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SERIES A, VOL. 202, pp. 1–69.

[PLATES 1–11.]

BAKERIAN LECTURE.

ON THE CONSTITUTION OF THE COPPER-TIN SERIES OF ALLOYS

BY

C. T. HEYCOCK, F.R.S.,

AND

F. H. NEVILLE, F.R.S.

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PHILOSOPHICAL TRANSACTIONS.

I. Bakerian Lecture.—*On the Constitution of the Copper-Tin Series of Alloys.*

By C. T. Heycock, *F.R.S.*, *and* F. H. Neville, *F.R.S.*

Received February 26,—Read February 26, 1903.

[Plates 1–11.]

Contents.

Section I.—Summary of Results.

Section II.—On the Solidification of a Metal.

Section III.—The Microscopic Study of the Alloys.

SECTION I.

Summary of Results.

The immediate origin of the present paper lay in a suggestion of the late Sir G. G. Stokes, made early in 1900, that we should attempt the microscopic examination of a few bronzes as an aid to the interpretation of the singularities of the freezing-point curve. This curve was at the time fairly accurately known, largely through the researches of the late Sir W. Roberts-Austen and Dr. Stansfield, published in 1895 and in 1897, and partly by our own work. Microscopic studies of the alloys had been also published by Dr. Charpy and by Mr. Stead, but, so far as we are aware, no attempt had been made to correlate the two lines of research, and the exact nature ot this group of alloys remained very obscure.

The ingots of alloy which we studied at first had been allowed to cool somewhat slowly and spontaneously in the furnace, so that there had been no sudden chill or alteration in the rate of cooling. Polished and etched sections of these ingots were found to contain very varied and complicated patterns that sometimes appeared to have no connection with the singularities of the freezing-point curve. For example, a tin-rich crystallisation which appeared to be primary, was found to *increase* to a maximum amount as we *descended* a branch of the curve, and in more than one region undeniable primary crystals which stood out in relief on the outside of the ingots were found, when polished half-through, to be full of smaller and quite different crystals. In fact, it became evident that the final patterns we were examining were of the nature of a palimpsest in which several different records were superposed, some of these being due to recrystallisations that had taken place after solidification. Two other considerations pointed to the same conclusion, the first was derived from the very valuable cooling curves, published by ROBERTS-AUSTEN and STANSFIELD in 1895, which revealed the fact that far below the temperature of solidification considerable evolutions of heat occurred in the alloys as they cooled. The second was derived from Professor ROOZEBOOM'S paper on the "Solidification of Mixed Crystals of Two Substances," published in the 'Zeitschrift für Physikalische Chemie,' of December, 1899. These two researches have been respectively the experimental and the theoretical basis from which the present work has grown, and the possibilities of interpretation which they promised have induced us to make a much more serious study of the bronzes than we originally intended.

It soon became clear that in order to understand the nature of the alloys it was essential to examine their structure at all temperatures, from the freezing-point downwards. We therefore adopted the plan of chilling small ingots at selected temperatures. We hoped that, as in the case of steel, the structure existing at a particular temperature would be so far stereotyped by the sudden cooling of the chill as to be recognisable under the microscope. This hope has been to a very large extent justified, most of the doubtful points as to the nature of the bronzes having been cleared up by the evidence derived from the chilled ingots. In February, 1901, we published in the 'Proceedings of the Royal Society' a short paper describing the method, and gave some photomicrographs illustrating the extraordinary changes that a solid alloy can undergo as it cools, and in December, 1901, we read before the Royal Society another short paper on the same subject. The latter paper contained a diagram giving a complete view of the conclusions we had arrived at, concerning the nature of the copper-tin alloys. The paper was published in the 'Proceedings,' vol. 69. The photomicrographs, which formed an important part of the evidence for the truth of the diagram, were exhibited by one of us when the paper was read, but were not included in the paper. The present paper does not represent any great advance beyond that of December, 1901, although the diagram (Plate 11) now given is in some minor points more accurate than the earlier one, and a change has been made in the notation. The main purpose of the present paper is to give the evidence for the correctness of our views, evidence which is largely drawn from the photographs of the chilled ingots.

The photographs are reproduced in Plates 1 to 9, containing figs. 1 to 101 arranged in order; opposite each plate is a table giving a brief description of the figures contained in it, the composition of the alloy, the method of etching the ingot, and the magnification employed in taking the photograph.

Before considering the photographs it will be necessary to discuss the cooling curves of Plate 10 and the equilibrium diagram of Plate 11. We shall thus be able to present an outline of our conclusions which will, we hope, render the bulk of the evidence, which is given further on, more intelligible. *We think that a reader wishing to understand the results of our work without desiring to weigh the evidence minutely would find Section I., and an examination of the plates and photographs referred to in Section I., almost sufficient for his purpose.*

The Cooling Curves.—(Plate 10.)

Although the pyrometric work of ROBERTS-AUSTEN and STANSFIELD gave us most valuable suggestions, we did not find it possible to use it quantitatively. This was partly due to the small size of their published curves, and partly to their being constructed on a thermometric scale different from the one employed by us. We therefore determined to repeat a good many of the cooling curves and to reconstruct the thermal diagram of the alloys. Plate 10 gives the more important of the cooling curves obtained by us, but we have in addition traced the cooling curves of alloys with more tin. Our curves are very similar to those of ROBERTS-AUSTEN and STANSFIELD, and we are not prepared to say that they contain any additional information, but they are in a form convenient for use with the present paper. They were traced by means of a platinum-resistance pyrometer and a Callendar recorder, in which a pen, controlled by the pyrometer, writes on a rotating drum.

In Plate 10 the horizontal ordinate is time, and it is reckoned from left to right, the vertical ordinate being temperature reckoned downwards. A scale of Centigrade degrees is placed at each end of the diagram, which will enable the temperature of an alloy at any point on its curve to be read off. It may be noticed that equal vertical distances do not quite correspond to equal ranges of temperature, but that the scale becomes more open as the temperature falls. This peculiarity arises from the curves having been traced automatically on the platinum scale. The curves are an exact copy half-size of those traced on the recorder.' The number at the head of each curve indicates the atomic percentage of tin in the alloy. In tracing a curve a mass of about 300 grammes of alloy was melted in a double or treble crucible and allowed to cool spontaneously with the pyrometer immersed in it. The time of tracing a curve was generally about two hours, and a little carbon was thrown on the surface of the ingot, to avoid oxidation, or, as an alternative, a little coal-gas was allowed to burn at the mouth of the crucible.

A detailed discussion of the various curves is not necessary here, as they will be referred to later on, but it may be worth while to say a few words about their general character. If a substance remained liquid throughout the whole range of cooling and underwent no chemical change we should expect its cooling curve to be a sloping line, probably somewhat steeper at high temperatures than at low ones, but free from abrupt changes of direction. The short upper branches of all the curves, near to where they are numbered, correspond to this cooling of a uniform liquid. But when solidification, or any other exothermic change, begins the rate of cooling will be abruptly decreased and the cooling curve will tend to become horizontal. This is well seen in the upper-most curve of Plate 10, the flat under the letters "Cu" being due to the isothermal solidification of the copper. The upper flat in the curve of Sn 4 is also due to the formation of solid, and in this case a slight surfusion must have occurred, the temperature of the liquid falling below the freezing-point, and then, by the evolution of the latent heat of solidification, being perceptibly raised. But the flat is shorter than with pure copper, and rapidly rounds off in consequence of the solidification not being an isothermal process. The solidification of Sn 4 is probably completed at 850°, and below that point there is no marked singularity in the cooling curve. But if we consider the curves of Sn 6, 8, 10, 12, or 14, we see that not only does the uppermost halt, the freezing-point, become lower and lower as the percentage of tin increases, but that some distance below this halt, at a temperature almost the same for all the curves, there is a second evolution of heat which becomes more and more marked with increasing content of tin. Moreover, in the curves of Sn 10 to Sn 15, there is a third evolution of heat at about 500°, and this, as we shall be able to prove, occurs in an absolutely solid alloy. Similarly Sn 17 is solid at 700°, but its cooling curve shows well marked heat evolution at a temperature below 500°. Valuable though cooling curves are for indicating critical points in the cooling, they have a defect; in order to make the whole period of tracing the curve a reasonable one, it is unavoidable that the cooling at the higher temperatures should be somewhat rapid, hence certain rather sluggish reactions do not complete themselves at the equilibrium temperature, and may indeed never become complete. One must, in consequence, exercise some caution in attempting to infer the magnitude of the heat evolution due to a particular change from the length of the flat it produces.

