula of the substance is:—



$$\begin{array}{l} C_8H_9C\text{—}NH \\ \quad\ \ \| \qquad\qquad \rangle CO. \\ CH_3C\text{—}NH \end{array}$$

It crystallizes in beautiful needles melting at 265° C. scarcely soluble in cold alcohol, ether, benzene, or chloroform, readily soluble in hot dilute alcohol.

$C_{12}H_{14}N_2O$. Calc N 12·2. Found N 12·6.

By the action of sodium amalgam and dilute acid on p.-methyl-ω-amido-acetophenone ammonia was split off, and the product had the characteristic odour of acetophenone.

I beg to return my thanks to Professor Gabriel, of the First Chemical Laboratory of the University of Berlin, at whose suggestion the work was undertaken.

XLII.

A THEORY OF THE MOLECULAR CONSTITUTION OF SUPERSATURATED SOLUTIONS. BY W. N. HARTLEY, F.R.S.

[Read MAY 22; Received for Publication MAY 31; Published AUGUST 3, 1901.]

THE salts which ordinarily are capable of forming supersaturated solutions have been ascertained to possess the following characters:—1st, they contain several molecules of water of crystallization, and form several different hydrates; 2ndly, they are much more soluble in hot than in cold water; 3rdly, they are capable of being suddenly solidified as a mass of crystals. For examples we have the following:—$Na_2SO_4 \cdot 10H_2O$, and the corresponding selenate, $Na_2CO_3 \cdot 10H_2O$, $Na_2HPO_4 \cdot 12H_2O$, and the corresponding arseniate, $Na_2B_4O_7 \cdot 10H_2O$: the alums, as for instance, $Al_23SO_4 \cdot 24H_2O$, $Na_2S_2O_3 \cdot 5H_2O$, and $NaC_2H_3O_2 \cdot 3H_2O$.

The formation of solutions of these salts by heating the solids with a minimum of water, their preservation by protecting them from dust, and their sudden crystallization accompanied by rise of temperature are well-known phenomena. For their solidification either a fragment of a crystal of the same salt, or one of the similar constitution and isomorphous with it, must be introduced into the liquid. Their behaviour has been carefully investigated by J. Millar Thomson.[1]

The anhydrous compounds will not cause crystallization; neither will a hydrate containing fewer molecules of water than belongs to the original salt. It is well known also that, if a solution of sodium sulphate which is supersaturated be cooled for some hours below 15° C., say at 10°, it deposits a small proportion of the salt with seven molecules of water instead of ten. From these and other facts which have come under observation,

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[1] Trans. Chem. Soc., 35, 1879, pp. 196–206. Also Thomson and W. P. Bloxam, Trans. Chem. Soc., 41, 1882, pp. 379–387.

during many years past, I have been accustomed, since 1882, to explain the cause of the phenomena by stating that the salt in solution is not that which crystallizes out suddenly; that which is formed in the solution by the action of heat is not the anhydrous compound, but a hydrated salt containing fewer molecules of water than the salt which was dissolved. It is essential that it should be more soluble at the higher temperature. The following are some of the facts which have led to this conclusion. Anhydrous salts much more soluble in hot than in cold water, such as potassium nitrate and silver nitrate, were not found to yield supersaturated solutions capable of sudden crystallization. If they are supersaturated when first cooled, such supersaturation is very slight, and the excess of salt in solution is gradually deposited, and is complete in twenty-four hours.

Soluble hydrated salts which have been completely dehydrated, such as sodium sulphate and manganese sulphate, if put into water, do not dissolve until they have first become hydrated again; the former salt then becomes the soluble hydrate with $10H_2O$, the latter the hydrate soluble, in one-third its weight of water, with $7H_2O$. When moistened with an insufficiency of water to form a solution, or even with an excess of water, they solidify to hard solid masses, apparently insoluble in water at 16° C.: this is particularly the case with the manganese salt. These hard masses only gradually become further hydrated and dissolved. A mixture of anhydrous manganese sulphate, with from 60 to 70 per cent. coarsely ground ferric oxide, sets quite hard, like Portland cement, and may remain in this condition under water without sensible diminution in quantity by solution, the hydration and subsequent solution being a slow process at the ordinary temperatures.

There are, in fact, several salts which, in the anhydrous condition, afford no evidence of being soluble in water to any extent while remaining in that state, though when they have once entered into combination with water they become extremely soluble. In confirmation of the statement made with respect to sodium sulphate let me refer to a classical memoir of M. H. Le Chatelier.[1]

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[1] "Recherches Expérimentales sur la constitution des matière hydrauliques." Extrait des Annales des Mines. May and June, 1887. Paris Vue. Ch. Dunod, 1887.

Anhydrous gypsum, or over-burnt plaster, is quite insoluble in water, but the mechanism of the crystallization of plaster of Paris $(CaSO_4)_2 \cdot H_2O$, during the process of setting, is the following. The partially dehydrated gypsum becomes at points in its mass, 1st, hydrated ; 2ndly, dissolved to supersaturation ; and 3rdly, crystallized $CaSO_4 \cdot 2H_2O$. When the hydration of a salt is slow, the supersaturation, on the contrary, becomes considerable. Anhydrous sodium sulphate sets in contact with water like dried gypsum, though it is a much more soluble salt. Coppet[1] has shown that this anhydrous salt, placed in presence of water, gives strongly supersaturated solutions, even when care is taken to prevent any rise of temperature ; and Le Chatelier has confirmed Coppet's observation of the formation of supersaturated solutions both with anhydrous sodium sulphate and carbonate. On p. 18, he describes a most ingenious experiment, showing how sodium sulphate when anhydrous, first dissolves and afterwards recrystallizes to a hard mass in presence of water, but at a considerable distance from the solid anhydrous salt which becomes hydrated and dissolved before it crystallizes. The whole operation was so conducted that no elevation of temperature beyond 0·5° C. could take place, and therefore heat did not cause the supersaturation of the solution. The conclusion drawn from all the facts quoted by Le Chatelier was, that crystallization, which accompanies the setting of all substances which harden in water, results from the previous production of a supersaturated solution. The hydration and subsequent solution of finely powdered manganous sulphate, $MnSO_4$, was observed by me in operations conducted on a manufacturing scale. In this case it cannot be alleged that there was no rise of temperature, but in operations conducted on a smaller scale, the substances being immersed in a large excess of water, there was no sensible increase, though undoubtedly, when no great excess of water was used, the combination of water with the anhydrous salt caused a considerable evolution of heat. The same salt mixed with ferric oxide, Fe_2O_3, when immersed in cold water, set so hard that even twenty-four hours afterwards it adhered so firmly to a large porcelain basin, the vessel was broken in endeavouring to detach the

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[1] *Comptes Rendus*, lxxiii., p. 1324.

mass. In fact it behaved very much like concrete in the manner of its hardening under water, though the fully hydrated salt $MnSO_4{\cdot}7H_2O$ is soluble, as I have already stated, in so small a proportion as one-third of its weight of water. There are, however, several well-defined hydrates of this sulphate which are crystalline, one $MnSO_4{\cdot}2H_2O$, and another $MnSO_4{\cdot}5H_2O$.

Many, if not all, sulphates and carbonates which form crystalline hydrates are insoluble in the anhydrous state, but become soluble when hydrated. This is also the case with several other salts; and the following are three conspicuous examples, namely, copper sulphate, cobalt iodide, and cupric bromide. The former salt is white and insoluble until it has combined with water, when it becomes blue and dissolves. The second in the anhydrous state is intensely black in colour; on absorbing water from the air it becomes the dark green dihydrate which is solid, and subsequently becomes a brown solution, and finally a red liquid. Conversely, on drying by a carefully regulated increase of temperature, the solution becomes a green crystallized dihydrate, and finally the green solid loses water, and becomes the intensely black compound, CoI_2. No solution of this black substance in water is known.

Cupric bromide, $CuBr_2$, which is exposed to the air, absorbs moisture without liquefaction; the solid substance with a steely metallic lustre becomes the dihydrate $CuBr_2{\cdot}2H_2O$, the change in composition being accompanied by a great increase in volume and a change in appearance from a crystallized lustrous substance to one with a dull black appearance like charcoal, and apparently amorphous. The further hydration results in production of the pentahydrate $CuBr_2{\cdot}5H_2O$ in the solid crystallized form, but rise of temperature of but a very few degrees causes dissociation of the latter salt whereby the dihydrate is produced, but the water liberated by dissociation from the pentahydrate forms a dark brown solution containing either the dihydrate or, if the temperature be raised, the anhydrous salt. It may be mentioned here that a hydrated cupric bromide, when dried over sulphuric acid in a desiccator, yielded a dull black substance with the composition of a monohydrate $CuBr_2{\cdot}H_2O$; but at temperatures between 48° F. and 50° F. there is very little tendency to form this substance when the salt is exposed to moist air, the di- and tri-hydrates being much more readily formed.

Evidence from Coloured Salts.

In a Paper recently published by the Society,[1] evidence is adduced of the existence, in solution, of salts in a definite state of hydration, and of changes in the state of hydration, following upon rise of temperature. A second contribution is in course of publication, "On the Conditions of Equilibrium of Deliquescent and Hygroscopic Salts, with respect to Atmospheric Moisture." In both these investigations the remarkable behaviour of cupric bromide is described. This salt crystallizes at temperatures below 15·5° C. as golden green, and also as rich dark green prisms, when of larger size, with the composition $CuBr_2·5H_2O$; it forms also a dihydrate $CuBr_2·2H_2O$, which is dull black, like charcoal, and an anhydrous salt, the crystals of which are black, with brilliant steely lustre. On concentrating the solution at or above 15° C., only the anhydrous salt can be obtained, and this only after a very high degree of concentration. The solution is black in thick layers, or of an intensely dark brown in thin layers. A saturated solution of cupric bromide was cooled by immersing the vessel containing it in ice. Its temperature fell to 2° C. without any sign of crystallization or solidification, and there was no change of colour by cooling. This latter fact indicates that the liquid had not undergone any change in its constitution. As but a little further concentration would cause the mass to solidify in the anhydrous condition, it appears as if this is a supersaturated solution of $CuBr_2$. Subsequently the temperature sank to 0·1° C., still without undergoing any change. On agitating the liquid by using the thermometer as a stirrer, it first deposited a few isolated golden green crystals of the salt $CuBr_2·5H_2O$, and then solidified to a magma of crystals in the brown mother liquor when the temperawas observed to rise to 3° C. These crystals could not be identified either with the pentahydrate or the anhydrous salt, and, as they were very perishable, they could not be submitted to any minute examination. Some of them were needle-shaped, and were probably small crystals of the pentahydrate; a larger proportion were rhombic plates, which is one of the forms of the anhydrous salt.

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[1] Transactions, vol. vii., (Series II.) p. 253, 1900.

Two determinations of the water they contained yielded numbers from which 1·4 and 2·01 per cent. of water was calculated. This does not correspond to any molecular proportion; the salt was therefore a mixture of the anhydrous $CuBr_2$ with a crystalline hydrate. When the temperature had sunk again to 2·3° C., there was a larger proportion of mother liquor to crystals, as if a considerable proportion of the solid had re-entered into solution.

In order to render the condition of the solution such that the pentahydrate might crystallize out, there were added to the whole quantity of crystals and mother liquor together 10 c.c. of water. The black crystals dissolved, and the liquid became of a cold yellowish brown colour. Continued agitation of the liquid at a temperature of about 1° C. caused no indication of crystallization or change in colour. About 50 c.c. of the mother liquor, poured off the first batch of black crystals, were mixed with the above solution in order to concentrate it, and the mixture was cooled down to 0·5° C., with frequent vigorous stirring, but no crystallization took place. The syrupy reddish brown solution drained from a mass of the black crystals, and which therefore was more concentrated than the yellowish-brown solution, did not show signs of crystallization after being kept for about two hours at a temperature of 0·5° C. with frequent stirring.

It may be mentioned here that the thermometer, a very delicate one, each degree being divided into tenths, which was made by Casella many years ago, was tested after these experiments, and the zero was found to be only 0·2° C. too high. A second thermometer marking degrees only, made by Geissler, showed a similar error.

The explanation of the phenomena, of which the foregoing is a detailed description, appears to me to be as follows. In the first instance, there was a completely saturated solution of the compound $CuBr_2$. After cooling down below 15° C., the liquid was a mixture of the dissolved anhydrous salt, with a small proportion of a solution of $CuBr_2{\cdot}5H_2O$, which latter salt crystallized out. A portion of the water which held the salt $CuBr_2$ in solution having combined and formed the compound $CuBr_2{\cdot}5H_2O$, the liquid then became a supersaturated solution of $CuBr_2$, and the rhombic crystals of this compound were deposited. As, however, the temperature rose about 3° C. owing to the heat evolved in the act of combination, a proportion of the salt redissolved and remained in solution as $CuBr_2$.

Attempts were then made to obtain a supersaturated solution of cobalt chloride which would crystallize suddenly. Several crystalline masses of the solid $CoCl_2{\cdot}6H_2O$ were placed in a tube and moistened with about 5 c.c. of water; then boiled, and the tube plugged with cotton wool as soon as steam escaped freely from the mouth of the tube. The solution was then quite blue, and it was allowed to cool. The uppermost layer of the liquid touching the glass appeared purple, the bubbles upon it were crimson, but the liquid below, when shaken up, was indigo-blue in colour and very dark. After two trials, another solution was made which remained for about four hours in a test-tube cooling, but it did not acquire the colour of the cold solution obtained by saturating cold water at 15° C. It was purple like a solution when heated to 53° C. This solution had a boiling point of 115° C. It was evident that the cobalt chloride in the liquid had not resumed the condition of a salt with the composition of $CoCl_2{\cdot}6H_2O$; otherwise it would have resumed its colour. Some crystals had separated and adhered to the glass, though the tube was plugged with cotton wool and had not been opened. It appears, therefore, that no supersaturated solution of the original salt could be preserved for any length of time. The crystals which separated were red and quite unlike the solution, though their colour was precisely the same as that of the solid hexahydrated salt, which they proved to be. After leaving the purple solution which had been poured off from the crystals for twenty-one hours the colour became deep crimson, darker than the crystals which had been deposited within it, and also darker than the saturated solution of cobalt chloride, $CoCl_2{\cdot}6HO$, which had been kept for some days at temperatures varying between 15° and 20° C. It appears, therefore, that the water dissociated by rise of temperature had not all recombined with the salt to form the original hydrate, but that some compound intermediate between this and the anhydrous salt was the substance which remained in solution. From the colour of the solution the state of hydration of the dissolved salt was $CoCl_2{\cdot}4H_2O$.

The theory which I had formed of the constitution of supersaturated solutions has been recently confirmed by M. G. Wyrouboff in a memoir, " Recherches sur les Solutions."[1]

He has worked on four salts which form hydrates with different proportions of water, and has investigated the solubility of these hydrates at different temperatures. These are nickel sulphate, cerium sulphate, thorium sulphate, and potassium-cadmium sulphate.

There are no fewer than four different forms of nickel sulphate : — (1) $NiSO_4 \cdot 7H_2O$, orthorhombic, emerald green; (2) $NiSo_4 \cdot 6H_2O$, cubic, bluish green; (3) $NiSO_4 \cdot 6H_2O$, clinorhombic, yellowish green; (4) $NiSO_4 \cdot 5H_2O$, crystalline system not described, a bluish salt *which effloresces.*

The solubility of these salts increases from the first to the third, which crystallizes at 70° C. The fourth salt is even more soluble; it is formed by evaporation at 100° C., and precipitation from the concentrated solution by the addition of alcohol. It has been shown by Lecocq de Boisbaudran that, by the introduction of a fragment of a crystal of $CoSO_4 \cdot 6H_2O$, or $FeSO_4 \cdot 6H_2O$, into a supersaturated solution of nickel sulphate, the clinorhombic form of the salt $NiSO_4 \cdot 6H_2O$ is separated. The interpretation of this phenomenon is, that the salt in solution is $NiSO_4 \cdot 5H_2O$, but the salt which crystallizes out is the clinorhombic $NiSO_4 \cdot 6H_2O$, which is less soluble.

In 1887, Dr. W. W. J. Nicol[2] brought forward the view formerly advanced by Lœwel,[3] that solutions usually regarded as supersaturated are not really so, but owe their formation to the fact that the salt dissolved is not the same as that which crystallizes out. He further states that no well authenticated cases of supersaturation of a solution of a salt which crystallizes without water is known to him.

As I have already pointed out, the supersaturation of solutions of anhydrous compounds, which do not form crystalline hydrates, is not so considerable as to be a well-marked phenomenon even when the salt is much more soluble in hot than in cold water; and such supersaturated solutions do not exhibit the marked peculiarities characteristic of solutions of hydrated compounds—as, for

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[1] Bulletin de la Société Chimique de Paris, 3° serie, t. xxv.-xxvi., p. 105, 1901.

[2] Chem. Soc. Trans., vol. 51, p. 389.

[3] Ann. Chem. Phys. [3], 49-51.

instance, crystallizing to a solid mass by the introduction of an already formed crystal or a fragment of the same. The facts of the case may be better understood by reference to a paper "On the Determination of the Solubilities and Specific Gravities of certain Salts of Sodium and Potassium," by Page and Keightley.[1]

The determination by saturation at a higher temperature and subsequent cooling proved that a state of supersaturation obtains less or more in every instance; but, in the case of these anhydrous salts, this phenomenon cannot be attributed to different degrees of hydration, as in the case of sodium sulphate. The fact that solutions so prepared exhibit a greater density at 15·6° C. than those maintained at that temperature from the outset, has a probable explanation in what may be termed "the attraction of solution"; or in other words, "the indisposition of the salt to change its state by virtue of the attraction of the mass in solution."

The extent to which supersaturation can exist is shown by the subjoined figures, which were very exactly determined, and are quoted from the original communication.

Solution prepared by digestion of the salts at a constantly maintained temperature of 15·6° C.			Solution prepared by saturation at 100° C. and subsequent cooling to 15·6° C.		
Salt.	Sp. Gravity.	100 parts of water dissolved.	Salt.	Sp. Gravity.	100 parts of water dissolved.
NaCl	1204·03	35·76	NaCl	1206·93	36·26
KCl	1171·10	32·88	KCl	1171·82	33·06
$NaNO_3$	1137·81	84·21	$NaNO_3$	1378·43	84·69
KNO_3	1141·23	26·04	KNO_3	1142·23	26·30
KNO_3 and		40·39			
$NaNO_3$ together		15·29			

Nicol's work is important, inasmuch as he furnishes evidence to disprove any analogy between the phenomenon of superfusion and that of supersaturation of a solution. Supersaturated solutions were prepared by dissolving cold dehydrated salts in cold water, and such solutions were found to be identical, so far as the quantity of dissolved salt is concerned, with solutions prepared by the aid of heat. He ascribed the formation of supersaturated solutions to the existence in solution of the anhydrous salt. According to this view, supersaturated solutions differ in no way

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[1] Jour. Chem. Soc., vol. xxv., 1872, p. 566.

from ordinary solutions; they are merely saturated or non-saturated solutions of the anhydrous salt, combination to form the hydrate taking place only at the moment of crystallization. It will then be seen that the view put forward by Nicol is essentially different from mine in the following particulars. For reasons already stated it appears to me—1st, that the anhydrous salt must become hydrated before it can enter into solution; 2ndly, that the hydrated compound, which is a crystalline salt existing in the so-called supersaturated solution, is not the hydrate that crystallizes out when a crystal is introduced; and 3rdly, that the phenomenon of supersaturation is a manifestation of differences in solubility of two distinct crystalline hydrates at a given temperature, which may be quite different in the extent of their hydration, and one of which may be formed from the other at the moment of crystallization by some considerable proportion, if not the whole, of the solvent water, entering into combination with the hydrate in solution, whereby the newly formed compound becomes insoluble and separates as a crystalline mass.

My attention has been drawn to a more recent communication by Dr. Nicol,[1] in which he returns to the subject of supersaturation of solutions of salts which do not combine with water to form crystalline hydrates.

The question he states is generally regarded as undecided, notwithstanding that there are many excellent examples of supersaturation among organic compounds, from which the possibility of forming hydrates or analogous compounds is excluded, and consequently the explanation, which proves satisfactory for salts containing water, is in this case not applicable. It may be remarked here that chemists engaged in the manufacture of organic compounds have long since recognised the fact that these substances frequently exhibit the phenomenon of supersaturation, though in some cases at least it has been doubted whether they were not cases of superfusion. Phenol is a conspicuous example, as it is usual to crystallize it in large masses by the introduction of a ready formed crystal of the substance.

There are other cases, such as that of potassium hydrogen tartrate, in which the substance is formed in solution, and

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[1] Zeitschrift für Anorganische Chemie, vol. xv., 1897, p. 397.

crystallization takes place on agitation, or scratching the surface of the containing vessel. The phenomena appear to be altogether different from those of such hydrates as sodium sulphate, which do not crystallize by shaking or other means of agitation. Glycerol,[1] again, is a substance which, by a very low temperature and continual vibration, becomes crystallized, but its persistence in a liquid state, notwithstanding low temperatures, must be due to what is ordinary called superfusion.

The instances quoted by Nicol are acetanilide, hydroquinol, acetamide, malonic acid, mandelic acid, resorcinol, tartaric acid, and citric acid.

In this latter example, water plays an important part; and no fewer than four different crystalline forms of citric acid have been recognised.

The following general statement has been formulated by Nicol as applicable both to anhydrous and hydrated compounds, to supersaturation of solutions, and to superfusion :—

"As soon as the conditions of the experiments are such as to admit of two allotropic modifications of the dissolved or of the molten substance, then the occurrence of supersaturation, or of superfusion respectively becomes possible."

The word 'allotropic' is used in a wider sense here than is usual, since it is applied to different crystalline modifications of one and the same substance, which are conditional on the presence or absence of molecules of other substances, as, for example, water of crystallization. It is further stated, with respect to substances which combine with water :—

"I. Supersaturation of a solution is occasioned by allotropy, which is conditional upon the presence of molecules foreign to the salt, particularly water of crystallization."

"II. Supersaturation is occasioned by the existence of allotropic (whether enantiotropic or monotropic) forms."

In the latter case the behaviour of potassium nitrate, ammonium nitrate, and silver nitrate is considered, as also the organic substances before mentioned. The anhydrous salts are said to form supersaturated solutions; but each can, in the anhydrous state, exist in two different crystalline forms, one of which is unstable,

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[1] Jour. Chem Soc., xxix., p. 384. Gladstone.

so that it easily passes into the other, and in so doing crystallizes completely, thus causing the whole of the solution to become solid.

Cases of supersaturation and crystallization of the former category (I.) appear to be capable of receiving the same explanation of their cause as that which I have given, and by that which is advanced by Wyrouboff, while those described under II. are such as were accurately described by Page and Keightley, but were found difficult of explanation because the transitional crystalline forms were not recognised. The reason of their crystallization, as explained by Nicol, applies equally well to the anhydrous inorganic salts as to the organic substances he dealt with, and on that account is full of interest.

I do not gather from Nicol's paper that he has explained the cause of the crystallization in these cases, but it may be inferred from analogy with the hydrated compounds that the reason why the transitional or unstable form crystallizes only in small quantity is because it is the more soluble modification of the compound. We thus see how it is possible that certain salts can form, and do form, supersaturated solutions, even when they are anhydrous, as, for instance, calcium carbonate, an instance cited by Le Chatelier, the different crystalline forms of the dimorphous salts having in all probability different degrees of solubility in cold water.

Note added in the Press.

I have recently verified by a few simple experiments some observations on copper sulphate made by me many years ago, and referred to in a course of lectures[1] delivered at the Royal Institution, but of which I find no details published. Three portions of the perfectly anhydrous salt, each weighing approximately 0·46 gr., were dropped into different quantities of cold water, and of a saturated solution of $CuSO_4 \cdot 5H_2O$.

(1). 0·46 gr. were placed in 0·5 c.c. of distilled water at 15° C. This is about twice as much as is necessary to form $CuSO_4 \cdot 5H_2O$. The liquid became warm, the white anhydrous salt caked, and only

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[1] "Air and its Relations to Life": London, 1876.

a very small portion of it dissolved to form a blue solution. The white anhydrous salt could be seen in the solution, it became hydrated very slowly; finally hydration seemed to cease, and the white salt remained insoluble in the solution of $CuSO_4{\cdot}5H_2O$ which was formed. After a period of rest for two hours, this portion of the salt was seen to have become crystallized, and of a very pale blue colour.

(2). 0·46 gr. was dropped into 5 c.c. of water at 15° C. The salt became hydrated, and dissolved to a clear blue solution in from five to ten minutes.

(3). 0·46 gr. was dropped into 5 c.c. of a freshly prepared saturated solution of $CuSO_4{\cdot}5H_2O$ made with cold water. The anhydrous salt did not dissolve or appreciably diminish in volume and it remained white. Even after standing for four hours very few crystals were seen under the microscope; nearly all the salt had remained amorphous and anhydrous.

(4). 0·46 gr. was added to 0·5 c.c. of cold water, shaken vigorously, poured into a watch-glass, and immediately examined under the microscope. The amorphous white opaque masses of the anhydrous compound were seen to become the nuclei for well-formed minute crystals to grow out of, until they became crystalline all through and transparent. It was observed that the solution formed became turbid sometimes when this experiment was repeated in a test tube, and then crystals were deposited, as if a hydrated salt entered in solution, and afterwards separated as crystals containing probably a larger proportion of water. Hydration, solution, and growth of crystals from the solution appears to be the order of the chemical change; while the formation of a liquid turbid from the separation of crystals indicates the phenomenon of supersaturation. Twenty-four hours after the last examination of the amorphous solid and the crystals in experiment (3), the solid matter was examined again. The number of crystals had greatly increased; they were small and appeared colourless. Some of the amorphous masses were semi-transparent and appeared of an extremely pale blue when drained from the cupric sulphate solution. A few crystals of the normal salt $CuSO_4{\cdot}5H_2O$ of much larger size, had grown, which had the usual appearance of such crystals.

The semi-transparent masses were apparently compact groups of very minute hydrated crystals which had grown upon nuclei of the amorphous sulphate. It was not determined whether these crystals were of the same composition as the normal salt or not, but it may be remarked that very similar groups were precipitated from a saturated solution of the normal salt by the addition of alcohol.

Why the saturated solution of the fully hydrated salt $CuSO_4 \cdot 5H_2O$ did not admit of the anhydrous cupric sulphate becoming hydrated except to a very limited extent, or, which is the same thing, very slowly, is to be explained by its inability to take into solution any more of the salt which is formed by the combination of the anhydrous compound with water (June 19th, 1901).

XLIII.

AWARD OF THE BOYLE MEDAL TO PROFESSOR THOMAS PRESTON, M.A., D.Sc., F.R.S., 1899.[1]

In recommending that the Boyle Medal be this year awarded to Professor Thomas Preston, the Science Committee have more especially in view the recent important advances which Professor Preston has effected in our knowledge of the phenomena attending radiation in a magnetic field, which work he has communicated to this Society during the last two years.

Your Committee in the first place desire to place on record their great regret at the unfortunate illness which alone has hindered Professor Preston from continuing the investigation. Meanwhile they submit that sufficient has been accomplished by Professor Preston to mark important advance in this field of research.

Early in 1897 the broadening of the spectral lines arising from radiation in a strong magnetic field was announced by Dr. P. Zeeman; and about the middle of that year, Dr. Zeeman further announced the fact that the triple nature of some of these lines had been established by aid of the differing polarisation of the central and lateral bands. This important experimental work was the first completely successful accomplishment of an experiment undertaken by Faraday, so long ago as 1862. The theoretical aspect of Zeeman's first experiments had been examined by Professor Lorentz and by Dr. Larmor. The threefold nature of the broadened lines as well as their polarisation phenomena had been predicted by these mathematicians, and also the probability that the change of wave-length introduced by the magnetic force should be proportional to the square of the wave-length of the affected lines.

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[1] The presentation took place at the Council Meeting of February the 8th, 1900, when the medal was handed by the Chairman (Right Hon. Viscount Powerscourt, K.P.) to Professor G. F. FitzGerald, F.T.C.D., F.R.S., on behalf of Professor Preston, who, owing to illness, was unable to be present.

Such, briefly, was the state of the inquiry, when Professor Preston—working with the Rowland Grating of the Royal University—brought his first research before this Society towards the close of 1897. ("Radiation Phenomena in a Strong Magnetic Field," Trans. R. D. S., vol. vi., Ser. II., 1898, p. 385.)

Members of this Society who were present on that occasion, will recollect that they were treated to no second-hand account of the phenomena, but were shown—a feat not before attempted—the triplication and quadruplication of the lines of cadmium and zinc by means of photographs projected on the screen.

In this communication, Professor Preston not only showed that he had attained a higher degree of resolution of the lines than had up to this been accomplished, but he was able to announce the existence of quartet and sextet forms for the first time. In his paper he seeks for explanation of the quartet variation from the normal triplet, and the fact that the difference of wave-length introduced by the magnetic force is not proportional generally to the square of the wave-length (as the simple theory seemed to suggest) was forced upon him at this early stage of his work.

Although these matters were laid before the Royal Dublin Society in December, 1897, Professor Preston can lay still earlier claim to these observations, as appears from a short communication to *Nature* in November of the same year. (*Nature*, vol. 57, 1898, p. 173.)

The second memoir on the subject appeared in the Transactions of the Royal Dublin Society for June, 1899 (vol. vii., Ser. II., pp. 7 *et seq.*), having been read by Professor Preston in January of that year.

He here offers an explanation of the quartet form analogous to Professor Fitz Gerald's suggestion that the ionic orbits will vibrate with definite period about their position of rest in the magnetic field, and records the observation that, for corresponding lines of the natural groups or series of Keyser and Runge, the theoretic condition obtains.

He further, in this communication, suggests a law which apparently involves the far-reaching conclusion that structural features in common are possessed by chemically related atoms. Although such a conclusion commends itself for other well-known reasons, so direct a proof as is involved in "Preston's Law," had hardly been hitherto adduced. This law he illustrates by the case of three substances:—magnesium, cadmium, and zinc. The law expresses the fact that not only are similar lines in the series of chemically related elements similarly modified by the magnetic field, but that the value

$$\frac{d\lambda}{\lambda^2}$$

is, in these cases, the same. The importance of this law, whether the theory of ions is accepted or not, is accentuated in M. Cotton's able review of the present state of the investigation. (Le Phénomène de Zeeman, *Scientia*, Oct. 1899.)

In the course of these researches Prof. Preston was gradually increasing the strength of his magnetic field, and lately was using a magnet built to his own design attaining a field of 40,000 cgs. units. The design of this magnet is original, but a published account of it has not yet appeared.

With the aid of this powerful instrument he was able to announce, in the addendum to his paper in the Trans. R. D. S. last referred to, that the quartet form hitherto noticed is really a sextet, the outer lines being feebly bipartite, that the normal triplets are not further resolved, and that the diffuse triplets are, in fact, nonets, consisting of unequally luminous lines.

Contemporaneously with these papers, others, mainly recapitulatory, appeared:—

Phil. Mag. xlv., 1898, p. 325.
,, ,, xlvii., 1899, p. 165.
Nature, vol. 59, Jan. 5, p. 224; March 23, p. 485; April 6, p. 533, 1899.

A clear and lucid account of the whole matter is also to be found in the report of Prof. Preston's lecture before the Royal Institution appearing in *Nature*, vol. 60, June 22, 1899, p. 175.

It is satisfactory to find how clearly in his later papers, Prof. Preston recognises the pioneer work of Dr. G. J. Stoney (upon whom this Society conferred the Boyle Medal last year).

On Dr. Stoney's conception of the ionic charge, originating by its orbital and orbital-apsidal motions, sequences of dual lines in the spectrum, much has since been founded. Dr. Larmor uses a similar conception to explain, as before referred to, the triplet produced by the influence of the magnetic field. Herein is indicated the present great interest of the research into magnetic radiation. It appears to place in the hands of the investigator a means of testing the adequacy of material theories. Beyond this, it is needless to observe, are ranged a host of problems awaiting solution in a dynamic conception of matter. To open this gateway of knowledge and reveal the light within, Prof. Preston has laboured earnestly and effectively.

We have in the foregoing referred to Professor Preston's leading work and to that specially qualifying him to receive the Boyle Medal, but before this work appeared, he was already known as a writer on science of high standing. His text-books on Light and Heat ("Theory of Light," Macmillan, 1890, 2nd. ed. 1895; "Theory of Heat," Macmillan, 1894) are at once characterised by a clear and pleasant style and a thorough grasp of the subjects treated. These works may each fairly claim to be advances on any previous English text-books of the same scope. The classical experiments of the earlier and central years of the century find sufficient notice, but are not given that undue prominence which detracts from the value of many text-books. The methods and precautions of Regnault and his school should be known to all students in their essential features, but the science student of to-day possesses agents and materials to aid him in his researches unknown to the preceding generations. Not only have these been given due prominence in Professor Preston's works, but they are accompanied by such able expositions of theoretical principles as render these text-books of more value to the modern student than perhaps any other works of the kind at present before the public.

Professor Preston is also the author, in part, of a well-known text-book on "Spherical Trigonometry" (Macmillan, Parts I. and II., 1885, 1886), as well as of several scientific papers which in this brief notice need only be referred to by title, but which are all marked by his ingenuity and thoroughness:—

"Application of the Parallelogram Law in Kinematics."—Proc. R.D.S., VIII., 1893–98, p. 469.

"On the Inversion of Centrobaric Bodies."—Proc R.D.S., V., 1886–87, p. 639.

"A Lecture Note on the Relation of the Theorem of Work to the Theorem of Moments."—Proc. R.D.S., VIII., 1893–98, p. 167.

"On the Continuity of Isothermal Transformation from the Liquid to the Gaseous State."—Trans. R.D.S., VI., 1896–98, Ser. II., p. 119.

"On the General Extension of Fourier's Theorem."—Phil. Mag., vol. 43, 1897, pp. 281 and 458.

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XLIV.

ON HAZE, DRY FOG, AND HAIL.

By W. N. HARTLEY, D.Sc., F.R.S.,

Royal College of Science, Dublin.

[Read November 20; Received for Publication, December 13, 1901; Published February 27, 1902.]

The work of Mr. John Aitken, F.R.S., on Dust, Fogs, and Clouds[1], led him to the conclusions which here follow :—first, that wherever water vapour condenses in the atmosphere, it always does so on some solid nucleus; secondly, that dust particles in the air form the nucleus on which vapour condenses.[2] The sources of atmospheric dust, besides ocean spray which becomes converted into a fine dust of salt, are the the products of combustion, together with almost all substances which are strongly heated, since these have been shown to contribute minute solid particles to the atmosphere. The fewer the dust particles, the more moisture condenses upon them, and they thus become heavier and fall. The more numerous they are, the less is the moisture condensed upon each of them, so that they remain suspended as fog, instead of falling as rain, hail, or sleet.

These islands are seldom free from cloud, rain, or fog, and minute quantities of dust, in a more or less moist condition, are nearly always present in the upper atmosphere. Observations on the number of dust particles in measured quantities of air have been made for some time past on the summit of Ben Nevis.

The prevailing winds with us are the west, south-west, and south; and the warm moist-laden air of the Atlantic is the cause of the condensation of aqueous vapour upon the dust particles.

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[1] Abstract, Proc. Roy. Soc. Edin., vol. xl., p. 14 (1880–1881).

[2] More recent experiments have shown that when air is filtered or washed so that it may be believed to be free from dust, a sudden expansion of saturated air causes the formation of a rain or mist. The expansion required being in the ratio $V_2/V_1 = 1{\cdot}252$, where V_1 is the initial and V_2 the final volume. This does not however affect the question of dust-laden air. C. T. R. Wilson, Phil. Trans. vol. 189, p. 265, 1897; also vol. 193, p. 289, 1900.

The dust particles themselves may have originated in salt spray from the ocean, carried up in equatorial regions, and from which the heat of the sun has evaporated the water. Consequently, a cloud may consist of moist crystals of salt; and by the accumulation of more water upon the nucleus or salt crystal, it may become a minute drop, consisting of a solution of salt. This may condense a still larger proportion of water, and become a drop of rain, and that this is the case there is evidence in the fact that rain-water always contains sodium chloride; but a drop of rain does not generally contain any appreciable solid nucleus insoluble in water, when the clouds from which it fell are travelling with our prevailing winds. Atmospheric dust may thus be said to be of two kinds, that which is soluble, and that which is insoluble in water.

Let us deal now with that which is insoluble.

At Palermo, on March 10th, 1901, a dense lurid cloud hung over the town, the sky appearing blood-red. There was a strong south wind, and drops of rain fell, having the appearance of blood.[1]

The phenomenon was attributed in that locality to red dust, carried up from the sands of the Sahara.[2]

At Naples showers of sand fell while the sky was of a deep red colour.

From Algiers, reports of a similar occurrence in North Africa were received.

Fine sand carried to a great height in the atmosphere is sustained by reason of the viscosity of the air and the minute dimensions of the particles. The condensation of moisture upon them increases their size and weight, and causes their descent as rain; otherwise they settle down more slowly, and travel farther by the operation of air currents.

Hellmann and Meinardus have shown the hours at which red and grey sand showers fell in North Germany, which came from the same source as that in Southern Europe.[3]

Several analyses have been made, and also examinations with the microscope, with the result that the dust was shown to contain

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[1] *The Times* newspaper.

[2] Nature, vol. 63, p. 471.

[3] Dr. Hellmann's Meteorologische Zeitschrift, "Der Staubfall vom 10. und 11. März 1901."

felspar and quartz sand, or in other words, it was a red felspathic sand, such as is found in the desert of Sahara and in Egypt.

Black rain falls occasionally at distances apparently remote from manufacturing centres. Rain of this character, accompanied by intense darkness, descended upon an area of nearly 500 square miles in the North of Ireland, in February, 1898, during a spell of north-easterly wind.[1]

In May, 1899, an equal area in central and south-western England received a similar fall.

The precise atmospheric conditions necessary for raising of dust or smoke into the upper parts of the atmosphere, and the concentration and descent over special areas, is not fully understood.

On December 27th, 1896, there occurred over Melbourne and a considerable area of Victoria, an unusually heavy fall of dust of a red colour, which was carried down by accompanying rain. This was examined microscopically, and found to contain diatomaceæ; it was therefore of terrestrial origin. Its chemical analysis, made by Mr. Thomas Steel, F.C.S., showed that it agreed closely with the composition of volcanic soils from such widely separated localities as Northern Queensland, New South Wales, and Fiji.[2]

In such facts we have abundant evidence of the transference of great bodies of dust from the Earth's surface to far distant regions by the operation of gentle air-currents. In February last, I communicated to the Royal Society a paper, by Mr. Ramage and myself, on the mineral constituents of dust and soot from various sources.[3]

Dust was separated from hail, rain, and sleet which fell in Dublin; volcanic dust came from different sources, and pumice from Krakatoa. We collected soot from different chimneys, flue-dust from gas works, from iron furnaces, and from copper-smelting works. Flue-dust from vitriol works, and iron pyrites from coal, also the dust from coal ashes were analysed. The localities from which the specimens came were situated in Ireland, England, Wales, the United States, New Zealand, Krakatoa, Vesuvius, and South America. We also examined meteorites

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[1] Nature, vol. 63, p. 472.

[2] Australasian Association for the Advancement of Science, January 10th, 1898.

[3] Proc. Roy. Soc., vol. 68, p. 97, 1901.

found in different localities; for one of the objects of this work was to ascertain whether meteoric dust descended upon the Earth, and this could only be done by ascertaining whether dust from terrestrial sources resembled in composition that known to be of meteoric origin.

The method of examination was by spectrographic analysis, which is of extreme delicacy, and practically the only means available for investigating the composition of complex substances, with very minute quantities of material, such as could be obtained from hail-stones and drops of rain. The largest quantity of material derived from such a source was 0·08 gr. The spectra photographed were obtained by burning in the oxyhydrogen flame the substance wrapped up in, or distributed over, the surface of an ashless filter-paper. From the number of lines observed belonging to the different elements which can be photographed in this way, also from their relative intensities, the proportions of the different substances present could be ascertained, and the different spectra could be compared. It thus became evident that different kinds of dust could be broadly classified according to their composition, and their origin ascertained. It may be well to remark, at this point, that arsenic and antimony cannot be detected by this method when present in minute proportions, and that a chemical method, such as Marsh's test, is more sensitive than either the spark or flame-spectrum of arsenic.

There are two samples of dust which, on inspection, appeared to be of an unusual character, to which attention may be particularly directed.

(I.) Solid matter which fell in or with hail in a hail-storm on Wednesday, April 14th, 1897, and was collected by Professor O'Reilly at a window facing the large open space of Stephen's Green, at the Royal College of Science, Dublin. It contained iron, sodium, lead, copper, silver, calcium, potassium, nickel, manganese (a trace); gallium and cobalt gave doubtful indications.

(II.) Solid matter from hail and sleet collected by Professor O'Reilly on plates upon a window-sill of the Royal College of Science, Dublin, during a very heavy shower, from 2.30 till 3 o'clock, in the afternoon of March 28th, 1896.

Total weight of the dust 0·1018 gramme, of which 0·08 gramme was burnt in the oxyhydrogen flame. The colour of the dust was steel-grey and it was magnetic. It contained iron, copper and sodium, lead calcium, potassium, manganese, nickel, silver, thallium (a trace), gallium, and rubidium (a trace), doubtful.

As II. contained thallium, a substance found in pyrites flue-dust, it is evident that it might be precipitated from the atmosphere in a neighbourhood where sulphuric acid is made; but as the flue-dust from vitriol works in Dublin contains a notable proportion of indium, the absence of this element precludes the possibility of I. and II. having come from them.

Volcanic dust is distinguished by the very small proportion of the heavy metals, lead and iron for example, and the principal constituents being lime, magnesia, and the alkalies.

Dust from the clouds shows a certain regularity in composition, whether it has fallen directly, or been carried down by rain, sleet, snow, or hail. Each specimen, out of several, appeared to contain the same proportions of iron, nickel, calcium, copper, potassium, and sodium. The proportion of carbonaceous matter is small. The samples collected from hail, sleet, and snow differ from one another, and differ widely from other specimens, by reason of the large proportions of lead which they contain.

It need scarcely be mentioned that different specimens of soot differ very widely in composition, even when taken from different chimneys in the same house. The quantity of the metals, such as iron, lead, copper, silver, &c., differs with the amount of carbon in the soot.

Having pondered over the subject, I will now proceed to state the conclusions arrived at after collecting together the results of numerous and varied observations.

Dry Dust.—Fume of whatever kind, condensing to solid matter, causes the formation of a dry dust, provided such condensation takes place in a dry air. Then the proportion of moisture condensed on the solid matter is small; the result, as Aitken has shown, is a mist or fog; if large, it is a cloud; if still larger it may become hail, rain, or snow, according to the temperature. Shortly, however, it may be stated that what appears as mist low down on a mountain, exists as snow at a greater elevation where the air is colder. Dry dust may be seen in the air as a distinct discoloration of the sky. It may arise from the blowing away of the pollen or the bloom from flowering plants, and this sometimes is seen in hot dry weather on the moors and mountains of Scotland, when the heather is in full bloom. Sometimes a dry dust may be observed in the upper stratum of the atmosphere, which largely consists of the spores of fungi, and with a moist air at lower levels and a high temperature, such a cloud becomes blight. Dry dust may also arise from the smoke of towns, or the condensation of fume from metallurgical works, or from the finer particles of dust from the smoke-shafts of factories, but which differs from smoke in its comparative freedom from carbonaceous matter. Such dust is visible in the neighbourhood of manufacturing towns.

Wet Dust.—Wet dust, such as that I now refer to, accompanies rain, hail, or snow in its descent upon the Earth. The dust from hail and sleet, suddenly precipitated, differed in composition from any other form of dust which was collected from the atmosphere in or near Dublin, during the course of the investigation referred to above, by reason of the large proportion of lead present. In this respect it resembles dust from the flue of an assaying furnace, where lead ores are constantly melted in considerable quantities, and lead fume is seen to rise from the crucibles when they are uncovered. It also resembles the dust from the flue of a gas-muffle furnace, in which lead is oxidised and volatilised when cupellation assays are made.

We could imagine the possibility of dust being brought down by means of sleet shortly after its escape from the laboratory chimney; but on careful consideration of the facts, this appears to have been impossible with the particular samples of dust which were obtained from sleet. With hail-stones, in which the mineral particles are the actual nuclei, and so are contained within the spherules of ice, such a source of fume as a neighbouring chimney cannot be considered as having provided them. At first sight the following fact appeared to be a possible explanation of the composition of this dust. About five miles to the south-east of Dublin lie the disused Ballycorus lead mines, in the neighbourhood of which lead smelting to a very limited extent is still carried on. The flue for condensing the fume runs up the surface of a hill for about half a mile, and terminates in a vertical shaft on the summit. When this hail, which has been mentioned, was collected, a small quantity of fume had been seen occasionally to escape from the shaft. Hail and sleet falling in Dublin came from the east or south-east, and therefore lead fume diffused through the air might possibly be mixed with any dust travelling with the wind upon which moisture would condense and freeze.

But hail appears to be formed in consequence of very strong local currents driving a body of air heavily charged with moisture to a great altitude, where the moisture is condensed upon the solid particles of dust in the form of ice.[1]

On careful consideration, it seems most improbable that the actual quantity of lead fume from the particular source specified could have been sufficient to diffuse through so vast a space at so great an elevation as the dark cloud was seen to occupy previous to the descent of the hail; and therefore some more extensive and copious source of dust of this composition and at a greater distance from where it fell must be looked for. Such a district is South Wales. In the Vale of Dowlais, in April, 1893, there being an easterly wind and a perfectly cloudless sky with bright sunshine for several consecutive days, it was noticed that the fume arising from the Bessemer works, in operation both there and at Merthyr Tydvil, ascended to a great height as a distinct foxy-red cloud before it dispersed. Since then the same occurrence has been noticed in other districts. It was remarked at the time as continuing in this state for some three or four hundred feet above the works; but this was really a minimum estimate made from sketches drawn on the spot, and it falls very considerably short of the height at which the dust diffused. A thin widely-extended haze appeared in the blue sky at what could not have been less than 4000 or 5000 feet above the Earth, if we may judge from the known distance of the observer from the source of the fume and the apparent height of the mountains of known altitudes and at similar distances. This haze showed no tendency to settle, but wafted slowly to the westward.