The Temperature Concentration Diagram.—(Plate 11.)

The information supplied by the cooling curves can be presented in another and for some purposes more convenient form by taking the composition of each alloy as the horizontal ordinate, and temperature as before for the vertical one. Our Plate 11 is constructed in this way. Here all the first halts of the cooling curves are used to form the "freezing-point curve" ABLCDEFGHIK. This has been very carefully investigated by ROBERTS-AUSTEN and by us. It contains angles at C, D, G, H, and I, which divide it into six branches, each corresponding to the crystallisation of a different solid. ROBERTS-AUSTEN and STANSFIELD have also shown that it is possible to draw a continuous curve through corresponding lower halts in the cooling curves of the alloys from Sn 15·5 to Sn 27, and thus obtain the curve C′XD′E′f, to which we, on other grounds, have added the branch *l* C′. The whole of this "transformation" curve, as the discoverers called it, has recently been traced by us from our own experiments, so that, as given in Plate 11, it is a confirmation but not a copy of that of ROBERTS-AUSTEN and STANSFIELD. The transformation curve has some analogy with the freezing-point curve, inasmuch as when the temperature of an alloy falls to that of a point on either of the two curves crystallisation commences, but while at the upper curve the new solid crystallises out of a uniform liquid, at the lower curve the phenomenon is a recrystallisation out of a body already solid and crystalline.

At the top of Plate 11 there are two scales, the upper gives the percentage by weight of tin in the alloy, and the scale of equal divisions slightly lower down gives the atomic percentage of tin. Compositions expressed in atomic per cents. have the advantage of being at once convertible into formulæ. Thus 25 atomic per cents. of tin, or, as we write it, Sn 25, implies Cu 75, and, therefore, the formula Cu_3Sn, and so on.*

One way of looking at the diagram is expressed by the statement that a vertical line stands for an alloy of a particular composition, irrespective of its temperature, while if we follow such a vertical line from the top to the bottom of the diagram we are, *diagrammatically*, watching the alloy cool.

The freezing-point curve ABLCDEFGHIK divides the area into two parts such that above the curve every alloy is a homogeneous liquid, while, immediately below, it is a mixture of solid and liquid. We shall in future abandon the term "freezing-point curve" and employ the term "liquidus," suggested for such a curve by Professor ROOZEBOOM.

The Solidus.

Professor ROOZEBOOM, in the paper already referred to, has defined another curve, the "solidus," which is the complement of the liquidus. Suppose an alloy, or any other mixture, caused to cool so slowly that all parts are, at every temperature, in true equilibrium with each other. Then when the temperature falls to the liquidus a little solid will be formed, and as the temperature continues to fall, more and more solid will form, until finally a temperature is reached at which the last drop of liquid solidifies and the mass becomes wholly solid. This temperature is a point on the "solidus," and the curve passes through the *solidifying*, as distinguished from the *freezing*, points of all the alloys represented on the diagram. Just as (in the concentration-temperature diagram we are considering) all points immediately above

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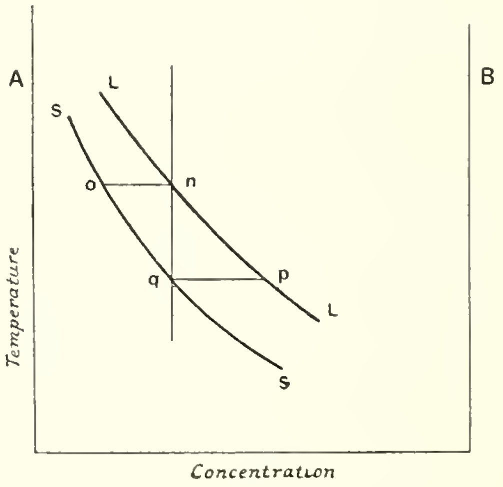
* In calculating the atomic percentage from the percentage by weight, the atomic weights employed were, Cu = 63·3, Sn = 118·1.

the liquidus represent liquid states, so all points immediately below the solidus represent wholly solid states of the system.* Points between the solidus and the liquidus stand for states of the system in which it is a mixture of solid and liquid.

The determination of the solidus by experiment is much more difficult than the determination of the liquidus. By stirring an alloy during solidification, and noting the temperature at which the stirrer becomes immovable, one gets a very rough approximation to a point on the solidus. A measurement from the cooling curve looks more promising, but is liable to prove very misleading. For example, in the cooling curve of Sn 12, solidification begins at the upper flat near 870°, but is far from complete at the end of that flat, continuing, of course with evolution of heat, to a little way below the end of the second flat at 790°. This temperature is a point on the solidus. Such cooling curves as those of Sn 4, Sn 17, or Sn 26 would leave the position of the solidus still more uncertain. It would seem that, assuming perfect equilibrium at all stages, the solidus must be identical with the "melting-point" curve, a point on the latter being defined as the temperature at which an alloy which is being very slowly heated begins to melt or form liquid. Here, again, on account of the impossibility of maintaining true equilibrium between the various crystals in a heterogeneous alloy, the experimental error would be large. We have attempted to determine points on the solidus by very slowly warming small rods of alloy and at the same time subjecting them to a slight strain, the temperature at which the rod breaks being taken as that of the solidus. These experiments have not given very consistent results, but they have been valuable in showing the high temperature up to which many of the alloys retain their rigidity.

We have found that by far the most satisfactory method of determining points on the solidus was through the study of polished and etched sections of chilled ingots of alloy. These show quite plainly how much of the ingot was liquid at the moment of chilling, and by chilling at successively lower and lower temperatures one can determine the temperature at which the whole ingot has become solid. In our Plate 11 the branches of the solidus were determined by such a study of the chilled alloys; for this purpose many chills were made in addition to those described in Section III.



Professor ROOZEBOOM defines the solidus differently, although the same curve is ultimately arrived at. As a clear understanding of Professor ROOZEBOOM'S view is essential for the argument of the present paper, perhaps we may be excused for restating it here.

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* It is more accurate to say that if we travel from A to I along the *solidus*, points on our right represent wholly solid states.

Let the figure be a portion of the concentration-temperature diagram of binary mixtures containing the two components A and B, the concentration being measured horizontally and the temperature vertically. The vertical line on the extreme left corresponds to pure A, and that on the extreme right to pure B, every other vertical line corresponding to a particular mixture. Now let the curve LL be a portion of the liquidus or freezing-point curve, and let us draw a vertical straight line, cutting LL in the point *n*. Let us consider the particular mixture represented by this vertical straight line, and think of it as cooling. When the temperature has fallen to the point *n*, the liquid mixture will be saturated, and if maintained slightly below this temperature it will, if surfusion be avoided, deposit a small quantity of a crystalline solid. This solid phase may be either the pure substance A, or a pure compound of A and B, or it may be, and this is the case we wish specially to consider, an isomorphous crystalline mixture of A and B or of compounds of the two.