In the Isle of Anglesey, in 1896, on the 23rd of May, the atmospheric conditions being precisely similar, that is to say with a feeble easterly or south-easterly wind and a cloudless blue sky, there appeared, high over Snowdon, commencing at about five

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[1] "Les phènomènes de l'atmosphère," p. 274, H. Mohn. Paris, 1884.

times the apparent height of the mountain, and extending as high again, a perfectly distinct blackish or grey haze subtending the angle of vision or about 30 degrees on a horizontal and vertical plane. There was nothing resembling it to be seen in any other part of the heavens, and the summit of Snowdon was perfectly clear. Such appearances in Ireland and Scotland have been noticed at much lower elevations, and they arise from manufacturing operations in the neighbourhood of Glasgow, Belfast, or Dublin. Down the Clyde, with an easterly wind, they have been seen as a thick dry haze to extend to Gourock and Dunoon. Occasionally over the sea a haze from steamer smoke is seen, but as a rule it lies much lower than the smoke of towns. Fume from the Bessemer process and from ferromanganese works contains chiefly iron and manganese, with very little, if any, lead; but where such fume can ascend, so also may the lead fume. Other instances of the transference of dust, soot, and fumes may be cited. Thus, on January 5th, 1901, with a very gentle easterly wind and a cloudless blue sky, the fume and smoke from the alkali district of Runcorn and Widnes, with the smoke also of Liverpool, was very distinctly observed from Holyhead to be carried out far into the St. George's Channel, at no great altitude, and descending apparently to not very far above the surface of the water. It presented the appearance of a reddish brown haze, and was not like that of steamer smoke, which is black or grey. It was evidently dry dust resulting from manufacturing operations carried on in the well-known industrial centres of Cheshire and Lancashire. The smoke of London may be observed high in the atmosphere as soon as one passes the Chiltern Hills, at or about Leighton Buzzard, when travelling southwards. The smoke of Alexandria and of the Vale of Leven is carried up Loch Lomond, and deposited upon the bracken on the western side of the Loch below Luss at a height of about 1000 to 1200 feet.

On January 7th, 1901, in Dublin and the district to the east of the city, the sky was overcast but without cloud, and there was a light current of air moving from the east, but no sign of fog near the Earth's surface. On the following day we received accounts of dense canopies of fog in London, and of similar atmospheric conditions in other parts of England. It appears, therefore, more than likely that this dry dust, smoke, or fume is carried in a body across the St. George's Channel, but at a great elevation. If the air-current amounts to a breeze, the dust is dispersed through a vast volume of air, and is not visible, and perhaps not otherwise capable of detection.

Taking these facts into consideration in connexion with what was observed in the South Wales district, the conclusion becomes inevitable that the haze was caused by dust originating with fume, which ascended during a period of anticyclone from one of the manufacturing centres of either South Wales, South Staffordshire, or possibly the pottery district of North Staffordshire.

Travelling slowly over St. George's Channel at an altitude of 10,000 to 15,000 feet, it may readily be understood that aqueous vapour could condense upon it and be precipitated as rain, snow, or hail. Metallurgical operations in the district around Swansea comprise lead and copper smelting; in the potteries lead oxide and alkalies volatilise from the kilns; in iron districts fume arises from Bessemer steel and ferromanganese works. A very reasonable explanation of the composition and origin of the nuclei of these hail-stones is afforded by these facts. It seems worth while to prosecute this inquiry somewhat further by examining dust collected from the neighbourhood of manufacturing towns, and afterwards in places far remote from them. I believe that from the spectrographic analysis of such dust it could be, in most cases, easily identified and traced to its source.

XLV.

THE NEBULA SURROUNDING NOVA PERSEI.

By W. E. WILSON, F.R.S.

[Read January 22; Received for Publication, February 12;
Published April 14, 1902.]

On the 22nd of last February a new star of the 1st magnitude was detected in the constellation Persei almost simultaneously by Dr. Anderson, of Edinburgh, and Mr. Ellard Gore, of Dublin. The outburst seems to have been exceedingly sudden, as that particular region of the sky was photographed in America on February 19th, only three days before, and there is not a trace of the star. The plate was given an exposure of over one hour, so that stars as faint as the 11th magnitude are clearly depicted on it.

The new star seems to have attained its maximum brilliancy a few days after its discovery, when it outshone stars of the 1st magnitude. It then rapidly waned, and, with some curious fluctuations in brilliancy, is now of about the 7th magnitude.

In September last, Mr. Ritchey, at the Yerkes Observatory, took a photograph of the Nova, using a reflecting telescope of two feet aperture, and giving the plate an exposure of about 4 hours. He thus found that the Nova was surrounded by a spiral nebula. This was an interesting discovery, as there is some suspicion that these new stars are connected in some way with nebulæ.

On November 9th and 13th Ritchey again photographed the Nova, giving his plates an exposure of about 7 hours. When these photographs were compared with the one of September 20th it was found that the nebula had altered in shape, and expanded in size. This was a most startling discovery, and quite unique in astronomical annals. The only possible explanation seemed to be that the nebula was the result of some terrific explosion of which the Nova was the origin, and that it was in fact expanding in volume like smoke after it leaves the mouth of a cannon. But it was soon seen that either the Nova must be comparatively close to the Earth, or else that the velocity by which the nebula was expanding must be enormous. If we assume that the Nova is as close to us as the nearest fixed star, the velocity necessary to account for this apparent expansion must be about 2000 miles per second. Such velocities are quite unknown and most improbable.

Early last month the idea occurred to me that this apparent expansion might be due to the illumination of the solid particles of the nebula by the light sent out on the occasion of the outburst of the star, and that if this hypothesis were correct it was possible to calculate the distance of the star from the Earth by means of the observed angular growth of the illuminated ring which must spread out with the velocity of light.

I have since found that Professor Kapteyn has quite independently suggested the same idea, and he can undoubtedly claim priority in its publication.

Let D denote the distance of the Nova, and let L be the distance travelled over by light in a year of 365·25 days, *i.e.* a light year.

Let T be the time in *days* elapsed from the outbreak of the star to the date of the photograph, and let ρ be the radius of arc in seconds from the Nova to the edge of the nebula, then

$$\frac{D}{L} = \frac{206265}{365{\cdot}25} \cdot \frac{T}{\rho},$$

or,

$$D = [2{\cdot}75184] \times \frac{T}{\rho} \times L,$$

the figure in brackets being the logarithm of $\frac{206265}{365{\cdot}25}$.

The angular distance ρ of the point marked (A) in the photograph of September 20th is almost exactly 480″, and the time from the outbreak is 211 days. This makes the distance D of the Nova from the Earth 248 light years, or 15,780,000 times the distance from us of the Sun.

If the Sun were removed to this distance its light would be reduced to that of a star of the 10·24 magnitude, and would be, therefore, quite invisible, except in a telescope of considerable size. The brilliancy of the Nova at its maximum must have been extraordinary. As it appeared to us brighter than a 1st magnitude star it must have been more than 10,000 times brighter than the Sun.

The most serious question is: Would the nebula be capable of reflecting enough of the light from the Nova to be visible to us?

If we take $\frac{1}{5 \times 10^{10}}$ as the ratio of the light of a 1st magnitude star to that of the Sun, then the edge of the nebula being 430 times closer to the Nova than the Earth the light it would receive would be 430^2, or $\frac{430^2}{5 \times 10^{10}}$, or $\frac{1}{270500}$ of sunlight.

Taking Young's estimate of the light of the full Moon as equal to $\frac{1}{600000}$ of that of the Sun, the nebula would receive about 2·2 times the light of full Moon.

The nebula being of finite area its intrinsic brilliancy would not be reduced by its distance from the Earth, so that allowing for the "albido" of the nebula, or the amount of light its particles are able to reflect as one-half, its particles ought to be intrinsically as bright as the Moon. But the particles of the nebula are evidently widely separated in space from each other, as the nebula seems very transparent. We, therefore, would not probably receive anything like the light of moonlight. The intrinsic brilliancy of the nebula, from the very long exposures required to photograph it, is certainly not greater than an 18th magnitude star; and as the light of the Nova was about a 1st magnitude one, the amount of light reflected from the nebula seems to be only equal to $\frac{1}{6310000}$, and if we take the light of the Nova at its maximum as equal to 0·2 magnitude the ratio becomes $\frac{1}{13180000}$ of the light it received from the star.

I consider, therefore, that we have very strong grounds for thinking that the nebula is able to reflect enough light to become visible to us, and that this apparent expansion of the nebula is entirely due to the advance of the wave of light sent out by the outburst of the star.

It thus becomes possible for the first time to determine the distance of a star whose parallax is unknown.

XLVI.

METHOD OF OBSERVING THE ALTITUDE OF A CELESTIAL OBJECT AT SEA AT NIGHT-TIME OR WHEN THE HORIZON IS OBSCURED. BY J. JOLY, Sc.D., F.G.S., F.R.S., etc., Hon. Sec. R.D.S.

[Read February 19; Received for Publication February 21; Published May 14, 1902].

It is a common experience to find clear skies at night-time, presenting to the mariner what would be valuable opportunities for observation, if at the same time the horizon was available. This has led to the invention of many contrivances, depending on gravity or gyrostatic stability, designed to afford an artificial horizon. Any contrivances controlled by gravity must, however, possess vibrational properties which will render their use unreliable. If controlled by kinetic stability or by magnetic force, the correct setting of the instrument to horizontality presents difficulties and uncertainties which have not yet been surmounted.

The want being thus not easily supplied by mechanical contrivances, I describe in this paper a very simple mode of making observations when the horizon is obscured—a mode which demands, it may be said, no special apparatus and no experience or knowledge from the mariner that he does not already possess; while fairly approximate results are obtainable, which under such conditions as would necessitate the use of the method would doubtless possess considerable value.

I assume that the vessel is provided with the usual rescue-signals, as certified by the Board of Trade. These signals, when thrown overboard (being first perforated), burn in the water with a bright white light, visible in clear weather up to five miles, and burning in all states of wind and water for about half-an-hour.

To one of these is attached some three or four fathoms of marlin, with a small piece of scrap-iron or any other suitable object attached at its extremity. The signal, so fitted, will not drift appreciably with the wind when thrown overboard. Save for current-drift it will remain stationary at the spot where it is launched. As will be seen later, current-drift of the signal will not affect the value of the method of making observations now to be described, as the ship may be assumed to drift an equal amount, premising that we speak of ocean-currents.

We will assume the mariner is desirous of making a stellar observation at night, when the horizon is obscured. To this end he looks for a recognisable bright star. If nearly astern of his ship so much the better as regards diminishing the time required to make the observation. But the mariner may optionally prefer to select a star near his meridian.

Having decided on a suitable star, he takes its bearing, and, altering his course to the opposite bearing, he thus brings the star right astern. He now drops the rescue-signal overboard (having perforated it if necessary), and at the same time a reading of the log is taken.

Having sailed or steamed a distance of about a mile from the signal, as indicated by the log, he reads the angular elevation of the star over the signal, using the sextant in the usual manner. In effecting this reading it will increase the accuracy of the observation to heave-to; but this should not be necessary if the star is kept on the signal, as nearly as may be, by shifting the limb of the sextant gradually as the distance increases nearly to the mile; diminishing the angle till the word is given that the knot is run. The reading being taken, the ship is put back on her course.

In this operation it conduces to accuracy if, instead of running directly away from the signal on the exact bearing opposite to that first taken of the star, attention is paid to the fact that the star is not a fixed object, but is travelling east to west at the rate of about 1° in four minutes of time. The amount by which the ship's course must be altered to counteract this motion and to preserve the signal in the vertical plane containing the star will depend on the direction of the ship's course, being greatest when this is north and south. Unless the ship travels very slowly the error may be sufficiently corrected by keeping the ship's course a very little to the eastward of the first bearing; in general something less than $\frac{1}{4}$ point. The inaccuracy introduced by this procedure into the determination of distance as effected by the log is negligible.

The altitude so determined, of course, requires a larger subtractive correction for "dip" than would be required when using the visible horizon.

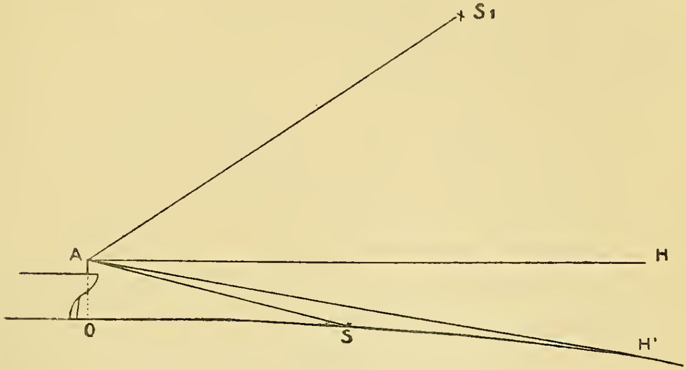

Fig. 1.

Let AH be the sensible horizon or tangent plane to the Earth's surface at the observer's position, and AH^1 the line touching the visible horizon vertically beneath the star S_1, and reaching the eye of the observer, whose height of eye above sea-level is OA: also let AS be the line extending from the observer's eye to the signal, which last is also vertically beneath the star. The usual correction for dip is the angle HAH^1; while that required by the use of the signal is the angle HAS. The angle HAS, of course, exceeds the normal dip by an amount depending on the proximity of the ship to the signal. Deducting it from the observed reading, S_1AS on the sextant (after this is corrected for instrumental error), the remainder S_1AH is the elevation of the object above the sensible horizon. The line OS follows, of course, the curvature of the Earth's surface. A short table of dips for objects nearer than the visible horizon is given in Norie's "Navigation," and in other works on navigation. A more extended table is desirable for the purpose of the present method. Such a table should read at least to minutes of arc.

In smooth water results of considerable accuracy would probably be obtained by the observation as described. If attention be paid to obtaining verticality of the star over the signal, and to obtaining a good reading of distance, and the ship's way be reduced when taking the reading, there seems no reason to expect a less degree of accuracy by this method than in the case of an altitude referred to the true horizon.

In rough water a correction, however, becomes necessary, which in extreme cases might render the results uncertain within three or four minutes.

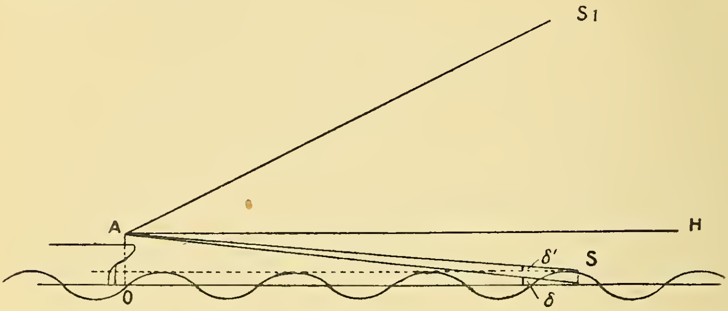

Fig. 2.

The diagram, fig. 2, shows that the dip δ′, which we read if we observe the signal when it is on top of a wave, is less than the true dip δ, or the angle that would be read if the signal floated at the mean-level of the sea. A little consideration shows that this is brought about by the fact that the wave brings the signal more nearly into the horizontal plane of the observer's eye, or, in other words, reduces the vertical height of the eye above the level of the signal by an amount equal to half the wave-height. Neglecting the Earth's curvature the tangent of the angle observed is no longer

$$\frac{OA}{OS} \text{ but } \frac{OA - \text{half wave-height}}{OS}.$$

The correction consists in deducting the estimated HALF *wave-height from the "height of eye," and then calculating the dip; or, if reference is made to the table of dips, entering this with the reduced height of eye and taking out the dip for the correct distance.*

As there is generally difficulty in arriving at a close estimate of wave-heights, even in daylight, and at night, when only by observation of the signal itself, when close to the ship, any estimate could be made, this difficulty is much increased, it is necessary to consider what magnitude of error might enter into observations made by this method in fairly steep seas. The table (see p. 564) of *maximum error*, due to wave-elevation, will give an idea as to the order of the errors arising where only a partial or incomplete correction for wave-elevation of the signal has been possible. The figures given in the table are, in short, the dips due to half the wave-heights. In other words, supposing the signal was always observed when on top of a wave (or, what comes to the same thing, the *least* altitude of the celestial object was taken), and no correction made for the elevation of the signal over mean sea-level, then the table gives the error affecting the angular elevation observed, and which would remain after the usual correction for dip in smooth water was applied to this angular elevation. The error is one of deficiency, and therefore the quantities in the table would be applied additively by way of correction. The table is carried so far as wave-heights of 12 feet, although it is probable that in such seas observation of any sort would be open to an equal degree of inaccuracy; and, indeed, the motion of the ship and its own elevation at the moments of observation would render any sort of angular observation liable to considerable error.

It will be seen from the table that in a swell of, say, six feet from crest to hollow, and in the case of an observation at a distance of one mile, the error, if neglected, would falsify a calculation of ship's position to the extent of about one mile and a-half. Thus in a meridian observation of a star bearing south the distance of the ship to northward is over estimated by this amount. It is evident, then, that in ordinary weather wave-elevation need not introduce any serious error, and would not count against the use of the method under such conditions and circumstances as would in general render its use desirable; that is, in circumstances where great accuracy was not required, but some fairly approximate idea of the mariner's whereabouts was desirable or imperative.

[TABLE.

Table *showing the Effects of Wave-elevation of the signal on the observed altitude.*

Height of Waves, crest to hollow : in feet.	Distance in Miles.				
		1	1½	2	3
2	46″	34″	23″	17″	11″
4	1′ 32″	1′ 8″	46″	34″	23″
6	2′ 16″	1′ 42″	1′ 8″	51″	34″
8	3′ 2″	2′ 16″	1′ 31″	1′ 8″	45″
10	3′ 46″	2′ 50″	1′ 53″	1′ 25″	56″
12	4′ 32″	3′ 23″	2′ 16″	1′ 42″	1′ 8″

In rough water it is more important to increase the distance from the signal than in smooth water. While half a mile, or even less, might give an accurate result in still water; in a sea-way, 1 mile or 1½ miles would be desirable. It is to be noticed that *some* correction reducing the amount of the error will generally be possible. Thus, if a six-foot sea is estimated erroneously to be an eight-foot sea, the error introduced is that arising from the subtraction of 4 feet instead of 3 feet from the height of eye. This, at 1 mile distance of observation, gives an error of about 34″ in the altitude, the altitude being over-estimated by this amount.

If the distance from the signal be erroneously determined, of course the dip will be incorrectly taken out. But this source of error need not be serious; for, with a good log, there is no reason to expect even as much as 5 per cent. error. If there was 5 per cent. error in a one-mile run the error will be about 40″ in the case of observations made from a height of eye of 24 feet. The error might be completely eliminated in smooth water by attaching the signal to a line, and paying-out the line, so that the signal was finally at an accurately known distance from the ship. This procedure appears to be needless in order to arrive at results possessing the degree of accuracy required.

An observation of the altitude of a known star will, in general, be an "ex-meridian," and may be reduced to give latitude in the usual manner. The mariner may, however, require to find his position by a Sumner problem. If a second known star is available, preferably not far from the first star, and he devotes a little longer time to the observation, this may be accomplished, the final accuracy depending chiefly on the state of the sea and the care with which he reads his distance and his angles.

The nature of the procedure in taking the altitudes of two stars to work a Sumner is as follows:—Having, as just described, taken the angular elevation of a star, S_1, above the signal, the ship is now put in such a course as will bring the second known star, S_2, vertically over the signal, while at the same time preserving unaltered the distance between the ship and the signal. The angular elevation of the second star above the signal is then observed, and the same correction for dips applied, when all the data for the problem are obtained.

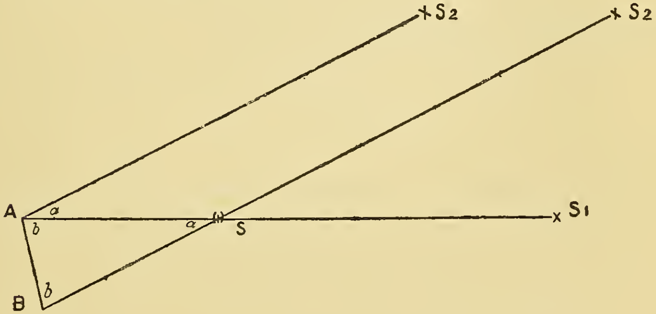

Fig. 3.

The figure, showing the successive positions of the ship projected on the horizontal, will explain the principles on which the ship's course is determined in going from the position where the first observation is made to that in which the second is made. S is the signal; S_1, the first star; A, the position of the ship when reading the angular elevation of S_1, above S as viewed from the ship. The second star, S_2, is seen in the direction AS_2 from the ship at A.

The observation of altitude at A being made, the bearings of the two stars are observed. The angle a is thus obtained. Now, if B is the required second position of the ship, the star S_2 will be sighted vertically over the signal, and the line BS_2 will be parallel to AS_2 (owing to the great distance of the star), and hence the angle at the vertex of the triangle ASB will be equal to the angle a (the horizontal angular separation of the two stars as seen from A). Now, the triangle ASB is isosceles, for BS is equal to AS. Hence the angles (b) at its base are equal and evidently

$$a + 2b = 180 \quad \text{or} \quad 2b = 180 - a \quad \text{and} \quad b = 90 - \frac{a}{2}.$$

The Rule for shaping the course from A is then as follows:—*With the bearing AS lay off the complement of $\frac{a}{2}$ and sail till S_2 is over S, when make the second observation ; a being the difference of the bearings of S_1* and *S_2 as observed from the place of first observation.* Of course S_2 is over S when the angular elevation is the least. In fairly calm weather a plumb line may be used to assist in placing the ship for the second observation. This is not *perfectly* accurate owing to the shift of the celestial objects in the interval required to run the distance AB.

For example, suppose S_1 bears *EbS*, and S_2 *NEbE½E*; the angle a is then 39° 20′ approximately, and $\frac{a}{2}$ 19° 40′ nearly. The complement of this is 70° 20′ or 6¼ points. The bearing of S_1 being *EbS*, we lay off 6¼ points to the south of *EbS*. The course is therefore *S¾E*; and this course is held till S_2 is over the signal.

The data now obtained are the altitudes of S_1 and S_2 above the horizon, the times of observation and the "run" over the distance AB, and made in the direction A to B, between the observations. This distance will have been measured by log, or, of course, it may be computed as the necessary elements of the triangle ASB are known. It may be that the run is negligible if the degree of accuracy required is not considerable. In the usual manner two latitudes are assumed between which or near to which we know the ship to be, and using the altitude and polar distance of S_1, we compute the longitudes corresponding to the assumption that the ship is actually in either of these latitudes. Secondly, using the altitude and polar distance of S_2, we again calculate two longitudes corresponding to the two latitudes. After plotting the results one of the "lines of position" is shifted for the run (if necessary), and the intersection of the two final lines of position gives the position of the ship.

The "double chronometer problem" may be also worked, using one assumed latitude only, and finding the lines of position by finding true bearings by Azimuth tables, using the declinations and calculated hour angles in the usual manner.

I have not in the title of this paper altogether restricted the method to observations made at night-time. In hazy weather, which at the same time may very probably be calm weather, the method is applicable to taking approximate altitudes of the sun. In this case the most suitable object to use as a signal would be a spherical or hemispherical bright tin float, but, as such must be specially provided, the use of any fairly bulky and conspicuous object might be resorted to successfully: as a piece of plank with an upright attached and a shape of any kind on top. This being "anchored" by a length of a few fathoms of marlin and attached sinker, is used as a signal. An ex-meridian (or meridian) observation is best made by sailing from the signal in the manner before described, and when a suitable distance is attained reading the elevation and noting time by "watch."