(The German word for such a phase, "Mischkrystalle," naturally translates itself as "mixed crystals," but this phrase is liable to be misunderstood, in so far as it may be taken to stand for a complex of two or more different kinds of crystals instead of for crystals all alike and each a homogeneous mixture of two components, the latter being the real meaning. We have, therefore, reluctantly decided to abandon the term and use instead the term "solid solution." This term implies that the two components are capable of being as uniformly mixed as in a liquid solution, and also implies the possibility of continuous variation in the percentage composition of the mixture. It does not imply the necessity of crystalline structure, and therein the phrase has a wider scope than the otherwise identical term "isomorphous mixture" or isomorphous crystal. But, so far as we know, all the solid solutions met with in alloys are crystalline, and we shall, therefore, use the three terms as synonymous. The idea does not exclude the possibility that the same crystal may, as is often the case, be made up of layers of different composition but, contrary to the views of some writers, we are disposed to think that such a structure is not essential, but is the result of imperfect equilibrium adjustments during the formation of the crystal; this, we believe, is the view of Professor ROOZEBOOM.)

Whether the solid phase which crystallises from the saturated liquid *n* be pure component, compound, or solid solution, it must, if left long enough in contact with the liquid at the constant temperature *n*, become homogeneous and of quite definite composition, for the phase rule forbids the possibility of two different solid phases being both in equilibrium with the same liquid except at points where two branches of the liquidus meet. If, therefore, the crystals were extracted and analysed, their composition and temperature could be represented by a point *o* on the diagram, the line *no* being horizontal. We know, moreover, that the solid phase will be richer in the component A than the liquid with which it is in equilibrium; in other words, that *o* will lie to the left of *n*. It is evident that, conjugate to every point on the liquidus, there is one and only one point analogous to *o*. The curve through all these points is the solidus as defined by ROOZEBOOM. In other words, if a horizontal line be drawn cutting the liquidus and the solidus, then the two intersections give the compositions of the liquid and solid phases that can exist in equilibrium at the temperature of the horizontal line. In all cases in which the two components form solid solutions the solidus is a sloping line.

The case where the solid phase is a pure component or a pure compound may be regarded as a limiting case in which the mutual solubility in the solid condition is indefinitely small. The solidus is then the vertical line through the fixed composition of the solid phase, while from another point of view it may be regarded as the horizontal line through a lower eutectic point or angle in the liquidus. This will become more evident if we follow ROOZEBOOM through his very important description of the complete solidification of a liquid which finally forms a uniform solid solution.

Returning again to the mixture represented by the vertical line through n, let us suppose that, after the formation of a very little of the solid phase defined by o, the system is allowed to cool very slowly. The separation of the o crystals will cause the residual liquid to be richer in B, that is, to be represented by a point on the liquidus a little to the right of n, and as more and more solid is formed, the point defining the residual liquid will travel more and more to the right. But such liquids will not be in equilibrium with the crystals first formed, and hence if sufficient time is allowed in the cooling, a continuous *re*-solution or transformation of the solid phase will go on, while at the same time it grows in amount. Finally, when the temperature q is reached, defined by the intersection of the vertical through n with the solidus, the system will, in the ideal case of perfect equilibrium adjustments, be a uniform crystalline solid solution, the crystals being surrounded by a vanishingly small amount of mother-liquid of the composition p, where p is defined as the intersection with the liquidus of the horizontal through q. Of course, in a real experiment, for which infinitely slow cooling is not possible, there will be a chance that the earlier crystals may never be wholly transformed, but may remain as cores richer in A than the solid outside them. In this case the temperature of complete solidification will be lower than the theoretical one given by the point q.

The fact, taught us by the phase-rule, that in a binary mixture in which only concentration and temperature are variable a particular liquid can in general only be in equilibrium with one solid phase makes it certain that the solidus as defined above is theoretically the same curve as the melting-point curve.

We can now proceed to consider the special form taken by the solidus in the copper-tin alloys. As determined by us through the study of chilled alloys, and drawn in Plate 11, the solidus consists of the broken line $Ablcmdef E_2E_3H'H''K'$. The angular points on this broken line, with the exception of m, are pretty accurately determined, but the exact shape of the branch Ab has been rendered uncertain by the impossibility of obtaining true equilibrium transformations during the cooling of the corresponding alloys, and the branches lc and $mdef$ may, from the same cause, be a few degrees too low. Again, we have drawn E_2E_3 as a vertical straight line, while it is possible that it may be slightly sloping and curved. The point H' is fairly certain, while we have not yet enough evidence to fix H''. But, on the whole, we have considerable confidence that the solidus, as we have drawn it, is a good first approximation to the truth.

The Substances occurring in the Alloys.

The diagram of Plate 11 also contains a number of thick vertical and horizontal lines which divide up the area below the liquidus into closed compartments. Each of these compartments embraces all the temperatures and percentages for which the alloys are in a particular state of aggregation, and the phases making up the aggregates are indicated for each compartment.

The following phases may occur :—

Liquid, which is found in every compartment that lies between the liquidus and the solidus ;

Crystals of five different types, which we designate α, β, γ, δ, η, and H ;

The substance crystallising along the branch IK of the liquidus, which must be pure, or nearly pure, tin.

The liquid may, of course, have any percentage weight of tin in it from 0 per cent. to 100 per cent. The α crystals are solid solutions, apparently isomorphous with pure copper. They may contain any percentage of tin not greater than 9 per cent. The β crystals are also solid solutions, perhaps isomorphous with the α. They range in composition from 22·5 per cent. of tin to about 27 per cent. No uniform solid solutions are formed with percentages of tin between 9 per cent. and 22·5 per cent. of tin. The γ crystals are also solid solutions of copper and tin or of compounds of the two metals. They do not appear to be isomorphous with the preceding. They range in composition from about 28 per cent. to about 57 per cent. of tin. The δ material possesses a well-marked crystalline character and is very constant in appearance in all the alloys in which it is found. It may be a solid solution of varying composition like the preceding, but we are disposed to think that it is more probably the pure compound Cu_4Sn. The η forms large crystalline plates, often bounded by plane faces making definite angles with each other. It occurs in all alloys between E and H, and in many of these alloys we have proved by isolation and analysis that it is the pure compound Cu_3Sn ; it also occurs in the alloys between D and E, here it has the same crystalline form, but there is some reason to think that it may be a solid solution of varying composition.

The H substance does not differ much in composition from the compound CuSn ; it plays an important part in anti-friction alloys. We have made many analyses of H, and find it very constant in composition ; but it contains a few per cent. more copper than corresponds to the formula CuSn ; it is probably CuSn containing some Cu_3Sn in solid solution.

The substances α, β, γ, η and H are found as primary crystals and mixed with liquid in ingots chilled between the liquidus and solidus ; the δ substance never crystallises from the liquid, but appears as a recrystallisation out of homogeneous solid β or γ. All these substances, except β and γ, are stable under certain circumstances at ordinary temperatures and are therefore found in slowly cooled unchilled ingots; on the other hand, the two latter are unstable at low temperatures, and are only found in certain chilled alloys.

The angle C of the liquidus indicates that the composition of the solid phase here changes abruptly,* for while the branch ABC corresponds to the solidus A*b*, the branch CD corresponds to the solidus *lc*. The angle at C was a great difficulty to us so long as we only examined alloys that had not been chilled, but ROOZEBOOM'S theory explains in the most perfect manner all the phenomena connected with this angle. It tells us that just above the temperature C the cooling saturated liquid deposits, and is in equilibrium with the α solid solution whose composition is given by the point *b*, while just below the temperature C the liquid forms β solid solution, much richer in tin and given in composition by the point *l*. Thus as the saturated liquid cools through the temperature C an isothermal transformation $\alpha_b + \text{liq}_C = \beta_l$ takes place. The heat evolved by this reaction is well marked in the cooling curves. No uniform solid solution of percentages between *b* and *l* can exist.

The angle D indicates another break in the series of solid solutions, and we have indicated a corresponding break between *c* and *m* in the solidus. The study of the chills in this region affords, as will be seen later, some evidence for the break *cm*, but this evidence is not altogether conclusive. However, we propose to speak of the solid solutions of the branch *mdef* as γ crystals, to distinguish them from the β crystals of the branch *lc*. Both the cooling curves and the microscope indicate that in alloys between Sn 17 and Sn 20 an isothermal exothermic reaction occurs when the temperature falls to that of the point D. This reaction must be either $\beta + \text{liq} = \gamma$, or $\beta = \gamma$. The first equation corresponds to our figure, in which *c* and *m* are separated, the second to the case of *m* and *c* being really coincident.