XLVII.

ON THE PROGRESSIVE DYNAMO-METAMORPHISM OF A PORPHYRITIC ANDESITE FROM COUNTY WICKLOW.

By HENRY J. SEYMOUR, B.A., F.G.S.

(Plates XXVI. and XXVII.)

[COMMUNICATED BY PERMISSION OF THE DIRECTOR OF H. M. GEOLOGICAL SURVEY.]

[Read March 19; Received for Publication March 21; Published June 28th, 1902.]

The object of the present communication is to describe an interesting case of the transformation of a porphyritic basic rock into a banded schist.[1] It is also put forward as an exceptionally clear example of an already recognised possible mode of origin of banded gneisses, by the effects of pressure and recrystallization acting on suitable non-homogeneous rock masses or complexes.

As has already been pointed out in another publication,[2] numerous outcrops of basic rocks occur within a zone, about a mile wide, along the western flanks of the Leinster granite between Brittas and Baltinglass. These rocks were formerly mapped as ashes (Ds.) on the Survey maps (old editions), their apparently bedded character—really a shear structure produced by pressure—being regarded by the earlier observers as pointing to a sedimentary origin. They are now mainly in the condition of hornblende and mica schists, and epidiorites, and were very probably pyroxenic varieties in their original condition, as is indicated by those examples which, owing to their having been outside the sphere of influence of the granite, have retained more or less their original structures.

One such example occurs, amongst other places at Ballinascorney Gap, west of Glenasmole, thin sections of the rock from this

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[1] I am indebted to my colleague Mr A. McHenry, for bringing under my notice the rock now described.

[2] "Summary of Progress," Geological Survey, 1899, pp. 71, 72, and 176.

locality showing that it was originally an augite-diorite, or dolerite without olivine.[1]

The amount of alteration produced on these rocks depends on their proximity to the granite. For example, the outcrops over a mile distant seem to be scarcely at all affected, while those somewhat nearer have usually been more or less re-crystallized into amphibole rocks. Those, however, near the granite have been, in common with the associated sediments, not only highly thermo-metamorphosed, but also considerably sheared. It may be here mentioned that the comparatively narrow extent of the zone of alteration on the western side of the granite of the Leinster chain, as compared with that on the eastern side, is due probably to the much steeper descent of the granite beneath the slates on the former side, as was first pointed out by Maxwell Close in 1877.[2] These basic rocks all probably belong to the same period, and occur apparently as intrusive sills, bosses, and dykes, in sediments believed to be of Lower Silurian (Ordovician) age. Some, however, may possibly be lava flows. The porphyritic type occurs locally usually as dykes in the more compact varieties (andesites). A similar association occurs at Lambay and Portrane, and the general identity and mode of occurrence of the basic rocks of these localities, and of those on the west of the Leinster granite, suggest that all belong to the same geological period, namely, *Bala*, according to the recent work of Messrs. Gardiner and Reynolds.[3] Though some interesting changes have been brought about in these older rocks by the granite, the present Paper is concerned only with one instance; having reference to some small outcrops in the neighbourhood of Donard (Co. Wicklow), noted at A and B on the accompanying sketch map of the district (p. 570). Donard is a small village, some six miles south-east of Dunlavin; and in the case of the outcrops just mentioned the results of both thermo- and dynamo-metamorphic action are well illustrated in the changes brought about in a porphyritic andesite developed here in some abundance. One outcrop of this rock occurs at Deerpark-hill (B), a little over a mile south of Donard, the other at Ballymooney-hill (A), about an

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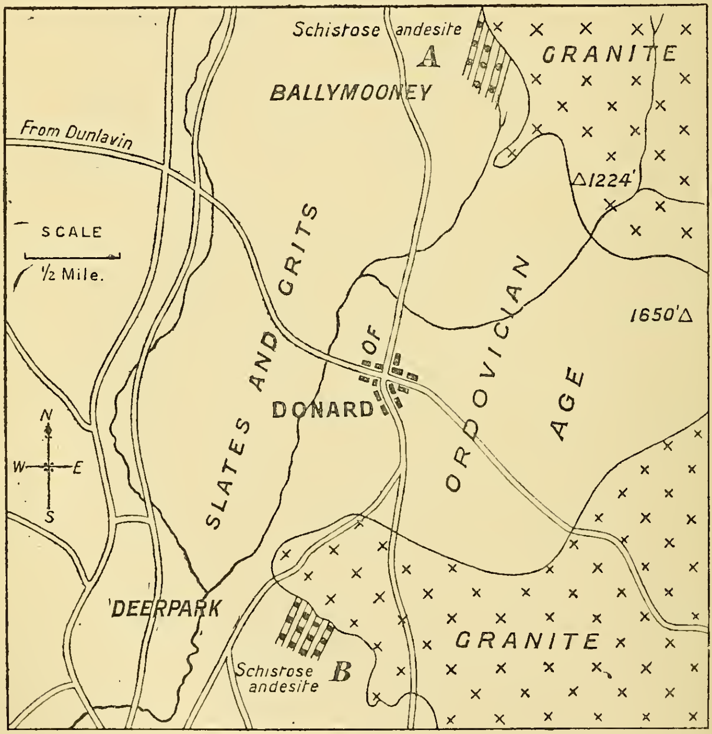
[1] "Summary of Progress," 1899, p. 177.

[2] Journ. Roy. Geol. Soc. Ireland. vol. v., p. 57.

[3] Quart. Journ. Geol. Soc., vol. liv., p. 147, 1898.

equal distance north of the same village. In the first-named locality the rock may be obtained in a practically unsheared condition, but at Ballymooney, where it occurs in greater quantity, it is everywhere highly sheared. The direction of shearing in both cases is approximately parallel to the axis of the granite mass, *i.e.* north-east and south-west, but a reference to the map below will explain how it is that the shearing has been apparently more intense in the northern than in the southern locality. At Deerpark a tongue of granite runs out from the main mass in a north-west direction, that is, across the general strike of the Ordovician slates, and at right angles also to the direction of shearing. On the ground this granite tongue forms a prominent rounded saddle-ridge, on the lower slopes of which occurs the porphyritic rock referred to. It is clear that, on the assumption that this granite mass resisted the shearing, a rock lying in such a position would be more protected from shearing effects than one occurring in an exposed position, as is the case



with the rock at Ballymooney. Hence, while the latter is highly schistose, the rock sheltered by the granite ridge is comparatively speaking, unaltered. In this locality, therefore, the rock may be obtained in a practically unsheared state; but it is yet very far from being in its original condition, for it has been completely thermo-metamorphosed by the granite. In its unaltered condition the rock was undoubtedly identical with the "Lambay porphyry," the well-known porphyritic andesite occurring on Lambay island and on the shore at Portrane.

The thermo-metamorphism of an andesite of similar type has been described in detail by Messrs. Harker and Marr,[1] and the rocks near Donard have gone through similar stages of alteration. The final result has been a complete re-crystallization of the original constituents of the ground-mass which now consists chiefly of a bronzy-brown mica, associated with a minutely crystalline mosaic of clear felspar and quartz only occasionally distinguishable from one another in thin sections under the microscope. Starting then with the Donard rock in this condition, its subsequent alteration by pressure may be readily traced in the field by the changes undergone by the porphyritic felspars, which stand out conspicuously on a weathered surface. Prior to any shearing effects these phenocrysts are seen to be arranged in an irregular manner (fig. 1, Pl. XXVI.), and form stumpy prisms of varying size up to a maximum of 1·5 × 1 × 0·5 cm. scattered singly or less often in glomero-porphyritic groups (fig. 1, Pl. XXVII.) throughout the rock. The crystals on a fresh fracture are rather brownish in colour owing to numerous secondary inclusions, but still show several parallel light reflecting bands due to repeated twinning. The first modification produced by pressure is to cause these plagioclases (andesine or labradorite) to arrange themselves in a direction with their longer axes approximately parallel to one another (fig. 2, Pl. XXVI.). They are in this condition not very much elongated, though their cross-sections have become somewhat flattened. The next stage consists in the gradual drawing out of the crystals which become longer and longer (fig. 3, Pl. XXVII.), till finally they become leaf or torpedo-shaped, flattened lenticles up to 6 cm. or more long, about 1 cm. broad, and varying in thickness at various points from 0·1 to 1 mm.

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[1] Quart. Journ. Geol. Soc., vol. xlvii., pp. 293-300.

The length of one of these lenticles depends on whether it has resulted from the elongation of a single crystal, or of a glomero-porphyritic group, being naturally longer in the latter case. The final result is the production of a banded rock composed of alternating dark (biotite) and light (felspar) laminæ which presents, on a minute scale, the characteristic structures of a banded gneiss (fig. 4, Pl. XXVII.)

Under the microscope the first sign of the effects of pressure in the felspars is the production of strain shadows, which is followed by fracture and strain slip cleavage. A continuance of the pressure results in a certain amount of granulation, after which the lengthening process goes on apparently by solution and recrystallization to the final stage. In this the original crystal of plagioclase is reduced to a granular mosaic the individual grains of which show little or no strain shadows, being largely re-crystallized material, consisting of water-clear quartz and felspar, with biotite, and some secondary muscovite. Accompanying these are secondary crystals of colourless epidote and zoisite.

In this condition the ground only differs from the sheared crystals in the relative abundance of secondary biotite, and the original rock has been reduced to one consisting of practically uniform-sized grains, a rather characteristic structure of gneisses and schists.

The biotites are all orientated parallel to the direction of shearing, except where they occur between the felspathic lenticles. In these positions they often stand in a direction at right angles to the direction of shear. It is very remarkable that in no instance are the ends of two adjoining sheared lenticles of original felspar welded together, so to speak, by the mashing action which the rock has undergone. They are invariably separated by a thin film of the matrix (fig. 4, Pl. XXVII.), and nowhere, so far as can be seen, has any mechanical mixture of the felspar and the ground been produced, both maintaining their separate individualities to the end. This seems to show that the rock at all times moved practically as a solid, and never approached the molten condition.

The ground of the rock, however, which started practically in the condition as regards texture to which the plagioclase phenocrysts were eventually reduced, in turn produced new structures while these phenocrysts were being stretched out. The one most noticeable is the tendency to form larger crystalline constituents, especially in the case of the biotite. A section of the rock in the final stage shows frequent knots or bunches of this mineral in the ground, the individual crystals of which are of much larger size than usual, and considerably larger than those of the ground at the expense of the smaller individuals of which they have been developed. The occurrence of larger biotite crystals in the late stage of the dynamic alteration of the Donard rock was noted by me in 1899[1], but its significance was not recognised till after reading recently a Paper by Van Hise[2] dealing with metamorphism. This author notes, in discussing re-crystallization, that, as the process of granulation goes on, a stage is reached beyond which the particles do not become more finely granulated, but a reverse process takes place, and instead of becoming smaller they become larger. He regards the coarsely crystalline, perfectly schistose rocks, nearly free from strain shadows as representing the most advanced stages of metamorphism.

The age of the shearing movement which has effected the Donard rock above described is clearly contemporaneous with that of the intrusion of the Leinster granite. Professor Sollas[3] believes that the granite laccolite was injected in successive sheets *pari passu* with the folding of its Ordovician cover, and that this movement continued for some time, and was very slow. Evidence is adduced for this by the presence of fractured contact minerals (garnets) produced in the neighbouring slates surrounding the granite mass.

Confirmatory evidence is afforded by the Donard rock, for the shearing has been evidently superimposed on a rock already metamorphosed by contact with the granite. When it was slightly sheared, an intrusion of granite took place, veins from which (still found unsheared in the Deerpark area) traversed the basic rocks. Other veins of aplite have, however, been highly sheared in the northern locality (Ballymooney) due to further movement after their intrusion. Veins of quartz cutting the basic rocks are also sheared by the same movement and in the same direction, but it is uncertain whether these quartz veins are of granitic or earlier origin.

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[1] "Summary of Progress," 1899, p. 178.

[2] Bull. Geol. Soc. Am., vol. 9, 1898.

[3] Proc. Geologists' Assoc., vol. xiii., 1893.

In conclusion, a banded and perfectly crystalline gneiss appears on the foregoing evidence to be capable of being produced solely by "mass-dynamic" agencies, acting on a non-homogeneous rock, as one type of which we may regard the porphyritic andesite described in the present paper.

EXPLANATION OF PLATES.

PLATE XXVI.

Fig.

1.—Weathered surface (54 × 42 cms. approx.),[1] of the porphyritic andesite at Deerpark (B), showing irregular arrangement of the felspar phenocrysts in the right-hand top corner. Part of the rock is slightly sheared.

2.—Surface of rock (67 × 52 cms.) approx.) near the last, showing first signs of alteration by pressure in the general parallelism of the felspar crystals, A quartz vein, sheared by the same movement, is shown in the upper portion of the photograph.

PLATE XXVII.

Fig.

1.—Photo. of hand-specimen (18 × 8 cms.), showing glomero-porphyritic arrangement of the felspar crystals on weathered surface.

2.—Photo. of hand-specimen (8 × 4 cms.), showing flattened cross-sections of the felspars in an intermediate stage of elongation.

3.—Photo. of hand-specimen (11 × 7 cms.), showing appearance of the felspars in a direction parallel to that of elongation, and almost in the final stage of alteration.

4.—Photo. of part of hand-specimen (15 × 5 cms.), showing banded character of the schist produced by the effects of pressure and re-crystallization from the porphyritic andesite (fig. 1).

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[1] The dimensions given in brackets are those of the original specimens, or portions of specimens, shown in the photographs.

XLVIII.

SOME RESULTS OF GLACIAL DRAINAGE ROUND MONTPELIER HILL, CO. DUBLIN. By W. B. WRIGHT, B.A.

(Plates XXVIII. and XXIX.)

[COMMUNICATED BY PROFESSOR J. JOLY, F.R.S., HON. SEC. R.D.S.]

[Read June 18; Received for Publication June 20; Published September 20, 1902.]

In many places on the northern slopes of the Dublin Mountains there occur curious deep valleys, which cut across the spurs of the hills, and which cannot be accounted for with the present topography. Their general character, moreover, is such as to suggest that they have been cut by running water at a period geologically not very remote; and it is hence necessary to imagine some agency not only capable of modifying the ground sufficiently to cause such a flow of water, but also capable of being removed in the comparatively short time since elapsed. A very typical example, and one with many interesting associated phenomena, happened to come within the area allotted to me to survey during last summer, and I was hence enabled to examine it in detail.

While seeking an explanation of these phenomena, my attention was called to various papers in which similar gaps recently observed in other portions of the British Isles and in America were described, and the explanation adopted in these cases seemed to apply equally well in that which I am about to describe.[1]

In all these cases the gullies were explained either by the action of water ponded back against the hills by the ice-sheet, and

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[1] Hermann Leroy Fairchild: "Glacial Lakes of Western New York." Bulletin Geol. Soc. America, vol. vi., pp. 353–74.

G. W. Lamplugh: "Annual Report of the Geological Survey and Museum of Practical Geology for the Year ending December 31, 1895. Appendix to the 43rd Report of the Department of Science and Art, p. 13. Brit. Assoc. for the Advancement of Science. The Isle of Man. An Appendix to the Handbook of 1896. Part ii., Geology, p. 179.

Percy F. Kendall: "On the Glacial Drainage of Yorkshire." Rep. Brit. Assoc., 1899, Dover.

Thomas L. Watson: "Some High Levels in the Post-Glacial Development of the draining directly across the ridges, as overflows from lakes held in between the ice margin and the bare land, or as having been cut by rivers flowing on the surface of the ice-sheet, just as the ridges emerged from it.

Certain passages were also brought to my notice by Mr. Lamplugh, which are of interest as showing that even the earlier local geologists took note of these gaps, and recognized the difficulty of accounting for them. As early as 1811, in Stephens and Fitton's Mineralogy of the Vicinity of Dublin[1] the following passage occurs:—

"At the foot of the mountains near this place" (*i.e.* Dundrum) "is one of the fissures already mentioned as somewhat resembling the Scalp in structure, the course of which is from west to east, parallel to the face of the mountain." There is also a description of the Scalp, and the foot-note—"Fissures similar to the Scalp though on a much smaller scale occur in other parts of the granite tract near Dublin, as at the foot of the mountains above Dundrum, and elsewhere. The mode of their formation offers an interesting subject of inquiry."

John Scouler, in 1838, in a paper "On the Raised Beaches near Dublin," has the following passage:—

"There is also another very curious phenomenon which, I think, may be associated with the preceding one" (*i.e.* the high level shelly gravels). "Besides the valleys, whose streams discharge themselves into the Bay of Dublin, and which we have seen have all been formerly blocked up by transported matter, there is another set of valleys, or more correctly ravines, which have a general easterly and westerly direction, and are consequently nearly at right angles to the valleys containing transported matter, and these ravines are all destitute of any beds of gravel or detritus carried for a distance. The valleys or gaps which possess this negative character are the Scalp, the Dargle,

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Finger Lakes of New York. Appendix B. Report of the Director of the New York State Museum, 1899." Review in Journal of Geology.

J. E. Wilson: "On a Glacial 'Extra-Morainic' Lake occupying the Valley of the Bradford Beck." Rep. Brit. Assoc., 1900, Bradford, p. 755.

Albert Jowett, M.SC., and Herbert B. Muff: "A Preliminary Note on the Glaciation of the Keighly and Bradford District." Rep. Brit. Assoc., 1900, Bradford, p. 756.

[1] "Notes on the Mineralogy of part of the Vicinity of Dublin, taken principally from the Papers of the late Rev. Walter Stephens, A.M.," by William Fitton. London, 1811.

and the Glen of the Downs; the first cuts across both the granite axis and the strata of micaceous schist which recline against it; the second is nearly parallel to the first, and the third has cut through strata of quartz-rock. All these ravines contain vast detached blocks of the adjacent rocks, granite in the first, and quartz in the second. Now it appears probable that the formation of these ravines was subsequent to the deposition of the shelly gravels; for had they existed along with the valleys containing transported matter, it is difficult to conceive how they should now be so thoroughly destitute of all vestiges of it, especially when it is remembered, that none of these ravines ever possessed any stream which could carry off their contents. As many of the shelly gravels occupy a higher level than these valleys, it is inconceivable if both orders of valleys were contemporary, and both equally under the water, as must have been the case, upon what principle of selection one set were the receptacles of transported matter while the others escaped? It therefore appears probable that the ravines were of later origin and are with the shattered blocks which are still *in situ*, the indications of the nature of that force which has elevated the shelly beds into their actual position."[1]

The Rev. Maxwell Close[2] also drew attention to these curious valleys, and recognized that they were directly connected with the other glacial phenomena of the district, suggesting that they might have been formed by the excavating action of ice. He remarked on "the straightness and better definition of those valleys on the east side of the mountain range; the fact that their cols are often situated to the west of what seems to have been the original position of the watersheds of the passes: the last two peculiarities are precisely what might be induced by a glacial flood of sufficient denuding efficacy, coming from the north-west, partly dammed up by the long mountain barrier, and pouring over the crest thereof down the steeper slope of its lee-side."

The transverse gully, which is the most striking feature in the small area here described, trenches completely across the lowest

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[1] "Account of Certain Elevated Hills of Gravel, containing Marine Shells, which occur in the County of Dublin," by John Scouler, Journ. Geol. Soc., Dublin, vol. i., p. 266.

[2] Rev. Maxwell H. Close, "Notes on the General Glaciation of the Rocks in the Neighbourhood of Dublin," Journ. Roy. Geol. Soc. of Ireland, vol. i., p. 3, 1864.

point of the ridge connecting Montpelier Hill with the main mass of the Dublin Mountains to the south. Small streams enter it near the ends, and flow east and west from it, but at its summit it is quite dry, and it is this absence of any adequate eroding agent which is the most remarkable characteristic of this and other similar gaps. The form of the ground at both ends of the pass indicates that, previous to the Glacial Period, shallow valleys had been excavated in the hillside on both slopes of the ridge, and atmospheric erosion, aided by the wash of rain, seems to have lowered in some degree the narrow portion of the ridge separating their head waters. In the shallow depression thus formed, the deep notch has been cut which now unites the heads of the two valleys. It is about 500 yards long, and has sides from 90 to 100 feet high, sloping at angles varying from 25 to 35 degrees, composed in the western part of slate and in the eastern part of granite, the gorge traversing the junction of the two formations, and apparently having no reference to the solid structure. The highest point of the floor is 1035 feet above the Ordnance datum line, and about 100 feet higher than the tops of the lower mounds mentioned below as occurring at the mouth of the Piperstown Valley. The form of the floor is so irregular, that no deduction can be made from its slope as to the direction in which the eroding water flowed. This is principally owing to the large amount of talus which has fallen in from the sides. The pass proper is continued in an easterly direction as a comparatively shallow but fairly steep-sided gully, partly excavated in drift and partly in granite, running down the slope into the Killakee Valley, and forming a trench in one side of the shallow depression which formerly existed here.

The stream which flows from the west end of the gap pours into a slightly larger stream coming from the south, the valley of which, at the point of junction, turns sharply to the west and opens out into Glenasmole. It is this valley, in which the village of Piperstown lies, that contains the most remarkable deposit of gravels in the district. From the mouth of the Piperstown Valley westward there stretches away the smooth gently-sloping plain of boulder-clay which fills up the lower part of Glenasmole. The gravels set in in a fairly straight line across the mouth of the valley and appear to lie on the boulder clay. Immediately to the east of this line they rise suddenly from the plain into two very

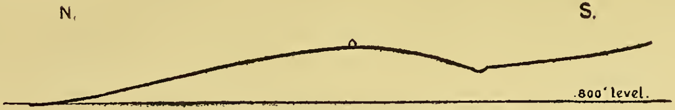

FIG. 1.—Section across Montpelier Hill.
True scale, .

FIG. 2.—Transverse section of pass at summit.
True scale, $\frac{1}{4}$-in. to chain.

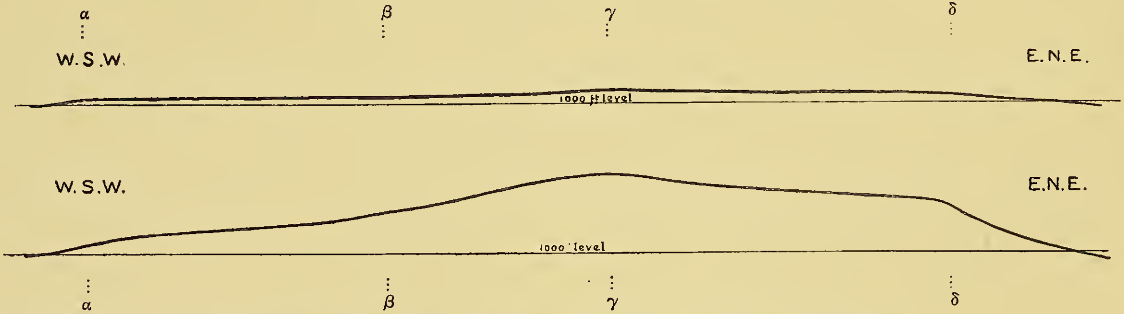

FIG. 3.—Section along the floor of the pass shown (1) to a true scale, (2) with an exaggerated vertical scale.
From α to β the pass is fairly wide, and near β a small stream enters which flows west.
From β to δ it is narrow with steep boulder-strewn sides, and the floor has probably been considerably raised by the talus from them.
At the summit γ is a tiny alluvial cone from a streamlet now dried up.
At δ the pass proper ends, and is continued east as a sloping gully (see p. 578); here also are the mounds of granitic debris from the gap.

remarkable mounds, between which the stream flows. Where these mounds abut upon the hills, they, like the boulder-clay, are covered over to a certain extent with local wash from the slopes above. The gravels themselves are well stratified and waterworn, and consist, for the most part, of limestone, but also contain a considerable proportion of granite, slate and greenstone. No shell fragments have been found in them, but as they are known to occur in similar gravels at Annmount, about 400 yards further westward, this is owing most likely to the smallness of the exposures, which hardly reach below the weathered surface. When traced eastward up the Piperstown valley these gravels form a series of mounds, rising gradually on the slopes as we ascend the valley. They thin out in its head and on the moor to the south of Montpelier Hill into a mere sprinkling of pebbles on the rocky surface. Even here, however, they rise occasionally into small mounds. They extend thus in places nearly up to the 1250 feet contour, the upper limit appearing to be indicated here and there by a faint rise of the surface. A strip of the moor from 50–100 yards wide lying alongside the deep transverse gully above described is quite devoid of gravel. This thin deposit extends completely over the ridge, and merges with those in the Killakee valley on the far side.