Thus the branch ABLC of the liquidus deposits α solid solutions, the branch CD deposits β solid solutions, and the branch DEFG deposits γ solid solutions.

The branch GH of the liquidus deposits crystalline plates of the substance η, which in this region consists of nearly or quite pure Cu_3Sn.

The branch HI deposits crystals of the substance H, which is certainly very near in composition to CuSn, although it has a slight excess of copper, probably due to a small amount of η in solid solution.

The liquid of the branch IK deposits crystals that must be very nearly pure tin.

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* During the experiments for the determination of the liquidus, described in a previous paper ('Phil. Trans.,' A, vol. 189, p. 50), the cooling alloy was sometimes stirred by means of a hand stirrer during the freezing-point experiments. On such occasions we noticed a marked difference between the precipitates formed a little above and a little below C; above C the solid forming was soft, and we compared it to mud, but as soon as the temperature C was reached the precipitate became hard and gritty, and we compared it to a sharp sand.

Below the lines A*blcdef*, E_3H' and $H''K'$ the alloys are wholly solid, if they have been cooled with extreme slowness; we have succeeded in verifying this fact, but, unless great care is taken to ensure slow cooling before the chill, alloys chilled a little below these lines, which together make up the solidus, will be found to contain liquid at the moment of chilling.

Classification of the Alloys into Groups.

Vertical lines through the points B, L, C, D, E, *f*, G, H, I, divide the alloys into groups having special qualities. We will trace the complete cooling of an alloy from each group.

(1.) The AB alloys, containing less than 5 atomic per cents. of tin, that is less than 9 per cent. by weight. When these alloys begin to solidify they form, while above the line A*b*, a mixture of α crystals and liquid (fig. 2). When the temperature of an alloy has fallen below the line A*b*, it consists of uniform α crystals embedded in a very little of a tin-rich mother-substance, which owes its existence to imperfect adjustment of the equilibrium between solid and liquid during the last stages of solidification. This small residue of liquid is absorbed by the α crystals at temperatures a little below *b*C and modifies the margin of these crystals, but in spite of some deceptive appearances, these alloys, at all temperatures below A*b*, consist substantially of one phase, namely, the uniform solid solution α (fig. 7).

(2.) The BL alloys, containing from 5 to 13·5 atomic per cents. of tin, that is from 9 to 22·5 per cent. by weight. These alloys, like the preceding group, commence their solidification by the formation of α crystals. but these never fill the whole volume, for when the temperature C (790°) is reached the reaction

$$\alpha_b + \text{liq}_C = \beta_l$$

commences and continues until all the C liquid is exhausted. (The sub-indices *b*, C, *l*, indicate the compositions of the particular kind of α, liquid and β respectively that take part in the reaction.)

Thus, when the temperature falls below C, assuming that the ingot has been kept long enough at the C temperature, the alloy is wholly solid and consists of α crystals of the percentage *b* embedded in β crystals of the percentage *l*. These β crystals are uniform, and at lower temperatures play the part of a mother substance to the α crystals, which grow at the expense of the β while the solid alloy cools through the range of temperature *bb'*. This growth in the solid is very remarkable in alloys near the composition *l*, and accounts for the fantastic angular shapes seen in the α combs of the slowly cooled and unchilled alloys. Fig. 27, Plate 3, an ingot of Sn 13·5, chilled at 558°, is a good example of this effect. The α combs are light and the uniform solid β out of which they have grown, is dark. When the temperature falls below 500° (the eutectic line of ROBERTS-AUSTEN and STANSFIELD), the residual β

decomposes into a very minute complex (fig. 19) of α and the tin-rich body δ, which we strongly suspect is the compound Cu_4Sn. Thus at all temperatures below $b'C'$ this group of alloys consists of the complex $\alpha + \delta$.

(3.) The LC alloys, containing from 13·5 to 15·5 atomic per cents., that is from 22·5 to 25·5 per cent. by weight of tin. These alloys commence their solidification by the formation of α crystals, but this process soon ceases, for at the C temperature the α is wholly changed into β of the l percentage, and then this β reacts along the lines lc and CD with the residual liquid in the manner described on p. 8. When the temperature has fallen to the solidus lc, the alloy is a uniform solid solution. It is a mass of β crystals, chemically identical, but forming crystalline grains differently oriented and therefore showing, after etching, differences of brightness on tilting or rotating. This uniform solid solution continues to exist until the temperature falls below the line lC', which is comparable to a freezing-point curve, inasmuch as on cooling to a point on this line, the uniform β becomes saturated with α, and below the line the α crystallises out in large copper-rich crystals. Finally, as before at 500°, the residual β breaks up into the C′ complex. Below the $b'C'$ line these alloys, like the preceding, consist of the complex of $\alpha + \delta$. An examination of the photographs we give of Sn 14 (Plate 3) will be found to confirm these statements. The C′ complex has often, of course, been previously observed in unchilled alloys, but, so far as we know, without its real nature being discovered.

(4.) The CD alloys, containing from 15·5 to 20 atomic per cents. of tin, that is from 25·5 to 31·8 per cent. by weight. These alloys begin to solidify by forming large, comparatively copper-rich combs of β immersed in a liquid considerably richer in tin, and, as far as Sn 16·5, the alloys when just solid, are a uniform mass of β crystals. Although the alloys from Sn 16·5 to Sn 20 form similar β crystals during the first stages of solidification, these crystals never entirely fill the ingots, and below the temperature D they are transformed into what appears to be uniform γ. The uniform character of the solidified alloys persists so long as the temperature is above the line C′XD′. These solid solutions are very homogeneous, and we have not been able to detect much, or any, difference between the appearance of the uniform β of Sn 16 at 700° and the uniform γ of Sn 18 at the same temperature, provided both alloys have been very slowly cooled.

In all the alloys of this group, when the temperature falls below C′XD′, the phase δ crystallises out in ribands at the borders of the crystal grains of the solid solution, as well as in the form of fern-leaf or rosette scattered through the grains. This crystallisation is well seen in the photographs of Sn 17, 18, and 19, that accompany the paper (see Plates 4 and 5). The δ, as seen in the photographs, is white; it contains a larger proportion of tin than the mother-solid round it, and the δ increases in amount as the percentage of tin in the whole alloy increases. The δ first appears in the ribands which border the grains, these ribands being produced at higher temperatures than the fern-leaf. We are disposed to think that this peculiarity is due to the fact that, in spite of the approximate uniformity of the alloy above the line C′XD′, there must be round each β grain an envelope, somewhat richer in tin than the grain itself, produced by the collection between the grains of the last traces of mother-liquid. These intergranular spaces would, therefore, as the temperature fell, be the first parts to become saturated with tin, and the tin-rich δ, in consequence, began to crystallise in these spaces. The substance between the crystals of δ is uniform until the temperature X is reached, when the residual solid solution breaks up into the C′ eutectic complex of α and δ. A careful examination of this complex with a high power proves it to be essentially the same in all alloys from Sn 6 to Sn 20. The photographs we give will, we think, justify this statement. The fact that the eutectic point C′ of the LC alloys is a little higher than the eutectic point X of the CD alloys is evident in the pyrometric curves of ROBERTS-AUSTEN and STANSFIELD, and we have also verified it, as may be seen in our cooling curves. But Professor ROOZEBOOM suggests that the true eutectic angle for all alloys from l to D′ is at C′, and that the apparent depression of X is a retardation due to the difficulty experienced by the α in crystallising without a nucleus of its own kind. Thus in the region XD_2D' the alloys are a complex of β (or γ) and δ, while below XD_2 they form a complex of α and δ.