A similar scanty deposit of gravel occurs on the top of Montpelier Hill, to the north of the gully. At one place it forms a mound of considerable size, in which a pit has been opened.

At the eastern end of the pass, at the point where it opens into the wide depression mentioned above as occurring at this side of the spur, are two mounds, or rather traces of mounds, lying one on each side of the gully, and composed, not of gravel, but of granitic and slaty debris, perhaps a portion of the material eroded from the pass. That on the north exists only as a mere swell on the otherwise even slope; that to the south is more noticeable. These appear to be in every way similar to a much larger deposit observed by Mr. Seymour in the pass of Glendoo, which, there is reason to suppose, has been deepened by the same agencies,[1] and this has led me to believe that they are in some way connected with the formation of the pass. The material was probably

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[1] "The Glacial Origin of Glendoo," W. B. Wright, Irish Naturalist, vol. IX., p. 96, 1902.

brought down by the torrent pouring through the pass, and checked at this point either by the ice-face, or by water held up by the ice-face, most likely the latter. The removal of the check would be followed by the subsequent erosion of the central portion of the deposit, leaving, as in the present case, mounds flanking the valley.

As the straightness of the line in which the gravels end off upon the boulder-clay platform at the mouth of the Piperstown Valley is suggestive of a barrier of some sort since removed, and as the great thickness of the gravels seems to indicate that they were deposited in comparatively still water, it seems not unreasonable, if the former existence of an ice-sheet be once granted, to suppose it to have been the barrier in question, and to have held up in the Piperstown Valley a temporary sheet of water, with an outlet through the pass into the Killakee Valley. The gravels seem to have been washed into this lake partly off or out of the ice itself, and partly from the hills, the torrents running between the ice and the bare hillside, playing, no doubt, an important part in their transport.

There is a complete absence of any trace of a shore line on the hill slopes above the gravels. This, however, is not to be wondered at when the smallness of the lake is considered. Professor Fairchild states that only the larger of the glacial lakes of western New York have shore lines, owing to the fact that it requires a wide expanse of water for waves to gather of sufficient force and volume to effect noticeable erosion.

At a later stage the continued shrinkage of the ice-barrier seems to have opened a passage for the waters of the lake at a lower level round the north side of Montpelier Hill, and their former route across the ridge was then abandoned, but not before they had excavated the trough above described. In their new course the waters have left their mark in a series of terraces and gashes in the hillside, which, in some cases at least, can be seen to be quite independent of the nature of the rock. These all slope from west to east, and seem to be more abundant, more steeply graded, and more sharply marked on the east side of the spurs which stretch north from the hill. They are all below the 1000 feet contour, and therefore below the floor of the gap; above this level the hill is comparatively smooth. On the north-west spur, about half-a-mile west of Montpelier House, there is a low saddle separating a small hill to the north from the rest of the spur. On the east side of this miniature col there has been considerable erosion, owing probably to the water having continued to pour over here until the ice sank to the same level on the outer side of the hill. The drainage seems to have been diverted in this way before it had time to trench right through the spur, and form a gap, such as has been described as occurring on a much larger scale on the south of the hill. The amount of erosion in each case is roughly proportional to the size of the rock-mass lying to the north, and this law seems to hold for all the dry gullies on the northern slopes of the Dublin Mountains.

In the valley in which Montpelier House stands there is a considerable deposit, filling up the whole of its bottom. At the surface nothing is seen except local hill wash, but several pits opened into it have revealed limestone gravel beneath, and it is probable that the local wash is only a surface layer overlying gravel of this nature. Some portion of this deposit has most likely been carried into the valley by the torrent which cut the small half-formed gap just mentioned.

Similar terraces on the spur above Ann Mount are more difficult to explain; their slope indicates a flow south-west, into Glenasmole, over the spur, which, if they are really cut by marginal waters, does not agree very well with the general drainage eastward towards the sea indicated elsewhere. A deposit of gravels at this place, at about the same level as the mounds at the mouth of the Piperstown valley, also indicates a flow in the same direction. A fine pit section in the mound shows cross-bedding dipping steeply to the south. The stream, however, which carried this gravel into the comparatively still water in which it was probably deposited may have flowed directly off the ice instead of along the margin.

In conclusion, I wish to express my thanks to Mr. Seymour for his assistance in the levelling operations necessary to determine the altitude and form of the floor of the pass, and to Mr. Lamplugh for much valuable assistance and information, and many suggestions, without which it would have been impossible for me to bring together and perceive the relation of the facts described above.

XLIX.

ON THE OCCURRENCE OF CASSITERITE IN THE TERTIARY GRANITE OF THE MOURNE MOUNTAINS, CO. DOWN.

By HENRY J. SEYMOUR, B.A., F.G.S.

[Read June 18; Received for Publication June 20; Published September 13, 1902.]

This communication is intended to put on record the occurrence of Cassiterite in a new locality in Ireland. The writer, while lately examining (in connexion with a revised Catalogue of Irish Minerals which he has in preparation) a collection of minerals from the Mourne Mountain district, made by Dr. E. A. Letts, Professor of Chemistry at the Queen's College, Belfast, had his attention directed by the latter to some specimens of beryl from Slieve-na-miskan, on which were implanted some very minute brownish-black crystals. These Dr. Letts had noticed when he collected the specimens, but had taken no further steps to identify. The writer being unable, through lack of facilities at the time, to diagnose the species, sent the material to the British Museum, where the mineral in question was determined by Mr. L. J. Spencer to be Cassiterite.

The crystals so identified are almost of microscopical dimensions, but more recently some good crystals, visible to the unaided eye, have been found amongst the material originally collected by Dr. Letts. They occur for the most part on the beryls (aquamarines), but are also found in the small drusy cavities in their immediate vicinity. The matrix is a much altered granite, in which the felspars are completely kaolinized, or washed away, and contains also secondary silica, so that the rock is much more quartzose than usual, and sometimes presents a spongy character.

This occurrence of Cassiterite in an undoubted Tertiary granite is, if not unique in the British Isles, at all events of very great interest, as tending to show the comparatively recent origin of some mineral lodes.

The only previous record of the occurrence of Cassiterite *in situ* in Ireland is contained in Griffith's "Report on the Metallic Mines of the Province of Leinster," 1828, where he says:— "With the exception of crystals of oxide of tin found in the gold wash at Croghan mountain by Mr. Mills, and those subsequently *found in the granite at Dalkey by Dr. Taylor*, the ores of tin have not hitherto been found in this district." The locality near Dalkey was the lead mine formerly worked in the confines of Victoria Park. William Mallet, in a paper on "The Minerals of the Auriferous Districts of Co. Wicklow,"[1] similarly records the occurrence of stream tin in the gravels of the Gold-mines river near Croghan Kinshela, associated with several other minerals, including gold, platinum, and wolfram. G. H. Kinahan,[2] in addition to the foregoing, mentions two other localities, one in Co. Cork and one in Kerry. In neither case is the occurrence sufficiently authenticated, and the presence of Cassiterite in both localities must be regarded at present as very doubtful.

The first record of the occurrence of Cassiterite in Ireland dates from 1796 (*circa*), when its discovery was announced by Weaver, who identified this mineral in the washings at Ballinvalley Gold Mines, associated with other heavy minerals. This discovery was reannounced at intervals during the next few decades by others, including Smith (1840) and Mallet (1851).[3]

Note added in the Press.

Since this note was written Dr. Joly informs me that he found some small crystals of Cassiterite in a much decomposed pebble of granite, taken out of the boulder clay near Greystones, several years ago.

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[1] Journ. Geol. Soc. Dublin, vol. iv. (1851), p. 269.

[2] "Economic Geology of Ireland," Scient. Proc. Roy. Dublin Soc., vol. v. (1886–7), pp. 200 and 207 (pp. 11 and 17 of the work as separately published).

[3] See London, Edinburgh, and Dublin Phil. Mag., vol. xix., 1841, pp. 27–31.

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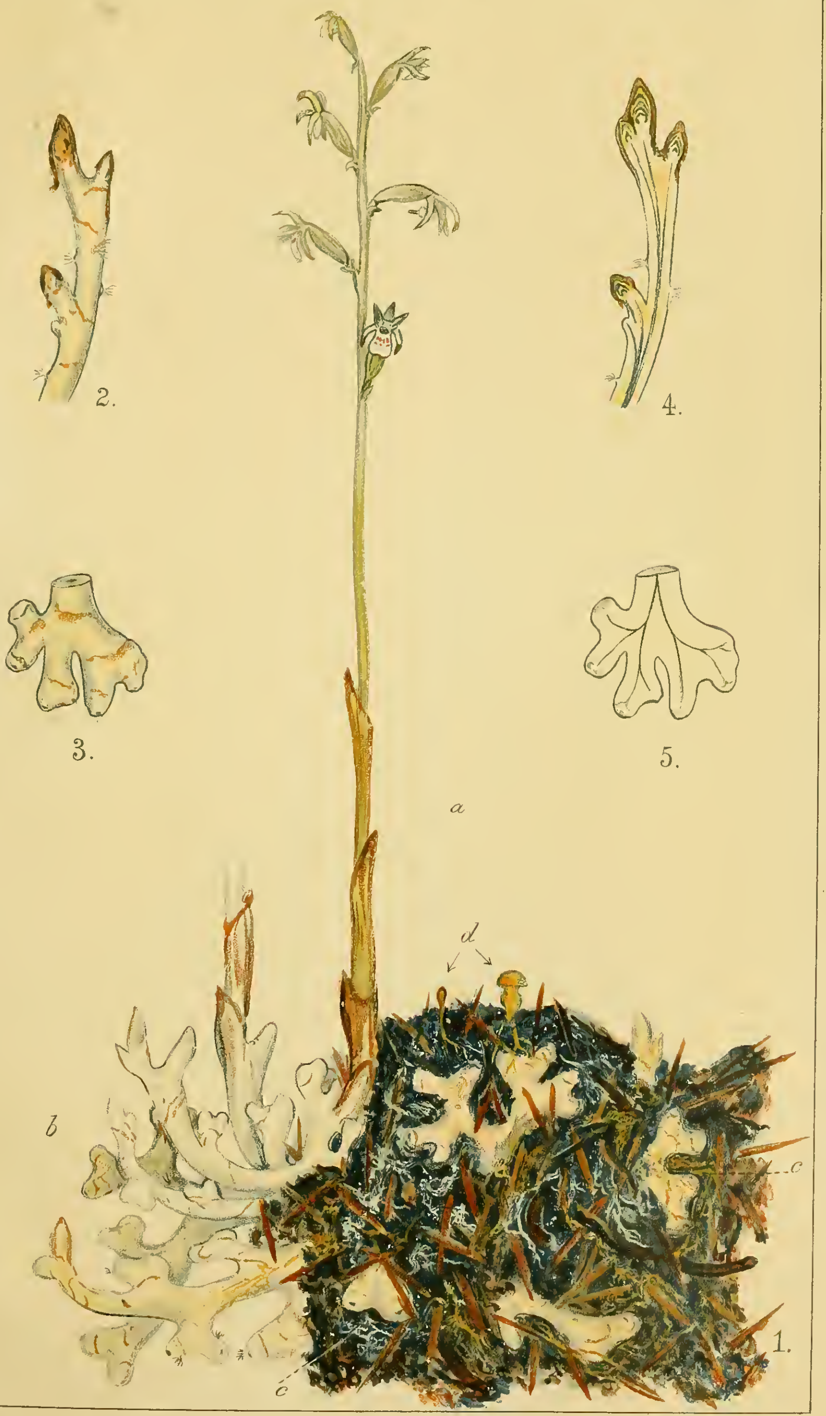
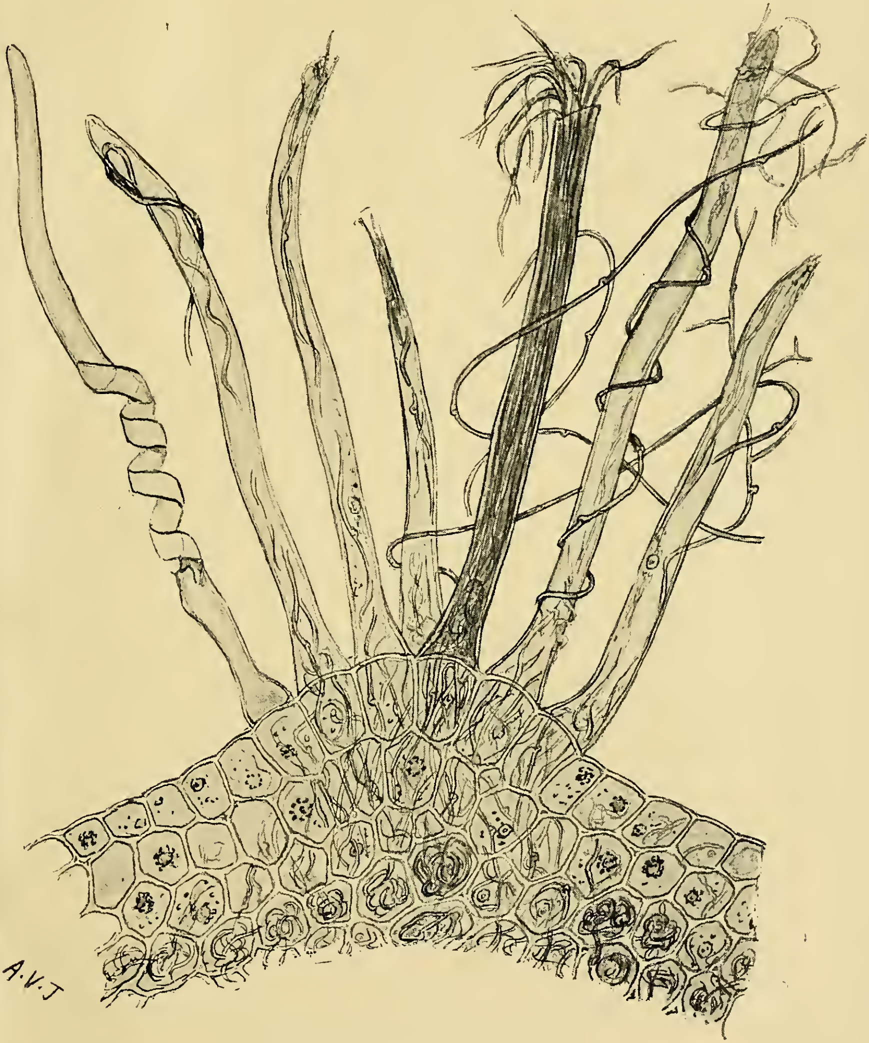
TO VOLUME IX

END OF VOL. IX.



A V Jennings
McFarlane & Erskine, Lith Edinr

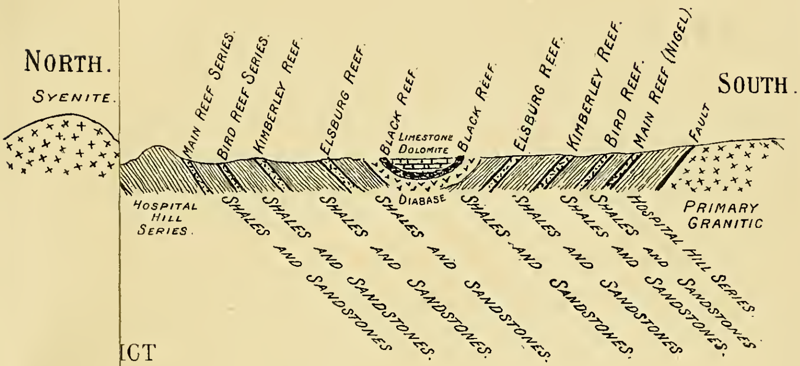
CORALLORHIZA INNATA *R. Br.*
AND ITS
"MYCORHIZA"



CORALLORHIZA.

Pr

PLATE III.



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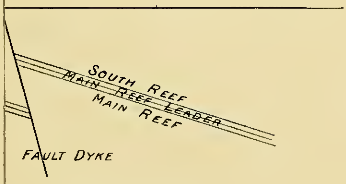
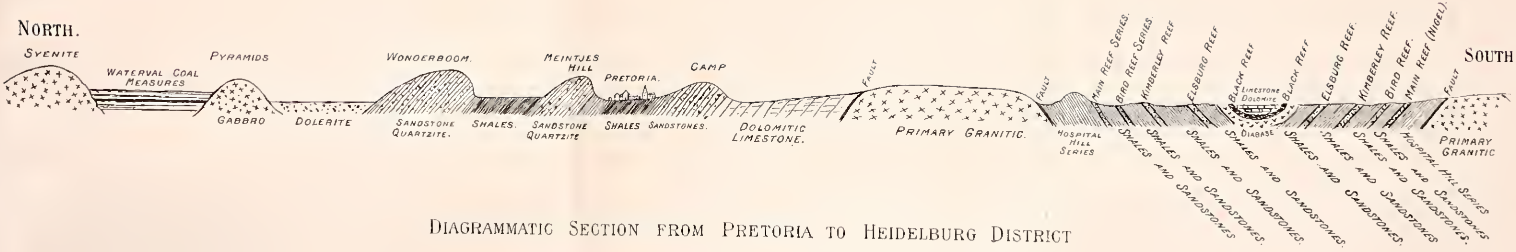


OVERTHRUSTS.



DIAGRAMMATIC SECTION FROM PRETORIA TO HEIDELBURG DISTRICT

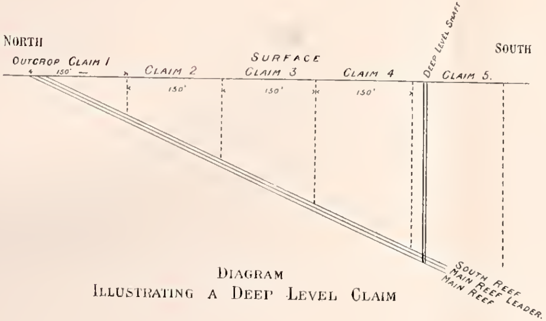


DIAGRAM
ILLUSTRATING A DEEP LEVEL CLAIM

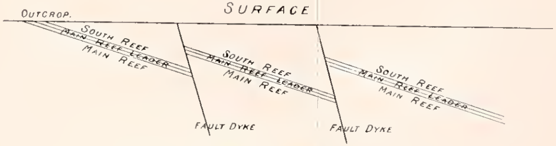
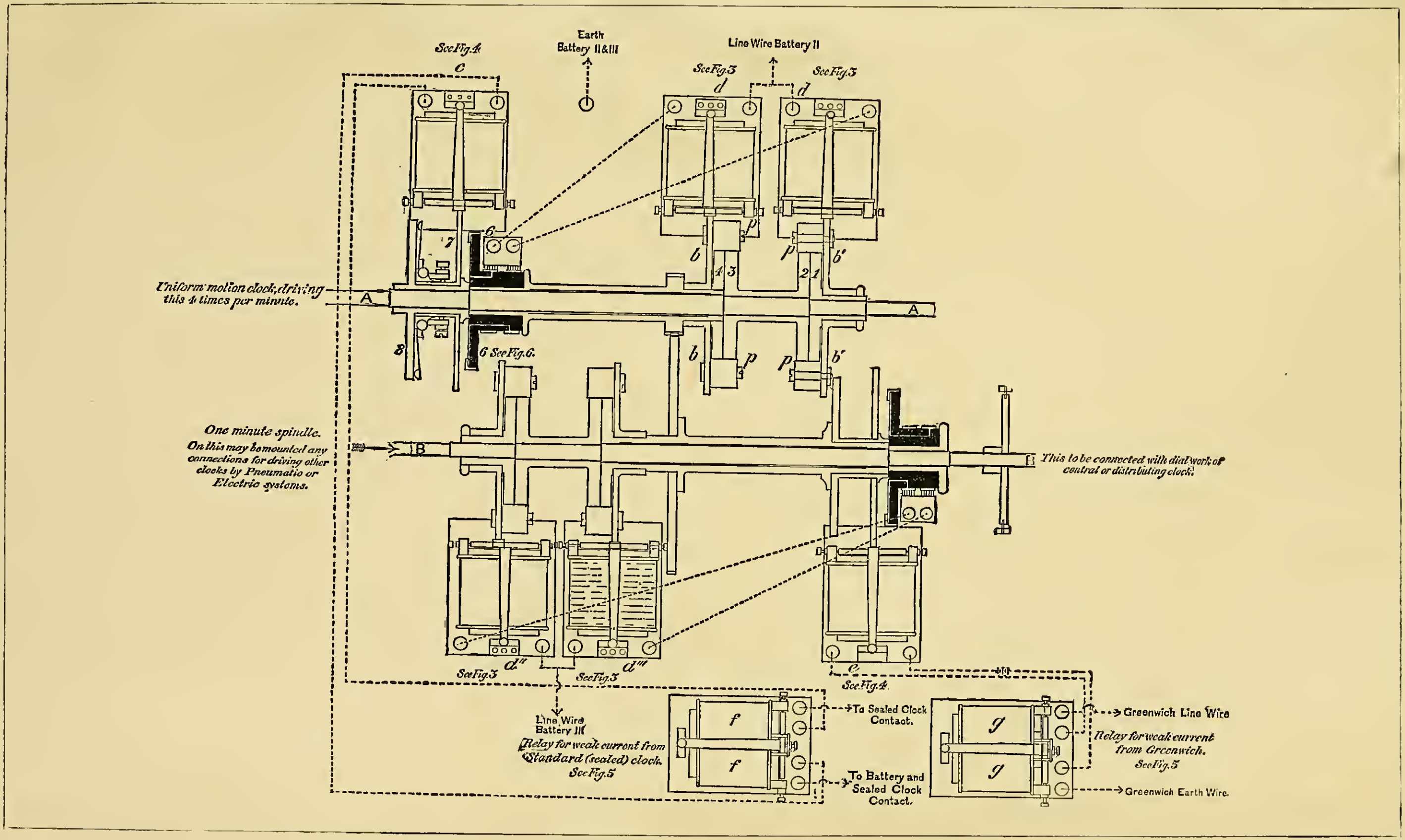


DIAGRAM ILLUSTRATING OVERTHRUSTS.



UNIFORM MOTION CLOCK, Etc.