The curves lC′XD′ record the equilibrium between the solids α and δ and the solid solution out of which they crystallise, and the method of examining chilled ingots has enabled us to follow the whole process in a very satisfactory manner. The α must be itself a solid solution, but we are strongly disposed to think that δ is the compound Cu_4Sn. The alloy Sn 20, although the cooling curve indicates that it undergoes a well-marked exothermic transformation at the D′ temperature, remains substantially uniform after the transformation. The fact that it has recrystallised is, however, shown in the ingots chilled below D′, by minute traces of the C′ eutectic visible between the large crystals of δ that almost entirely fill the ingot. It may be that the chemical compound Cu_4Sn does not exist above the temperature D′.

(5.) The DE alloys, containing from 20 to 25 atomic per cents. of tin, that is from 31·8 to 38·4 per cent. by weight. When chilled between the liquidus and the solidus, these alloys are found to contain primary combs of γ. On the solidus, these combs fill the alloy, and just below it they form a uniform solid solution, but it is very difficult in this region to prevent, by chilling, a commencement of the transformation proper to the D′E′ curve. However, our chilled ingots afford a considerable amount of evidence that the condition of the alloys at temperatures between *de* and D′E′ is that of a uniform solid solution. When the temperature falls below the curve D′E′, long, straight, very uniform bars separate out of the solid solution. These are richer in tin than the solid out of which they crystallise. They are dark in the photographs. Near D′ these bars are usually very slender and scanty, but they increase as we approach E′, and at that point they fill the whole alloy. These bars appear, from what one occasionally sees in some ingots, to be really plates seen edgeways, and their greater or less breadth is partly due to their varying inclination to the plane of the section. These plates, the first appearance of the η phase, must be either pure Cu_3Sn or solid solutions of Cu_4Sn and Cu_3Sn; we are not at present able to decide this point. Thus immediately below D′E′ the alloys are a complex of η and residual γ. But ROBERTS-AUSTEN and STANSFIELD have proved that when any of the DE alloys fall to the temperature D′ they evolve heat (see cooling curves of 20, 21, and 22). This must be due to the conversion of the residual γ into δ, so that below D′E″ the alloys form the complex $\delta + \eta$ (Plate 5, fig. 56).

(6.) The EF alloys, containing from 25 to rather more than 27 atomic per cents. of tin, that is, from 38·4 per cent. to 41 per cent. by weight. These go through the same stages of γ + liquid, then homogeneous γ, then $\gamma + \eta$; but when the temperature of the line *f*G is reached, the residual γ breaks up into η and liquid of the composition G. Thus these alloys present the somewhat rare phenomenon of the partial melting of a solid brought about by cooling it. The transformation $\gamma_f = \eta_{E'} + \text{liq}_G$, or, as we may safely write it, $\gamma_f = Cu_3Sn + \text{liq}_G$, is the transformation which causes the angle at G in the liquidus. It is accompanied by a large evolution of heat, well seen in the cooling curve of Sn 27.

It may be noted here that the triangular area *l*X*f* forms a region of uniform solid solutions, which could only have been discovered by the examination of chilled alloys, inasmuch as these solid solutions break up into two phases when slowly cooled.

(7.) The FG alloys, containing from 27·5 to 42 atomic per cents. of tin, that is, from 41 per cent. to 57·5 per cent. by weight. These, like the preceding, begin to solidify by forming the complex γ + liq (figs. 75 and 76), their state, when the G temperature is reached, being that of γ crystals of the *f* percentage and liquid of the G percentage. The isothermal transformation $\gamma = \eta$ + liq now commences, and completes itself abruptly with a heat evolution very well marked in the alloys near *f*. The alloys become perceptibly more liquid as the temperature falls,* and the microscope shows very well the change from the rounded, uniform γ combs to the complex of liquid between plates of η (figs. 73 and 74).

When an FG alloy has cooled below the G temperature the η continues to crystallise out of a liquid which is continually becoming richer in tin. This process goes on between the G temperature of about 630° and the H temperature of 400°. Below 400° the FG alloys follow the same course as the next group.

(8.) The GH alloys, containing from 42 to about 87·5 atomic per cents. of tin, that is, from 57·5 per cent. to 93 per cent. by weight. When these alloys begin to solidify they deposit plates of η, and this process continues until the liquid has the

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* This peculiarity was noticed during the operation of chilling the ingots: a little ingot of, say, Sn 28, chilled just above the G temperature, was not distorted by the sudden immersion in water employed to chill it, but a similar ingot chilled a little below G was converted into a mass resembling granulated zinc; this difference was observed more than once.

composition H and the temperature is 400°. At this temperature the η becomes less stable than the body H, and the reaction $\eta + \text{liq} = \gamma$ commences.

The reaction is closely analogous to that characteristic of the C point in the copper-rich alloys, and like it is a very slow one. The H at this temperature has a composition very near Sn 45; the η is still almost identical with Cu_3Sn. This reaction should complete itself isothermally until, for alloys to the left of H′ the liquid, and, for alloys to the right of H′, the η is wholly transformed. But as soon as the plates of η have become completely coated with H, the reaction, which is now a process of diffusion through the solid H, becomes extremely slow, and, with ordinary rates of cooling, it never reaches anything like completion. The result of this imperfect reaction is that the diagram contains four compartments in the space E_3SUH, in each of which one of the phases that are found would be absent if the equilibrium transformations had been completed. Professor Roozeboom has suggested the excellent plan of putting a bracket round the symbol of the phase that has no right to be present. We retain this notation because it indicates the ordinary condition of the alloys as most observers will find them; we have, however, succeeded, by maintaining the ingots for many days at a temperature a little below 400°, in completing the reactions and removing the third phase.

(9.) The HI alloys, containing from 87·5 to 98·3 atomic per cents. of tin, that is, from 93 per cent. to 99·1 per cent. by weight. In these alloys the solid first formed is H, and the diagram sufficiently explains itself.

(10.) The IK alloys, containing more than 98·3 atomic per cents. of tin. These alloys contain primary crystals of pure, or very nearly pure, tin in a eutectic made up of H and tin.

SECTION II.

On the Solidification of a Metal.

Our experience, and we believe it to be identical with that of most who have studied the subject, points to the comparative rarity of the formation of large crystals with plane faces during the solidification of a metal or alloy. The first solid structure is generally a crystal skeleton, which in its simplest form consists of a stem with radial branches projecting from it. This may be compared to a fir tree, and in many cases the branches are at right angles to the stem and to each other. Such a structure, when cut by a plane, gives rise to the fern-leaf or dendritic forms so often seen on the surface of cast metal, or in the etched and polished surface of a section of an ingot.

Let us think of the case in which such a crystal skeleton has been produced in an otherwise liquid mass of metal. As the branches give off what we may call twigs, and these may develop other systems of twigs, and so on indefinitely, it follows that from an original centre of crystallisation a uniformly oriented scaffolding may stretch out in three dimensions until it meets similar structures starting from other centres. The figures we give of an unchilled ingot of Sn 1, of the chill of Sn 6 at 966°, and of Sn 12 at 805°, all illustrate this process. If the centres of crystallisation were uniformly scattered through the liquid, and if the velocity of crystallisation were everywhere the same, we could predict the shape of the outer boundary of a crystal skeleton, but, as a rule, on account of unequal velocities of crystallisation, due to local temperature differences and other causes, the skeletons vary very much in size and shape. If the substance is a pure or nearly pure metal, or an alloy that solidifies to a uniform solid solution, the skeletons become solid by the thickening of the bars and the growth of new orders of twigs, and in the wholly solid ingot when cut and polished each skeleton is found to have given rise to a grain. The sections of the grains are irregular polygons, and, although the original skeleton can often no longer be detected in the polygon, yet a uniform orientation persists throughout a polygon and often causes it, when etched, to reflect light at a particular angle. Thus when parallel light falls on the surface, some polygons will appear dark and others bright, but each polygon will have a uniform degree of brightness throughout its area. The chill of Sn 2 at 957° (Plate 1, fig. 3A) shows skeletons which have grown until they almost fill the whole alloy. The same surface (fig. 3) when illuminated by oblique light, shows that there are several grains differently oriented.

If the substance contains an impurity, which is not isomorphous with the material first solidifying, this impurity will be principally found as an envelope round each grain, and in a section of an ingot it will appear as a slender network round the polygons. Some of this mother-substance must, however, from the peculiar skeletal manner of growth of the grains, exist in minute particles enclosed in the grains, though it may not always be possible to detect it. If there is very little impurity it may not form a complete network round the polygons, but only be found in isolated patches where three polygons meet. The chill of Sn 28 (fig. 73), and the unchilled Sn 6 (fig. 12), are good examples of this. If there is a good deal of impurity, so that the substance first crystallising ceases to form before the metal is solid, and if the remainder of the liquid produces an entirely different solid, then the original skeletons never fill up, and can be detected in the polished and etched sections. They then appear as fern-leaf markings, as gridirons, or as combs, distinguished by colour or by texture from the mother-substance that solidified at a later stage. The chill of Sn 9 at 777° (Plate 2, fig. 15) is a good example of the phenomenon, the pale skeletons being composed of a copper-rich substance which ceased to form some time before the whole mass was solid. It is surrounded by, and sharply divided from, the tin-rich matter, dark in the figure, which solidified later. The existence of such combs in an alloy often enables us to form a correct inference as to the material that solidified first, but we shall see in the course of this paper that it is not always safe to assume that the material of the fern-leaf or comb pattern was the first to solidify.

Most of what we have said above is a matter of very general knowledge to students of metals, but as the argument of the present paper depends largely on the interpretation of the patterns seen in the etched surfaces, we have thought it well to state the more obvious rules for interpreting such patterns. The uniformly oriented scaffolding or grain is by some writers called a "crystal." We, on the whole, prefer the term "grain," or the more descriptive term, "crystal skeleton." Crystals of considerable size, with plane faces, are sometimes found in alloys; one at least of the substances described in the present paper is found in such crystals; we have also seen them in alloys of aluminium with nickel or with platinum.*

The Development of Pattern.

When there is a difference between the chemical composition of the combs and the matter surrounding them the pattern can be developed in several ways. If there is a difference in hardness, one of the two materials will be etched out by polishing and a pattern formed in relief. The pattern thus obtained is often very well seen when the surface is examined with a lens, but in the CuSn alloys we have not found it suitable for microscopic examination or photography. A better method with all the bronzes ranging from pure copper to the alloy with 25 atomic per cents. of tin, is to heat the polished surface cautiously by laying it on an iron plate over a small flame. The copper-rich parts of the alloy then oxidise more rapidly than the tin-rich parts, the tints orange, red, blue, white, red and blue appearing in succession in such a way that the copper-rich parts are always a tint ahead of the tin-rich. Very splendid patterns are thus obtainable in the case of the ABC alloys, and the method is most valuable in determining the parts richest in copper. BEHRENS and STEAD have both drawn attention to the applicability of this method of heat oxidation in the study of the bronzes. The chilled alloys, however, are in an unstable condition, and we have sometimes found that the heat needed to bring out pattern by oxidation produced changes in the structure of a chilled alloy. It is, therefore, best to commence the examination of a chilled alloy by a chemical method of etching.

Many re-agents are available for etching, the most suitable for a particular alloy depending on the position of that alloy in the series. Ammonia readily attacks, dissolves and darkens the copper-rich α combs of the ABC alloys, leaving the remainder of the surface, as a rule, a dead ivory white, and where, as in unchilled alloys of the region CD, there is α, or a copper-rich phase resembling α, that also is attacked. A prolonged exposure to strong ammonia generally brings out a striation in the β; ammonia does not touch alloys containing more than 20 atomic per cents. of tin. Strong hydrochloric acid is similar in its action to ammonia on the alloys from

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* What has been said above as to the formation of crystal skeletons does not preclude the possibility of the phenomenon, observed by LEHMANN, QUINKE, and others, that the solid skeletons may be preceded by the separation of droplets of an unstable liquid phase; the highest chills of the DE alloys strongly suggest this (fig. 54). See also the note, p. 19.

A to D, attacking and dissolving the copper-rich parts. With more tin than 25 atomic per cents. the action of the acid is reversed, the tin-rich parts being dissolved and the η and H bodies not being touched until all the excess of tin has been removed. It is improved in its action by the addition of small quantities of an oxidising agent such as bromine or ferric chloride. But the latter re-agent often reverses the light and shade of the pattern by what appears to be an electrolytic deposit on the tin-rich material. Such complications are not, however, confusing if one examines the same alloy in succession in different ways.

In the case of the alloys discussed in the present paper the different ways of bringing out pattern confirm each other and leave not the slightest doubt as to which part of an alloy is tin-rich or copper-rich. We find that for photographic purposes an etch with a dilute solution of ferric chloride acidulated with hydrochloric acid has been most frequently successful. Its principal drawback is the conscientious way in which this solution develops every polishing scratch, however minute.

Preparation of the Ingots.

We prepared the little ingots containing from five to ten grammes of alloy in three ways. The simplest was to melt the weighed materials, or the previously made alloy, under charcoal and to allow the ingot to cool spontaneously in the crucible, which remained in the furnace until cold. Such a process of cooling is more rapid at high temperatures than at low, but there is no abrupt chill or change in the rate of cooling. We call these "unchilled ingots." In our experiments the ingots generally took from two to three hours in cooling. The alloys prepared thus may be said to be in the ordinary state in which previous workers have examined them. We soon found, however, that the patterns in these unchilled ingots were too complicated to admit of a satisfactory interpretation, inasmuch as the records of successive changes were superposed on each other in the same ingot. We therefore adopted the plan of allowing a small ingot to cool somewhat slowly to a selected temperature and then chilling it by withdrawal from the furnace and instantaneous immersion in water. We thus stereotyped the larger structures that had formed during the slow cooling previous to the chill, and although we did not always prevent the changes that were due at lower temperatures, yet the very short period of time available for them caused the corresponding detail to be, in most cases, very small and readily distinguishable from that formed before the chill. We call these "chilled ingots" or "chills," and speak, for example, of "the chill at 775°," the temperature being that to which the alloy had fallen in the furnace before its extraction for chilling.

These chilled alloys gave us much valuable information, but we found that some of the transformations, especially those of the C, D and H temperatures, required a period of at least some hours to complete themselves, and that the cooling antecedent to most of our chills had not in general been slow enough to allow of complete transformation. In fact, when the cooling is spontaneous, that is, brought about by extinguishing the gas and allowing the ingot to cool in the furnace, although the total time spent in cooling may be considerable, yet the rate of cooling at the higher temperatures will always be rapid. We therefore made a series of chills, preceded by a cooling which was very slow from the freezing-point of the alloy down to the moment of chilling. We took especial care to ensure that the time of cooling through a range of a few degrees above and below the critical point C or D should last several hours. In these chills, which we call "slow-cooled chills," and sometimes indicate by the letters "s.c.c.," the detail formed before the chill is naturally large and the transformations at the critical points are much more complete.* This slow and regular cooling was obtained by carefully regulating the gas pressure and at the same time slowly and automatically cutting off the supply. (The arrangements for the automatic reduction of the gas supply are described in a paper in the 'Journal of the Chemical Society,' 1898, p. 714.) Some of these slow coolings required watching for twenty-four hours, and we are much indebted to Mr. W. FEARNSIDES for carrying them out. They would have been impossible without a temperature recorder such as that of Professor CALLENDAR, which we employed.

On the Melting Point and the Rigidity of the Alloys at High Temperatures.

Although the photomicrographs of the successive chills of an alloy enable us to determine with considerable accuracy the temperature at which the crystalline phase fills the whole volume of the ingot, this method gives us no information as to the solidity or rigidity of the solid phase at high temperatures. For example, in Sn_2, chilled at 1025° (fig. 2, Plate 1), large primary combs of oriented and therefore crystalline substance certainly existed at the temperature of 1025°, and the chill at 957° (fig. 3) shows that the crystals at this temperature occupy almost the entire volume; but the question whether at such high temperatures the crystals are rigid, like ordinary crystals, or plastic like the so-called liquid crystals, must be attacked by other methods.† Our attempts to determine the melting-point, as distinguished from the freezing-point, though unsuccessful in their primary object, which was to prove that the solidus was identical with the melting-point curve, have established the great rigidity of the crystals, even at very high temperatures.