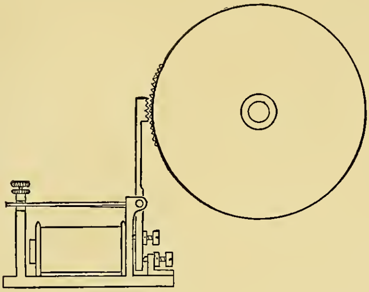


Fig. 1.

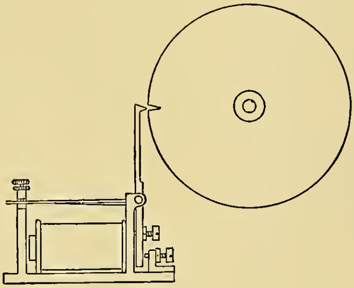


Fig. 2.

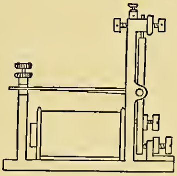


Fig. 3.

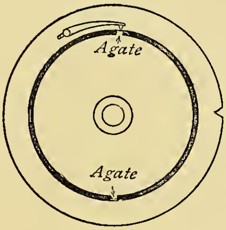


Fig. 4.

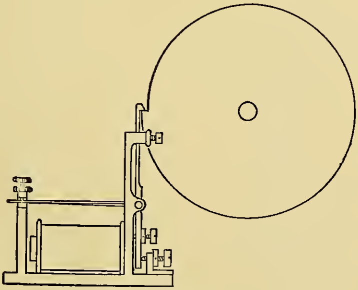


Fig. 5.

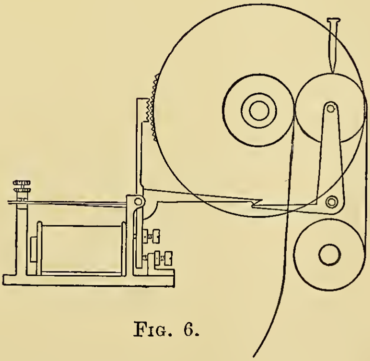
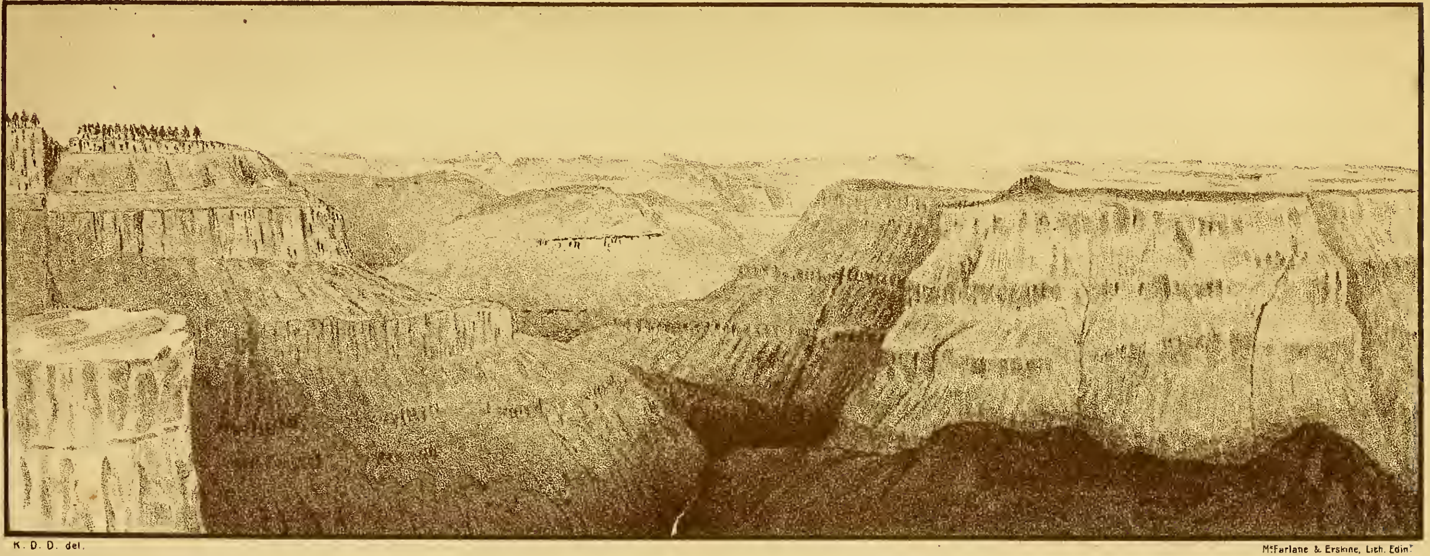


Fig. 6.

UNIFORM MOTION CLOCK, Etc.

K. D. D. del.
McFarlane & Erskine, Lith. Edin^r

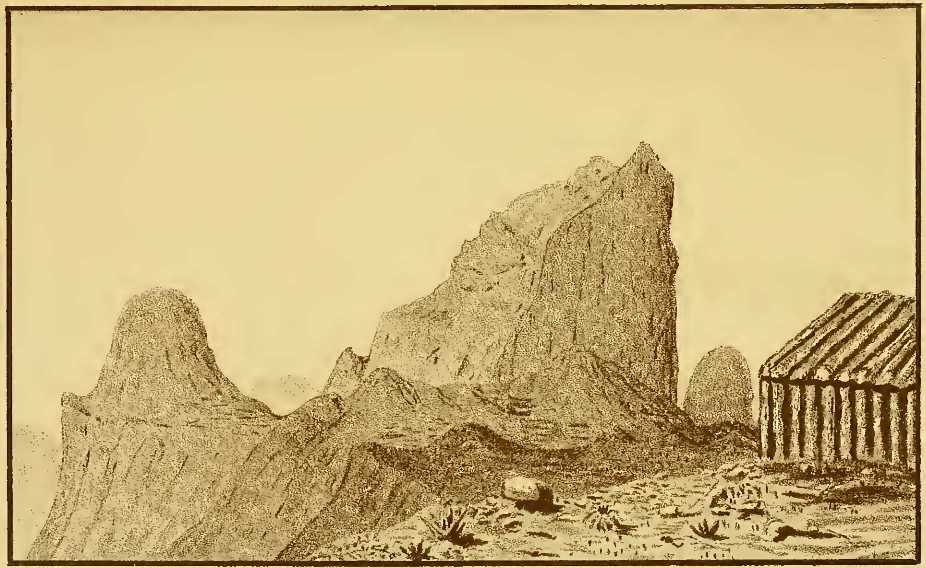
LA PUERTA BLANCA.—CHIHUAHUA. SHOWING COMMENCEMENT OF DRAINAGE ON THE MESA, AND FORMATION OF ROCK PILLAR.



K. D. D. del.

McFarlane & Erskine, Lith. Edin^r

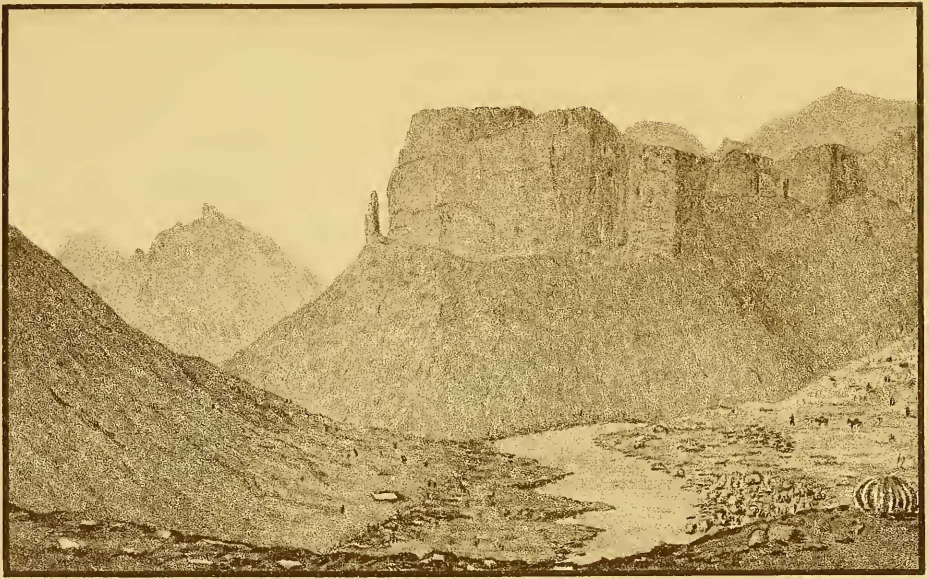
GRAND BARRANCA OF THE URIQUE RIVER, FROM
OJITO DE BARRANCA. ELEVATION 7200 FT



K. D. D. del.

McFarlane & Erskine, Lith. Edinr.

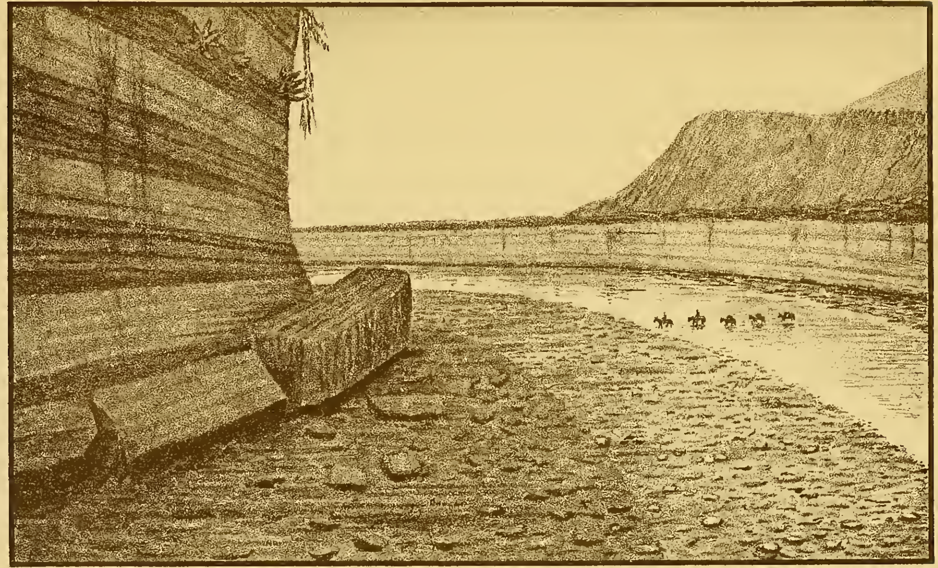
TOP OF THE CERRO DE VOLCAN, FROM DOCHINAHUI IN SONORA.



K. D. D. del.

McFarlane & Erskine Lith Edinr

THE RED BARRIER ROCK OF REALITO
FROM THE VILLAGE.



K. D. D. del.

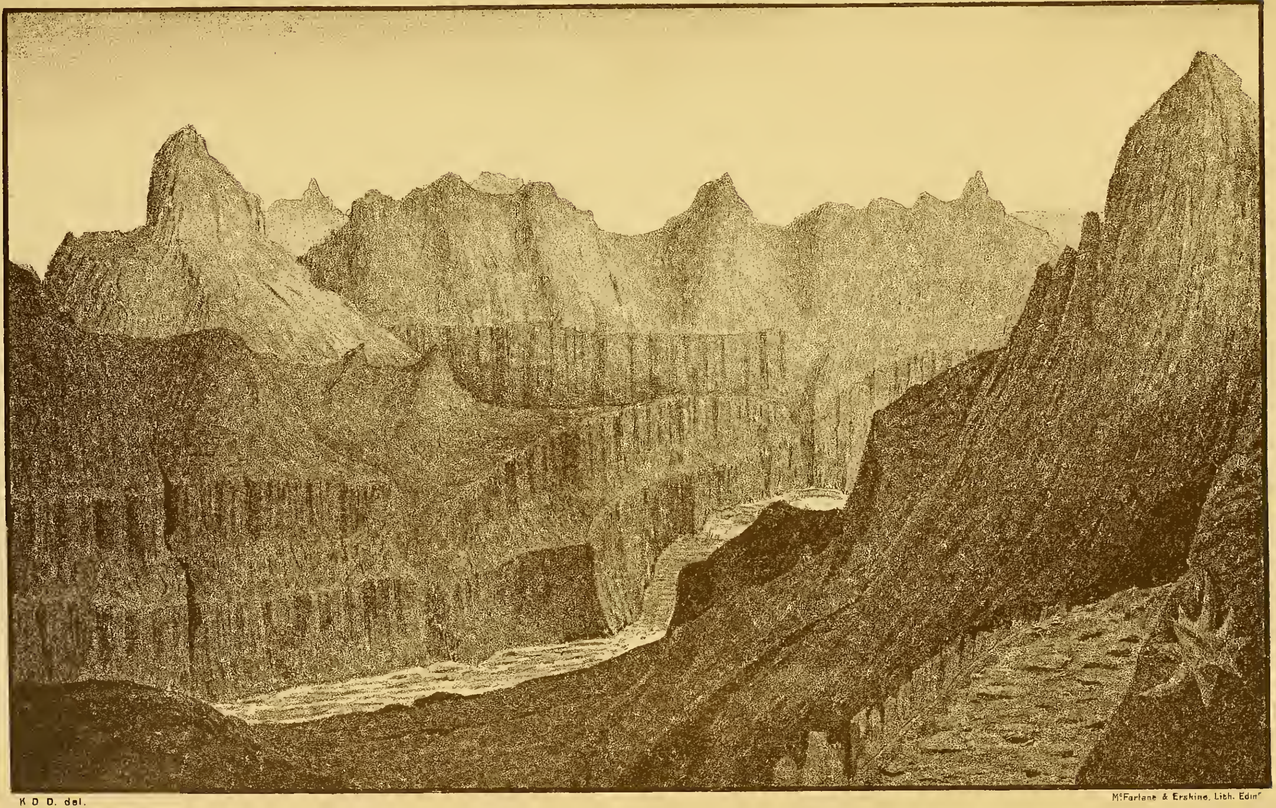
McFarlane & Erskine Lith. Edinr

RIVER CHANNEL THROUGH OLD LAKE BED,
LAKE TERRACE TO THE RIGHT. TAKEN NEAR TUBARES.

K. D. D. del.

M^cFarlane & Erskine, Lith. Edin^r.

ERODED EDGES OF OLD LAKE BEDS, BARRIER ROCK AND TERRACES IN DISTANCE. TAKEN FROM MISSION NEAR TUBARES.



K D D. del.

McFarlane & Erskine, Lith. Edinr

BATOPILLAS RIVER, FROM MOUNTAIN SIDE NEAR SAN JOSÉ.

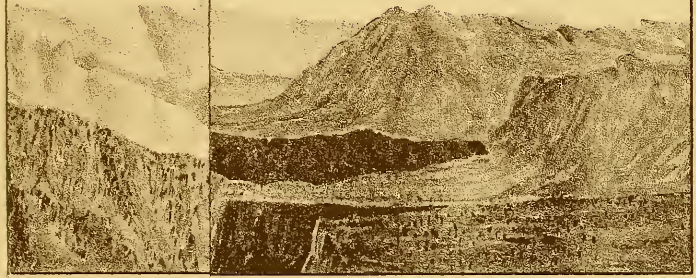
Plate XIII.

K. D. D del.

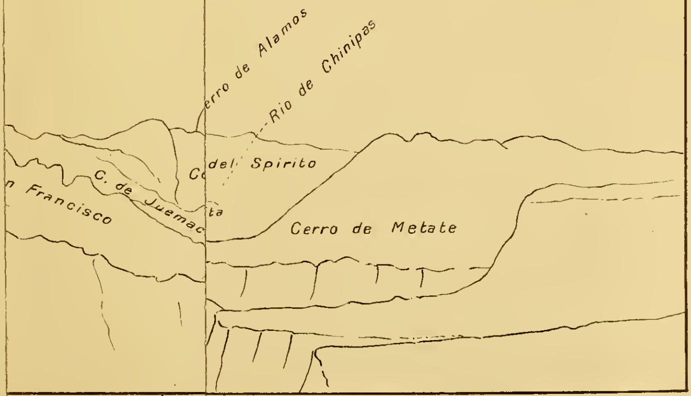
McFarlane & Erskine, Lith Edinr.

CANON OF THE RIO DE URIQUE, VIEW ACROSS AND UP THE VALLEY
FROM THE EAST SIDE NEAR GUAPALAINA.

Plate XIV.



McFarlane & Erskine Lith. Edinr.



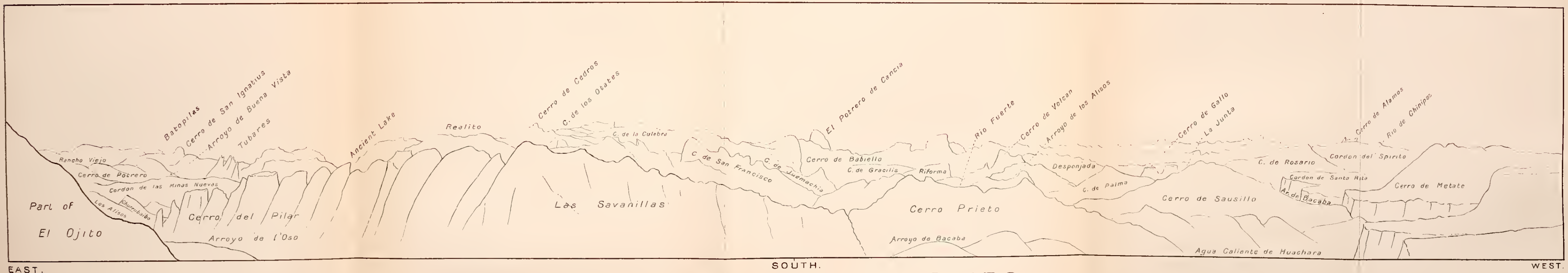
SOUTH WEST.

A FRO

Elevation

R. D. O. del.

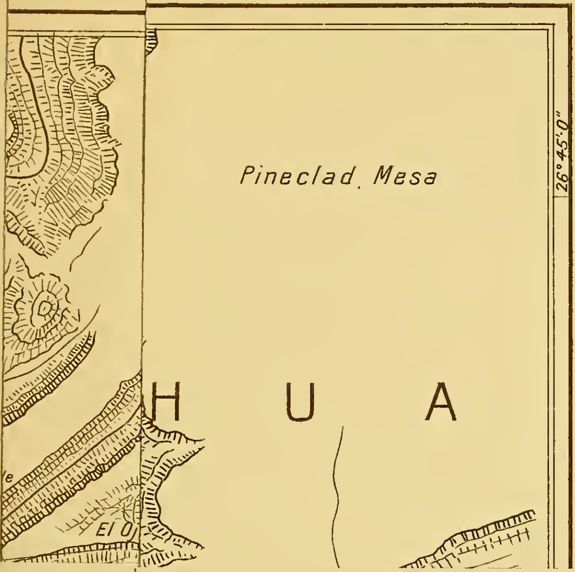
McFarlane & Erskine, Lith. Edin.



PANORAMA FROM EL OJITO

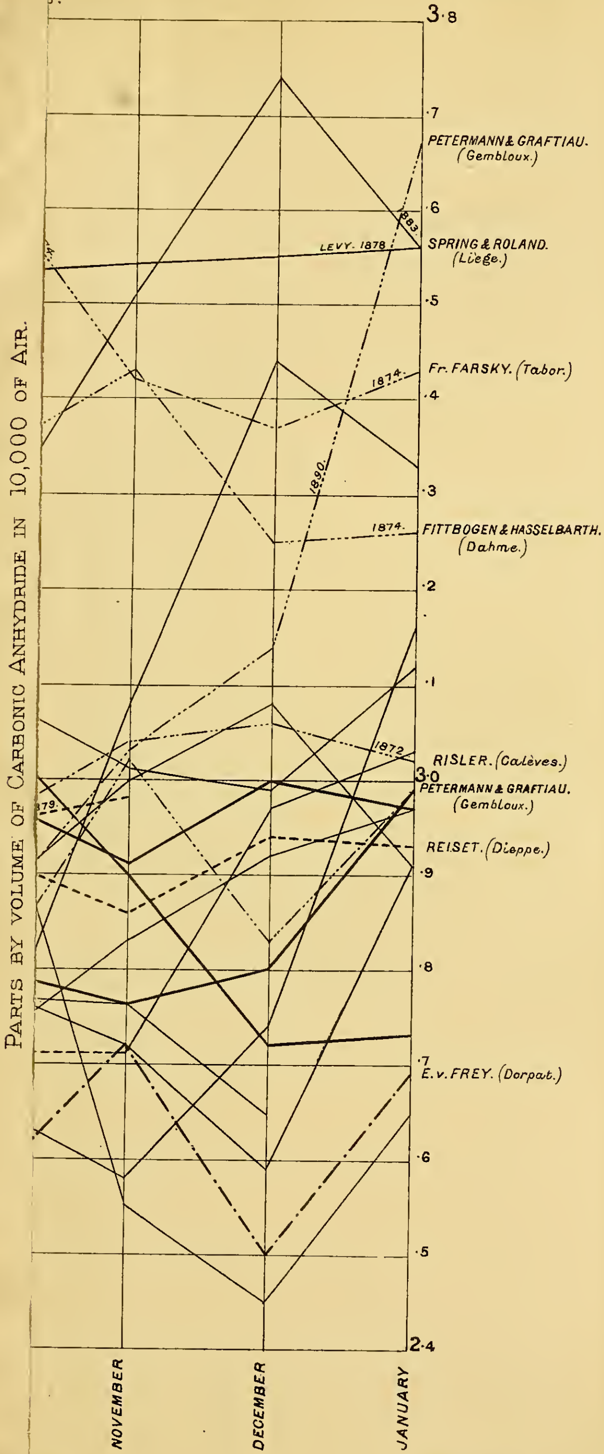
Elevation 6630 feet.

Plate XV.



FOOTHILLS OF THE SIERRA
WESTERN MEXICO
BY
K. Dryden Doyle.