We attempted to find the melting-points by two different methods. The first method was to subject a little bar of alloy to transverse strain while it was gradually

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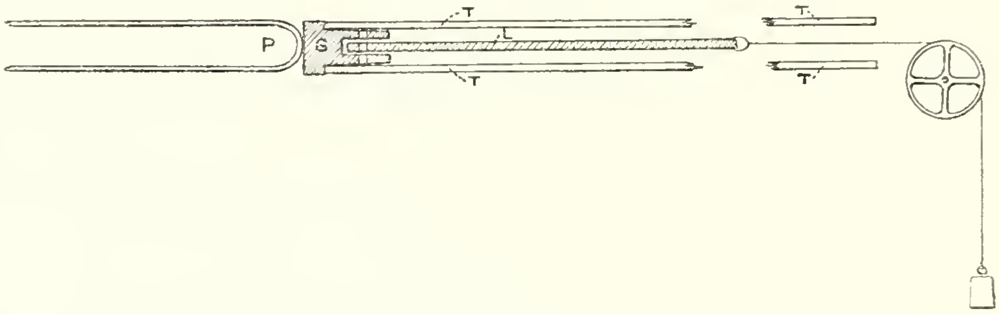
* When the cooling, before the chill, was exceptionally slow, the abbreviation v.s.c.c., for very slow cooled chill, is used.

† The rounded form of the lobes of the primary skeletons in many of the upper chills suggests the action of surface tension and therefore of some plasticity in the crystals, but the continual transformation undergone by a crystal of solid solution as it grows may account for the rounding without the assumption that the crystals are plastic.

heated to higher and higher temperatures, until finally it broke. The temperature was called the *breaking-point.*

The arrangement was as follows :—A porcelain tube, open at both ends, was fitted at one end with a cork or plug of soft graphite. (We are much indebted to Messrs. ALLBRIGHT and WILSON for their kindness in giving us a suitable sample of graphite.) The porcelain tube had a diameter of rather less than a centimetre, being identical



with the tubes containing the pyrometers. In the figure, G is the plug of graphite closing one end of the tube T. A saw-cut, about 2 millims. wide and a centimetre deep, was made longitudinally in the plug, and at right angles to the plane of the saw-cut a circular hole of about a millimetre in diameter was also drilled through the plug. A lath of graphite just fitting into the saw-cut, and with a corresponding hole drilled in it, passed along the axis of the porcelain tube. A little rod of the metal or alloy to be examined was fitted through the holes in the lath and the plug, as it were riveting them together. The lath and plug with the alloy were then fitted into the tube, and the tube introduced into a tubular electric furnace, and secured in that position. The outer end of the lath was connected with a string passing over a pulley and stretched by a 50-gramme weight, a transverse stress of definite amount being thus maintained on the rod of metal. A pyrometer P was pushed into the other end of the furnace, so that the end containing the coil was in contact with the outer end of the graphite plug, the end of the pyrometer and the plug being as nearly as possible in the middle of the furnace tube. The heating current was then started, and very slowly and automatically increased. By this arrangement the temperature of the rod of alloy was known at each moment and could be raised with any desired degree of slowness. Finally, the rod broke quite suddenly, the weight fell and started an electric alarm so that the breaking temperature might be noted.

The time occupied in heating the alloy up to its breaking temperature was three or four hours, or even longer. The graphite appeared to protect the metal perfectly against oxidation, and yet it burnt away so slowly that the same plug and lath were serviceable for several experiments.

In order to test the method we began by determining the breaking-points of pure metals. The following table gives the results. Column I. states the freezing-point, as determined by our pyrometers, and Column II. gives the breaking-point, as determined by the above method.

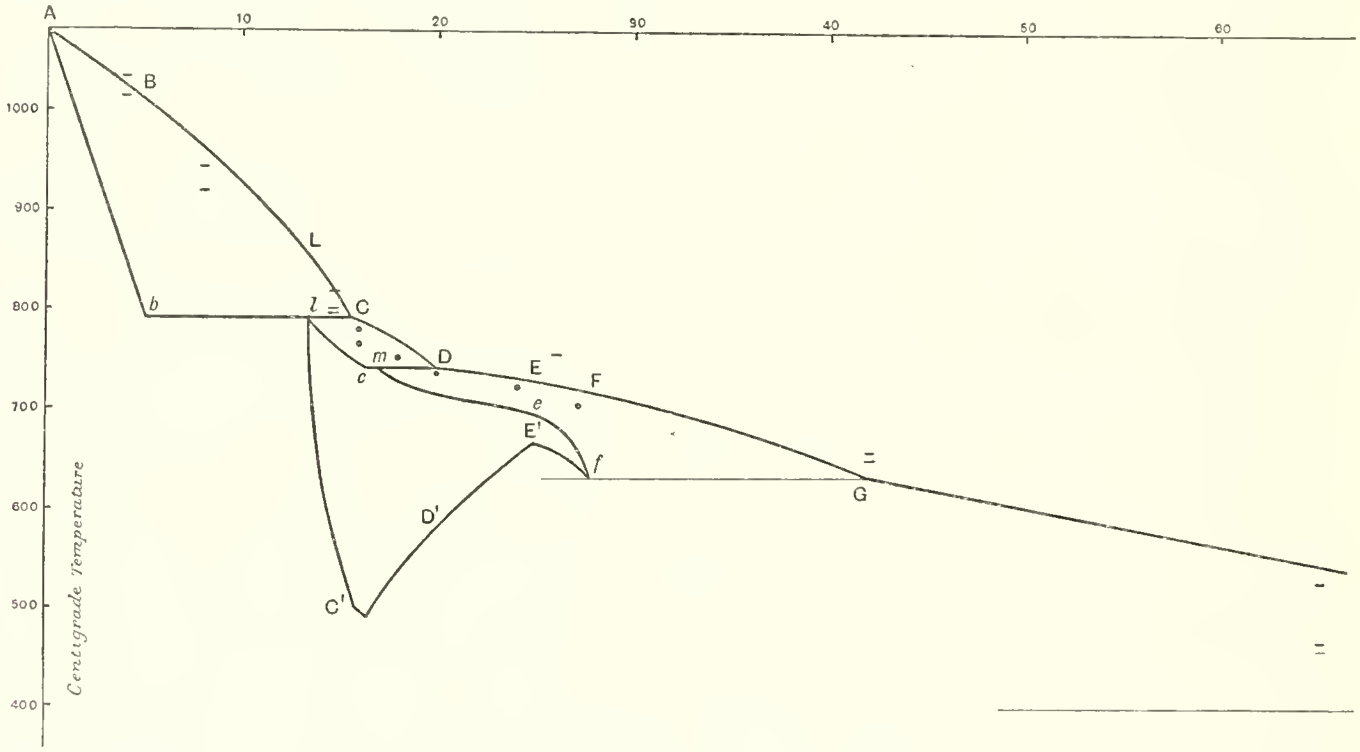
	Freezing-point.	Breaking-point.	Pull-out.
	°	°	°
Copper	1082	1084	—
Silver	961	972	—
	—	970	—
	—	969	—
	—	967	—
Aluminium	655	640	654
	—	637	654
	—	630	—
Magnesium	633	644	—
	—	650	—
	—	655	—
Antimony	630	—	630
	—	—	625
Zinc.	419	426	—
	—	426	—
Lead	327	—	332
Bismuth	266	—	272
Tin	232	—	235
		—	235

It will be seen from the table that, except in the case of aluminium, all the rods of metal broke at temperatures a little above the freezing-point. This peculiarity of aluminium is due to the fact that the metal has no constant temperature of solidification, but behaves more like a mixture than a pure substance.