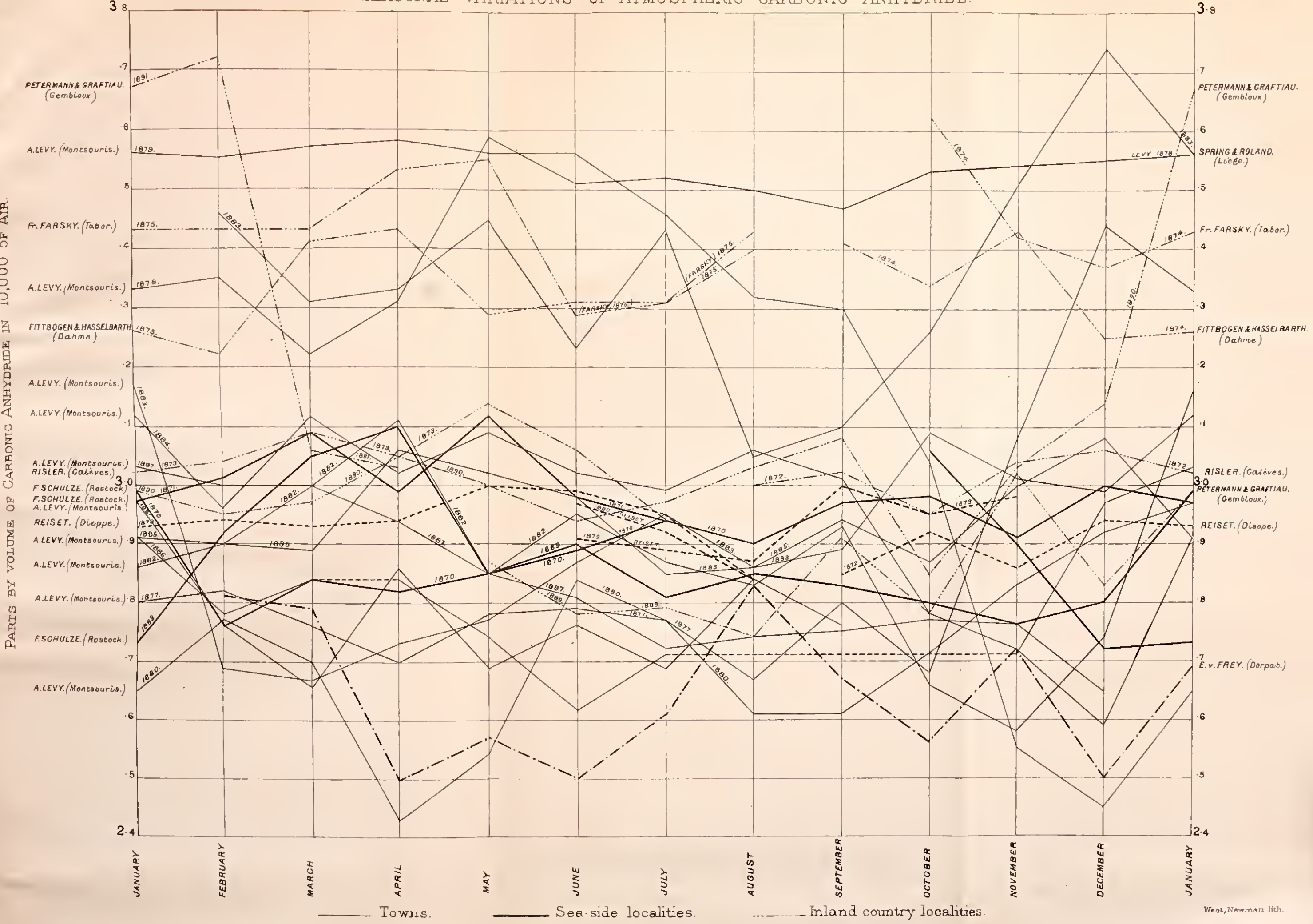
Plate XVI.



ties.

West, Newman lith.

SEASONAL VARIATIONS OF ATMOSPHERIC CARBONIC ANHYDRIDE.



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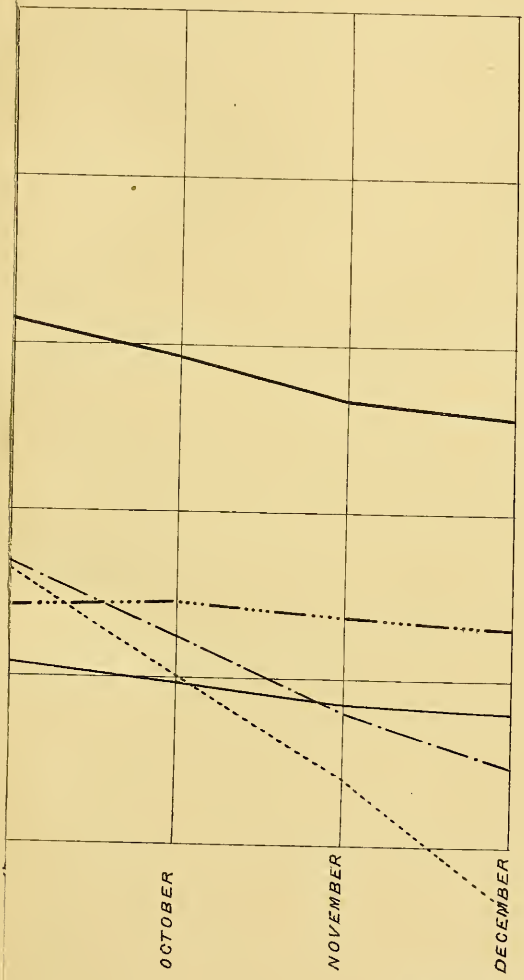
TEMPERATURE.

Plate XVII.

877-1879.)

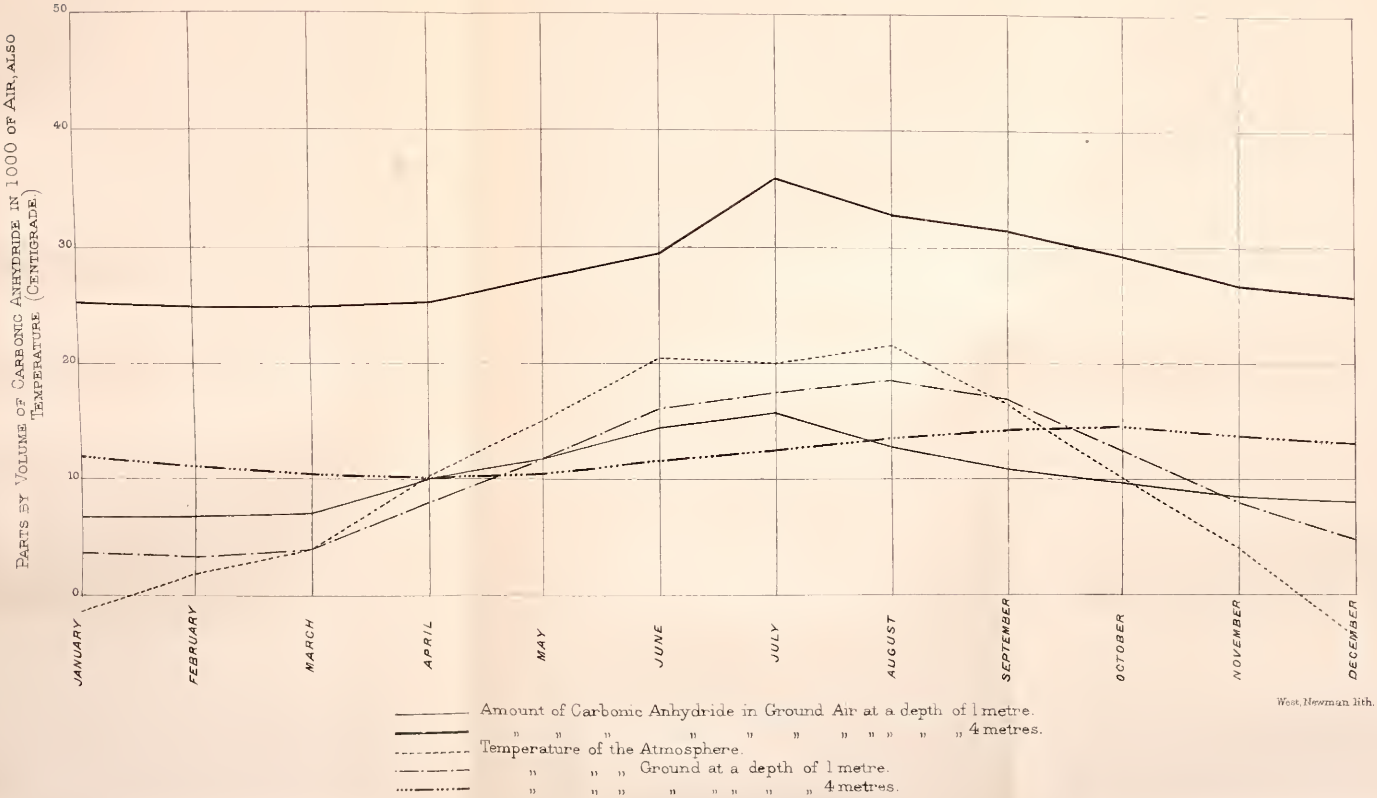


re.
res.

West, Newman lith.

THE AMOUNT OF CARBONIC ANHYDRIDE IN GROUND AIR IN RELATION TO TEMPERATURE.

(Calculated from Von Fodor's results at Buda-Pesth during the period 1877-1879.)

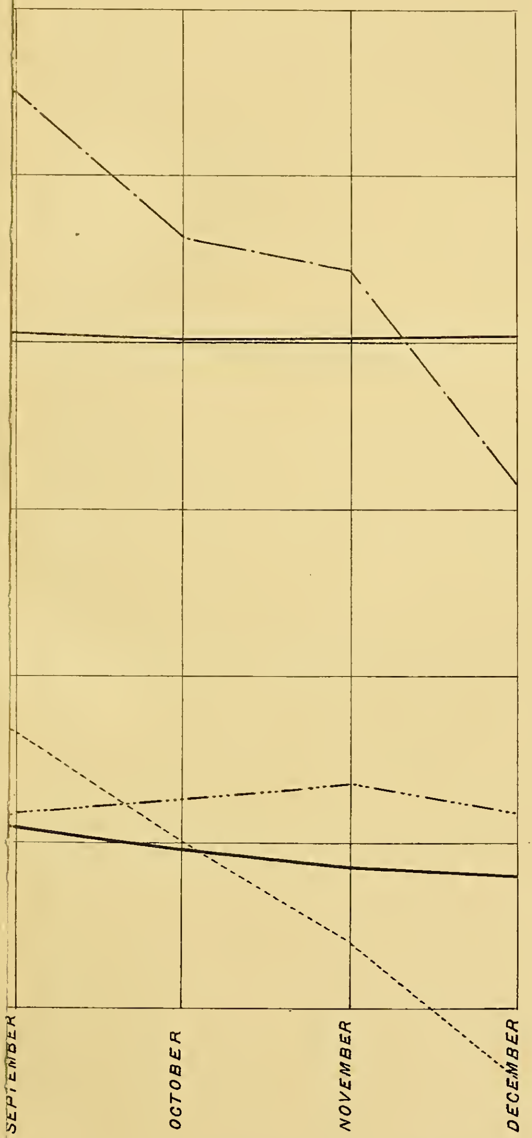


West, Newman lith.

ND AIR

Plate XVIII.

877-1879.)



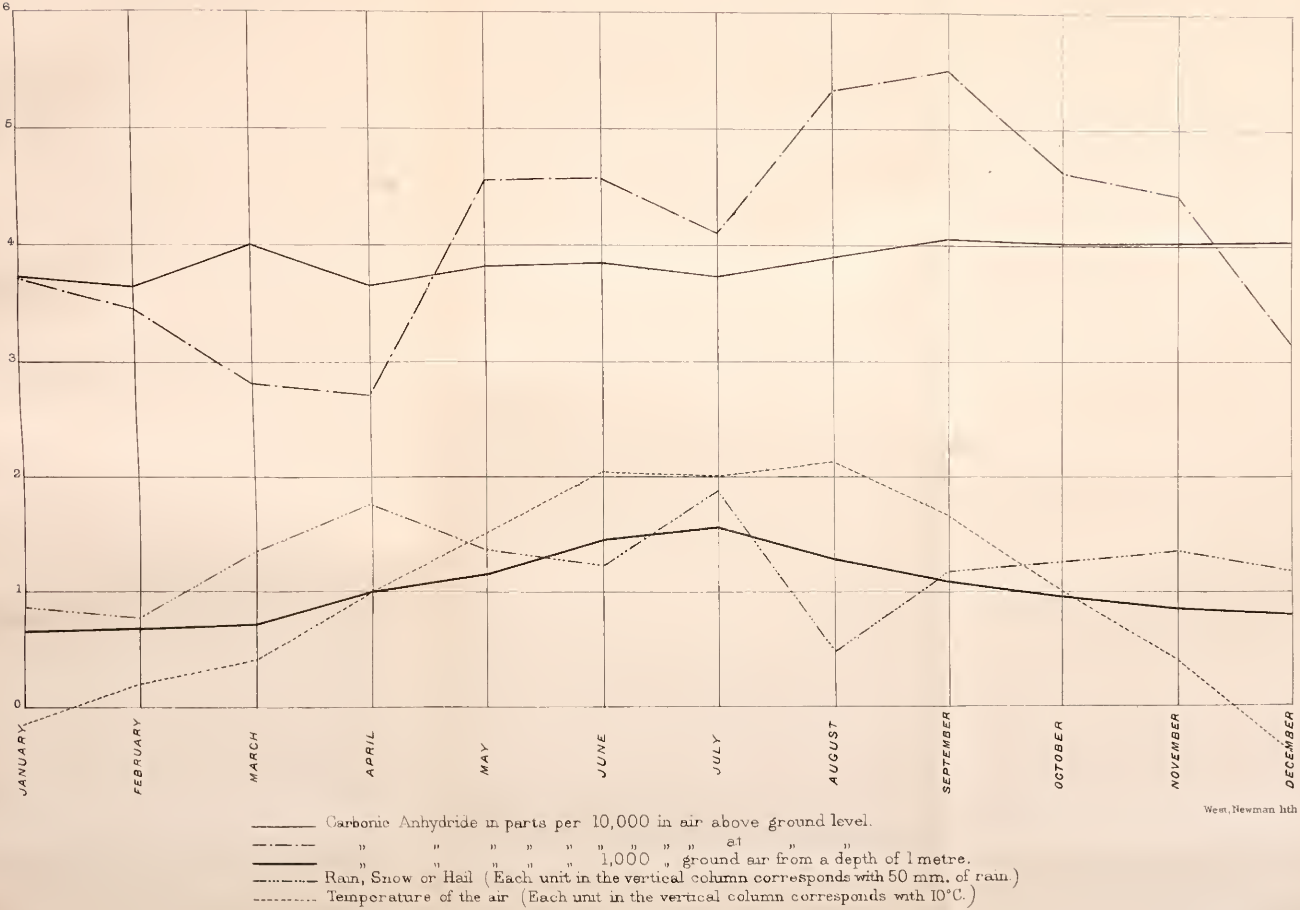
West, Newman lith

re.
. of rain.)
°C.)

Plate XVIII.

ATMOSPHERIC CARBONIC ANHYDRIDE IN RELATION TO GROUND AIR TEMPERATURE AND ATMOSPHERIC PRECIPITATES.

(Calculated from Von Fodor's results at Buda-Pesth. during the period 1877-1879.)



West, Newman lith

Fig 1. × 37

Fig. 2. × 12

G. C. delt. M^c^Farlane & Erskine, Lith. Edin^r

View of quarry opened near Drumboy. The vogesite dyke forms a dark mass crossing the foreground, and cutting the structural planes of the paler schists, which appear above.

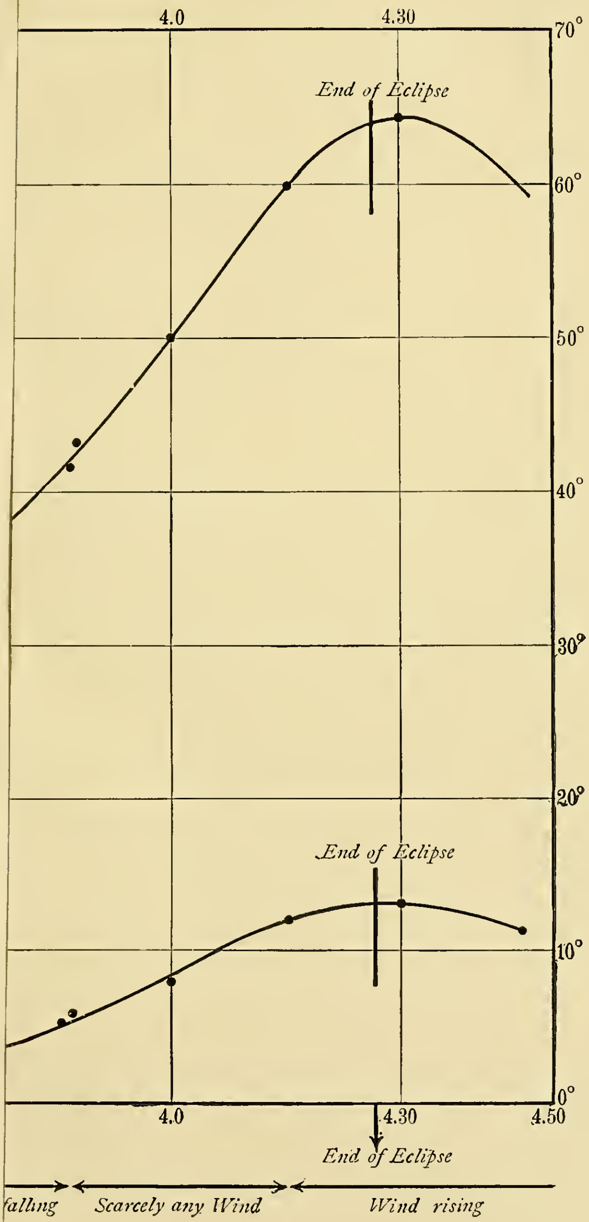
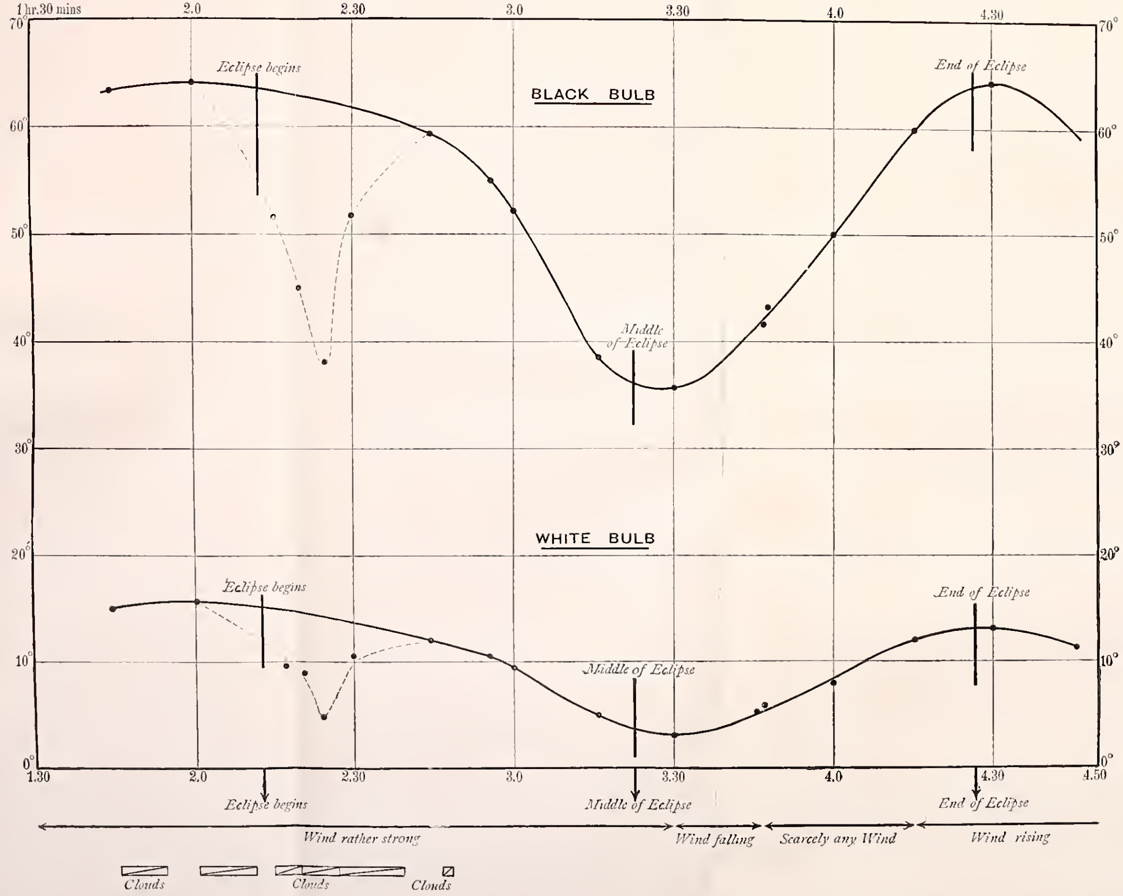
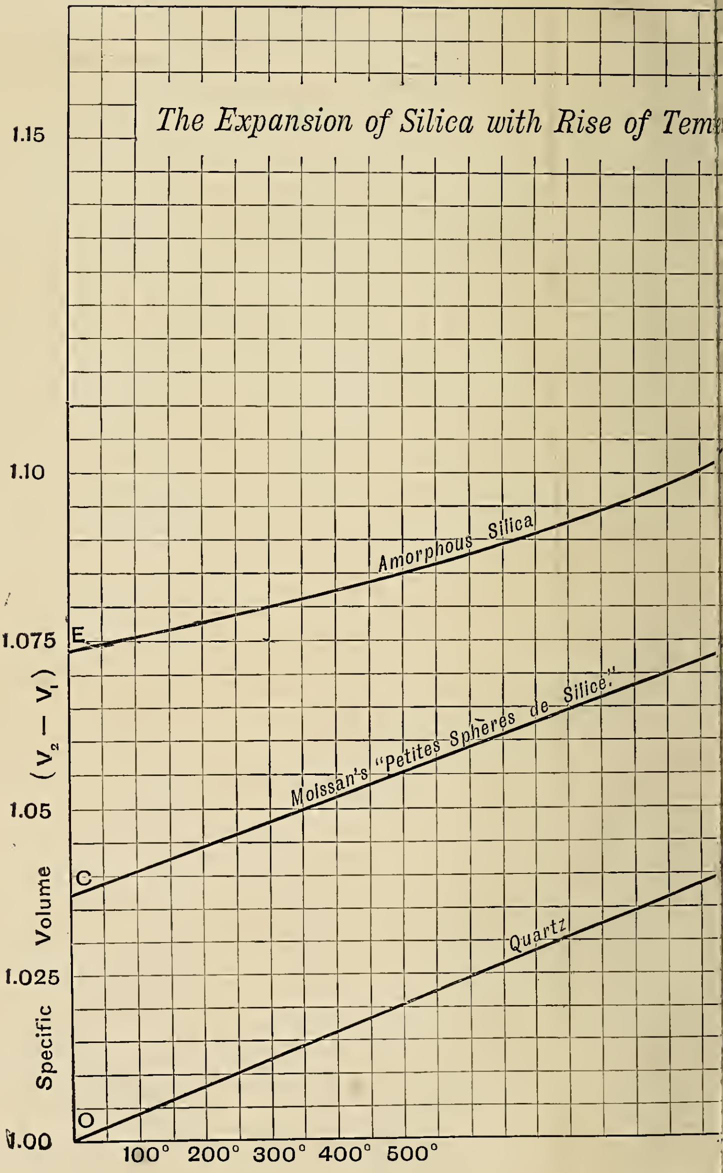
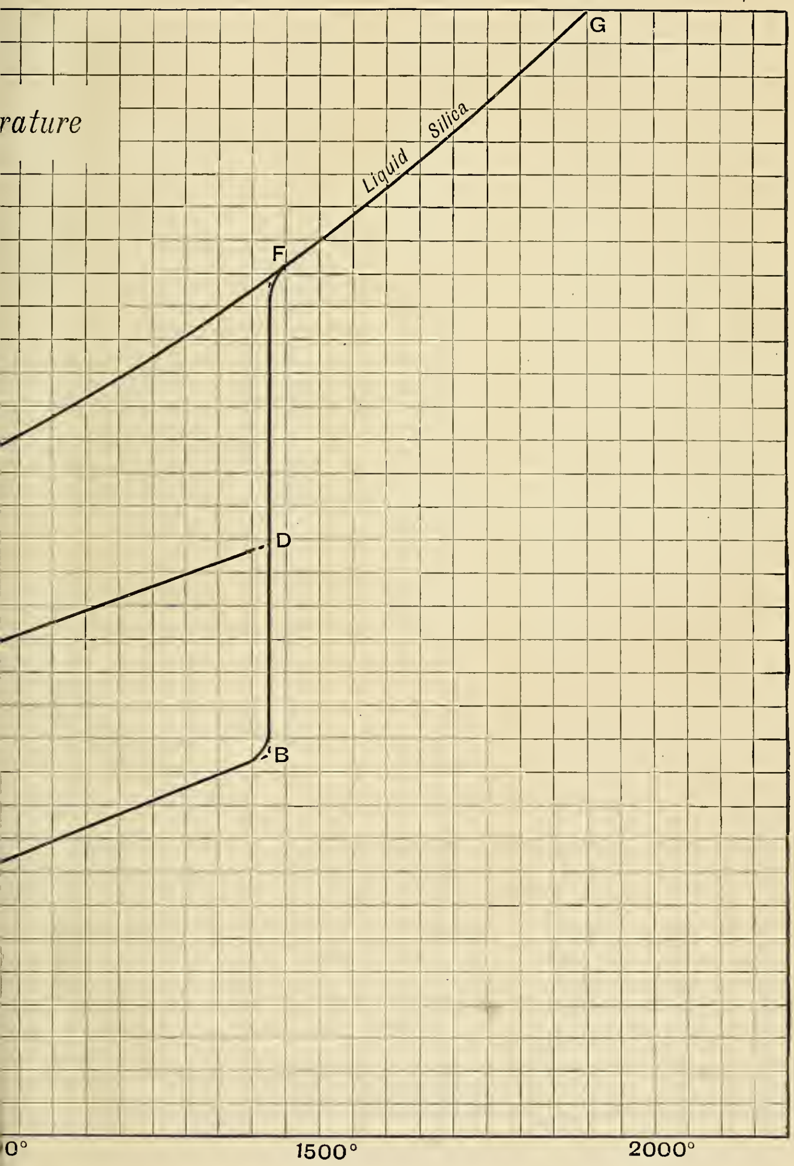
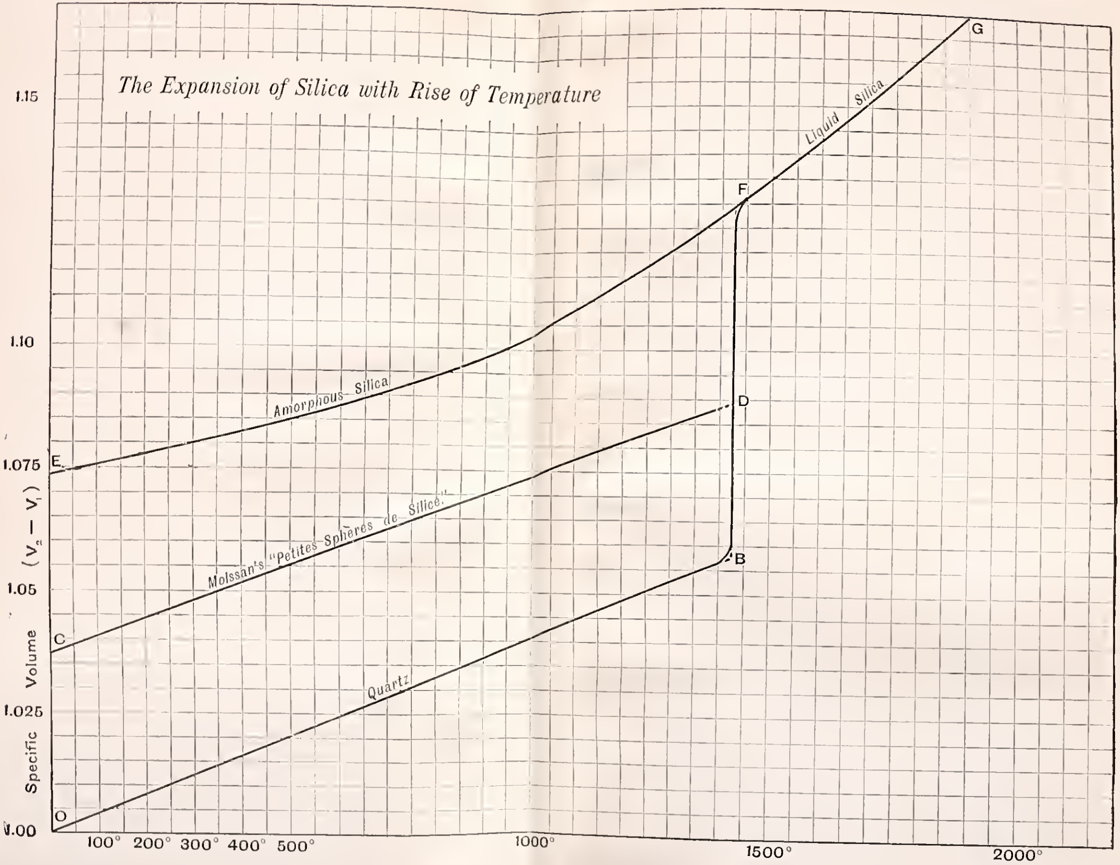

4.0
4.30
70°
60°
50°
40°
30°
20°
10°
0°
End of Eclipse
End of Eclipse
4.0
4.30
4.50
End of Eclipse
falling
Scarcely any Wind
Wind rising

Plate XXI. (*to face p.* 364.)




The Expansion of Silica with Rise of Tem
1.15
1.10
1.075
1.05
1.025
1.00
Specific Volume $(V_2 - V_1)$
100° 200° 300° 400° 500°
E
C
O
Amorphous Silica
Moissan's "Petites Sphères de Silice."
Quartz


rature
G
Liquid Silica
F
D
B
0°
1500°
2000°


The Expansion of Silica with Rise of Temperature
1.15
1.10
1.075
1.05
1.025
1.00
Specific Volume ($V_2 - V_1$)
100°
200°
300°
400°
500°
1000°
1500°
2000°
G
Liquid Silica
F
Amorphous Silica
D
E
Moissan's "Petites Sphères de Silice."
B
C
Quartz
O

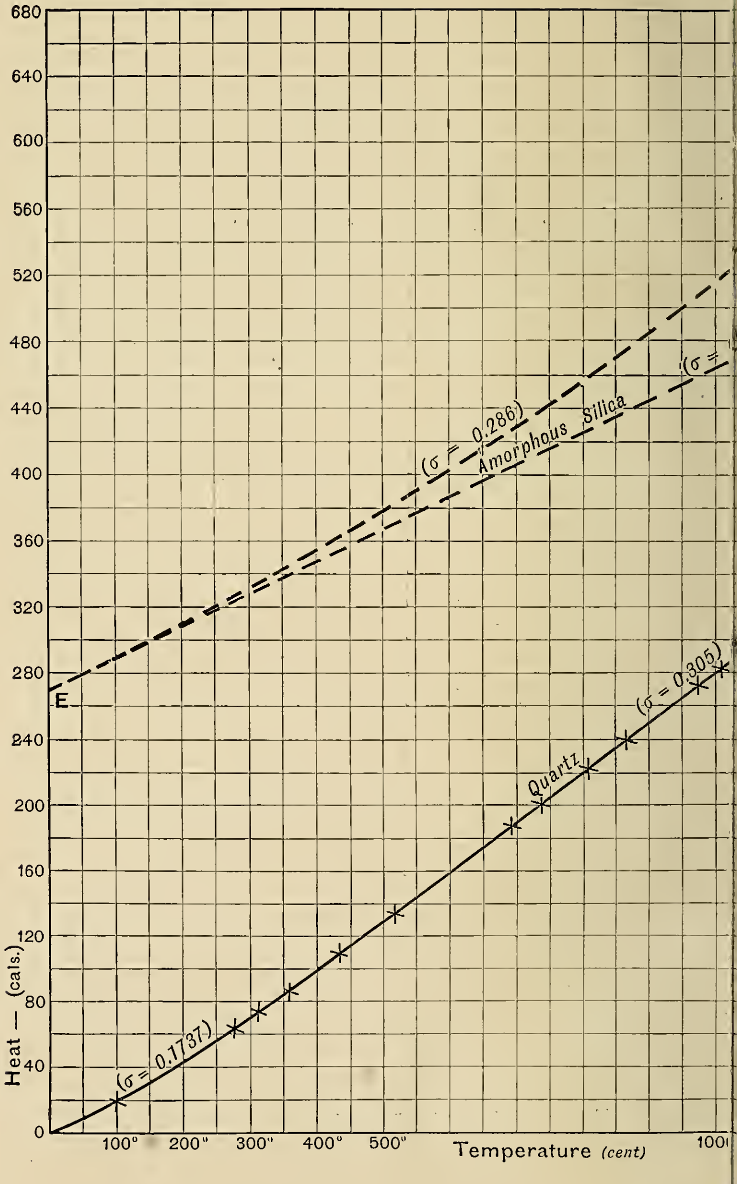
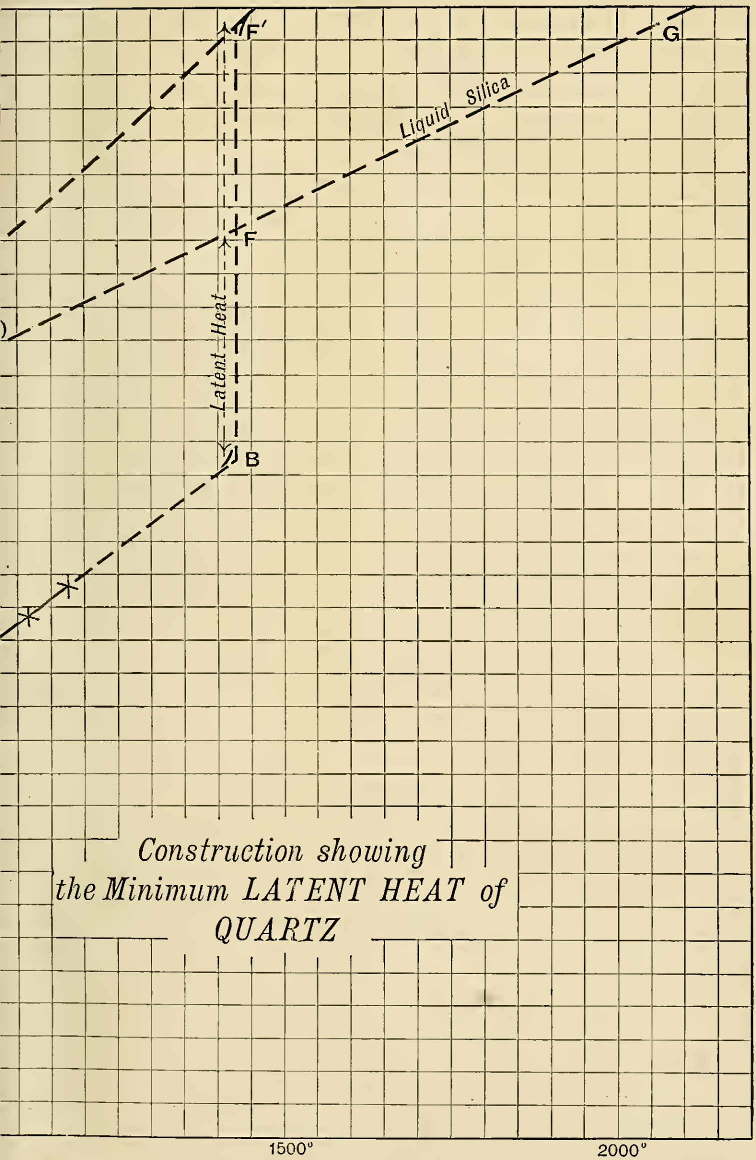
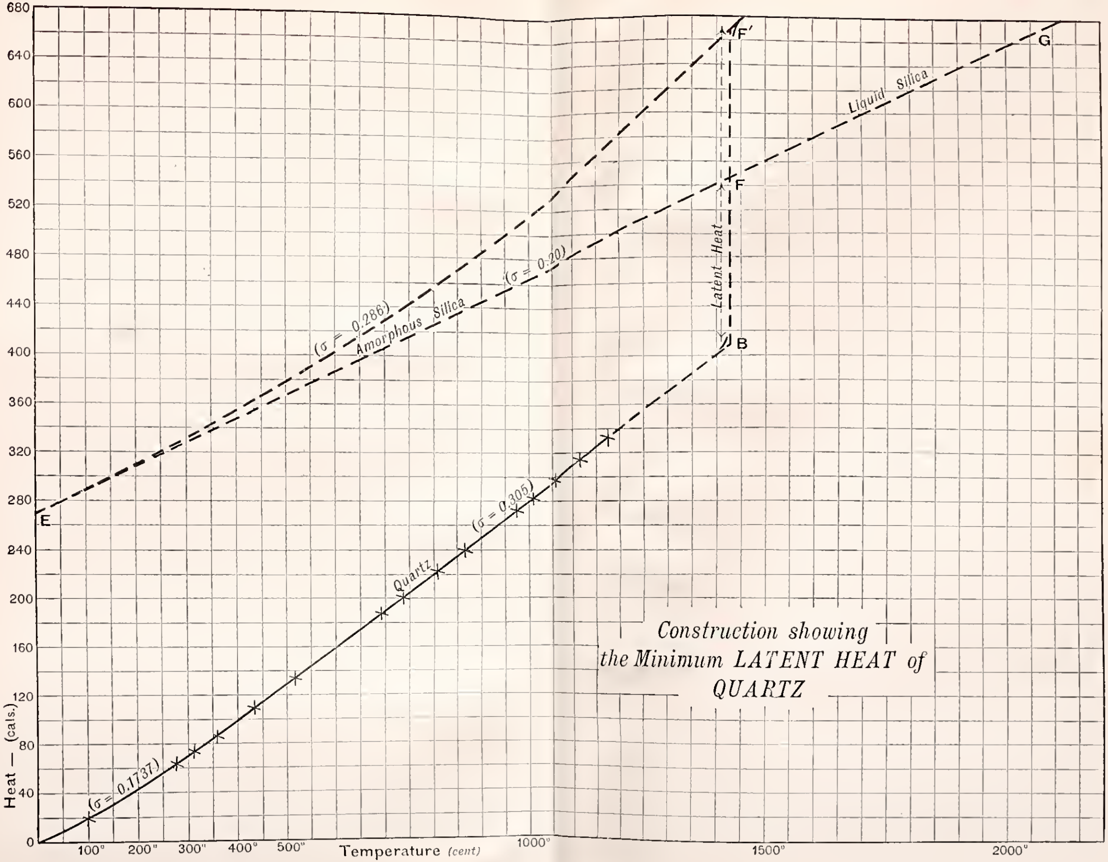

680
640
600
560
520
480
440
400
360
320
280
240
200
160
120
80
40
0
Heat — (cals.)
100°
200°
300°
400°
500°
100
Temperature (cent)
E
(σ = 0.286)
Amorphous Silica
(σ =
Quartz
(σ = 0.1737)
(σ = 0.305)

Plate XXIII.



Construction showing the Minimum LATENT HEAT of QUARTZ



Construction showing
the Minimum LATENT HEAT of
QUARTZ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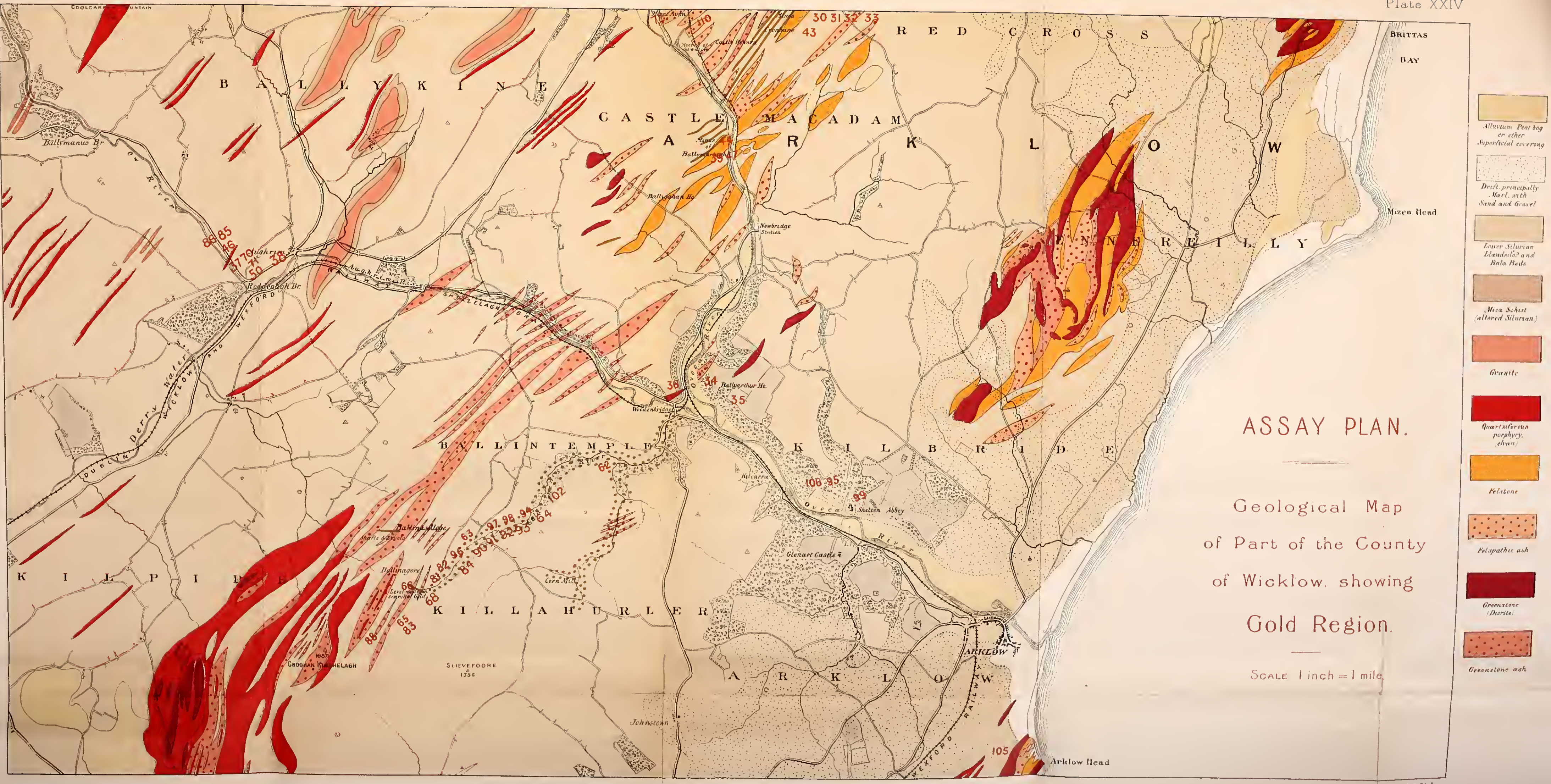
RD
D

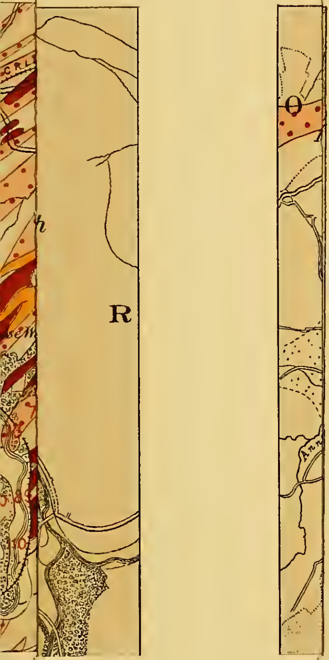


ASSAY PLAN.

Geological Map of Part of the County of Wicklow, showing Gold Region.

Scale 1 inch = 1 mile.

M'Farlane & Erskine, Lith. Edin.



▭ *Alluvium Peat bog, or other Superficial covering*

⁙ *Drift, principally Marl with Sand and Gravel*

▭ *Lower Silurian Llandeilo? and Bala Beds*

▭ *Mica Schist (Altered Silurian)*

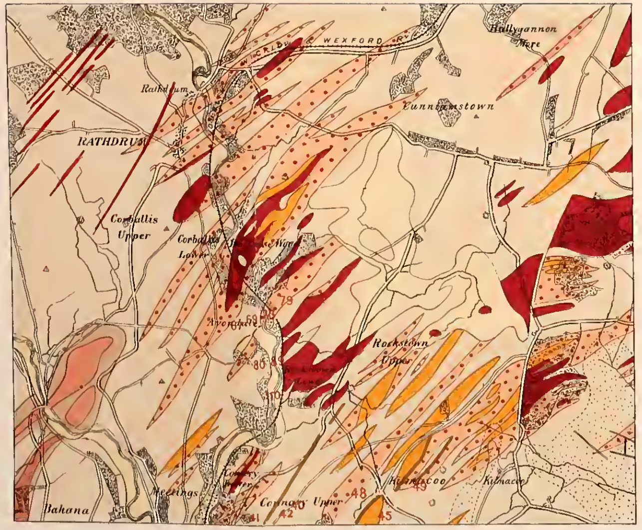
▭ *Granite*

🟥 *Quartziferous Porphyry, (elvan)*

🟧 *Felstone*

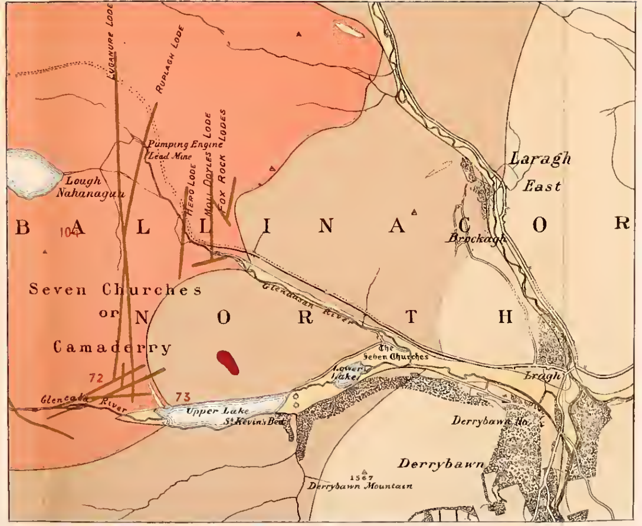
▨

A.



WICKLOW.

B.



WICKLOW.

C.

CLARE.

- ▭ *Alluvium Peat bog, or other Superficial covering*
- ░ *Drift, principally Marl with Sand and Gravel*
- ▭ *Lower Silurian Llandeilo? and Bala Beds*
- ▭ *Mica Schist (Altered Silurian)*
- ▭ *Granite*
- 🟥 *Quartziferous Porphyry, elvan*
- 🟧 *Felstone*
- ▨ *Felspathic ash*
- 🟥 *Greenstone Diorite*
- ▨ *Greenstone ash*

ASSAY PLANS.

Geological Maps of Part of the Counties of Wicklow, and Clare, Showing Gold Regions.

SCALE 1 inch = 1 mile.

FIG. 1.

View looking east from point marked A on map (Pl. XXIX.), showing the dry gap.

FIG. 2.

View looking west rom point marked B on map (Pl. XXIX.), showing the gravel mounds in the Piperstown Valley.

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OF THE

ROYAL DUBLIN SOCIETY.

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Quarto, Published in Parts, stitched.

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