The apparatus was withdrawn from the furnace as soon as the weight fell, and the residue of the rod was examined. As a rule the rod had completely melted into two or three round beads, but the rod of aluminium broke without melting.

The second method was a pull-out method similar to that employed by MEYER, RIDDLE and LAMB in the study of salts (' Ber.,' 1894, Jahrg. 27, p. 3129), and later by us ('Journ. Chem. Soc.,' 1895, p. 190). A Jena tube of about 5 millims. internal bore was sealed at one end and the end slightly enlarged into a bulb. A gramme or two of the metal or alloy was then melted in the tube so as to fill the little bulb, and, while the metal was still liquid, an iron wire was pushed into the metal so that the end was immersed. When the metal had solidified, the iron wire became firmly fixed in the metal, and on account of the bulbous shape of the end of the tube the ingot was also fixed in the tube. The tube was then placed vertically, so that the lower end containing the metal was immersed in a bath of molten tin. The upper end of the wire projecting out of the tube was connected with a string passing over a pulley and stretched as before by a 50-gramme weight. A pyrometer was placed in the bath of tin and the temperature slowly raised, until the wire was pulled out of the metal. We called this the "pull-out" temperature. In some cases the end of the iron wire was bent into a little hook before immersion in the metal, in other cases the end was straight; both gave the same results. The heating was not, as a rule, so slow as in the bar-breaking experiments, the time of heating not, as a rule, exceeding an hour. But in the case of Sn 27 a slow heating of several hours was tried ; it gave exactly the same pull-out temperature as a much more rapid heating had given.

The results for pure metals are stated in the third column of the table. They are in very fair agreement with the freezing-points. It is rather curious that the result for aluminium should be practically the same as the freezing-point. We then applied both methods to a few alloys. The results are shown below, the breaks by short horizontal lines, and the pull-outs by round dots. It is evident that the alloys remain practically rigid up to temperatures well above our solidus, indeed nearly up to the liquidus. We infer from these results that the alloy gives way, not when the eutectic, or other mother-substance, between the primary combs begins to melt, but at considerably higher temperatures, when a good deal of the primary has itself been dissolved. The skeleton crystals of the solid phase must form a sufficiently rigid framework to prevent the breaking of the bar, or even the pull-out, although they are surrounded by liquid. From the nature of the equilibrium in the region between the solidus and the liquidus it is quite conceivable that the rigid scaffolding might become more infusible by the draining away of the liquid from the bars. Thus the temperature we were measuring was necessarily indefinite, but depended more on the melting-point of the solid phase than on the commencement of liquefaction.



The experiments failed to throw any light on the position of the solidus, but they have proved that the skeletons of the solid phase are, even at the temperatures between the solidus and the liquidus, rigid structures and not plastic masses. This fact, together with the photographs which indicate when the solid phase fills the ingot, entitles us to say that *below the solidus Ablcmdef, as drawn by us, the alloys, though they may be at a bright red heat, are rigid solids. Hence any crystallisations taking place below the solidus occur in an already solid and crystalline body.*

SECTION III.

THE MICROSCOPIC STUDY OF THE ALLOYS.

Identification of the Substances as seen in the Photographs.

The α Material.—This is the only substance present in unchilled alloys of the AB group. It is best seen in chilled ingots, appearing in the form of isolated combs or skeletons in the chills taken above the solidus, for example, in figs. 2 and 3A, where it is the darker part, and in fig. 6, where it is the somewhat lighter part. The α also forms the primary crystallisation in the BL alloys, as in fig. 10, in which the α is dark, and fig. 11, in which it is the lighter part.

The rectangular network of raised crystals that covers the outside of the ingots of all the alloys from A to L is entirely composed of α. This network is evidently the substance that solidified first, from which the mother-liquid retired in consequence of contraction due either to cooling or solidification. Both in the raised network, and in such sections as that of figs. 10 and 28, one sees the very rectangular character of the skeletons; where the angle of intersection of two branches is not a right angle it is very frequently an angle of 60°, though for obvious reasons this cannot always be the case. It will be observed that in all ingots chilled above *b*C, or even a little lower, especially in the slowly cooled chills, the individual lobes are rounded; this is well seen in fig. 6. On the other hand, in the lower chills this roundness is absent, having been succeeded by an almost flamboyant angularity, well seen in fig. 22.

The α is much richer in copper than any other material found in the alloys; it is, consequently, softer than the tin-rich material surrounding it, and polishing alone develops the pattern. In the pattern thus obtained, the copper-rich α is red or yellow, and the tin-rich material is pure white. Prolonged polishing accentuates the pattern by oxidising the α to a deep red or purple, and in the method of developing the pattern by heat-oxidation, the α is always oxidised more rapidly than the surrounding material. Ammonia or hydrochloric acid attack, dissolve, and generally darken the α, leaving the tin-rich matter surrounding it a pure silvery white, as for example in fig. 3A. The acid solution of ferric chloride that we have used in etching the surfaces for the photographs we reproduce has a similar action on the alloys chilled well above *b*C, but when, as in the case of alloys chilled below this line the α is in contact with β, the α is paler than the β, this substance being often left very dark, as in figs. 15 and 16.

The α combs, at all events in ingots chilled below the solidus, often have another peculiarity; they are cored, that is to say, they contain an inner skeleton differing somewhat from the outer portions of the crystal. These cores oxidise more rapidly than the material outside them, and they are more rapidly attacked and darkened by such re-agents as ammonia. Hence they are evidently richer in copper than the outer parts of the crystals. The most striking and certain way of developing cores is to take a polished surface of an ingot of Sn 5 that has not been chilled nor very slowly cooled, and to heat-oxidise it. Oxidation through orange, red, blue to the white stage may not develop much pattern, the α combs, which up to Sn 6 almost entirely fill the field, remaining of a flat tint; but when the white stage is reached, the outlines of the combs may be here and there marked by a trace of mother-substance which has remained an indigo blue. If, however, we proceed to heat further, a pattern of deep red or blue cores will develop itself, while the surrounding α, probably three-fourths of the area, remains white. This colour combination does not photograph well, but we sometimes get the core pattern with the first orange, in which case it can be photographed. We show the effect in the photograph of the unchilled Sn 1 (fig. 1).

As visible in unchilled alloys, these cores have been described by STEAD and by CHARPY. The cores are not divided from the substance outside them by a sharp line, but by a blurred or graded zone, so that under a high power there seems to be no boundary at all. Herein the cores differ from the α combs, the margin of which, whenever visible, is a sharp line even under the highest powers. The v.s.c. chill of Sn 4 at 775°, fig. 8, shows the character of the cores. They are only seen in the ABL alloys, and in the AB group they can, by slow cooling, be made very faint, or by rapid cooling very well marked. A decidedly slowly cooled ingot of Sn 4, chilled at 800° and etched with HCl, fig. 5A, shows the complete α combs with sharp margins, but the darker cores, due to the earlier α, are also evident. These developed in the interval of time between etching and photographing, and are due to the more rapid air-oxidation of the copper-rich parts. This ingot was not cooled with the extreme slowness of that of fig. 7, hence a few dark spaces can be found that may have been due to a trace of mother-substance liquid at the moment of chilling.

When the cores have been developed by etching, their intensity depends very much on the nature of the etch and on the time that has elapsed between the etch and the examination; for example, the s.c. chill of Sn 6 at 805° can be so treated as to show well-marked cores or none. We must conclude, therefore, that though the presence of cores indicates some difference of composition, yet the intensity of the visible core cannot be taken as a measure of the difference in composition existing between it and the matter outside it.

The β Material.—This is always considerably richer in tin than the α, hence when both substances are present it is easy to distinguish them. This can be done by heat-oxidation when the α oxidises first, by etching with strong ammonia when the α is darkened and dissolved and the β left a pure ivory white, or by etching with acid ferric chloride. Ferric chloride, the re-agent we almost invariably employ in preparing the surfaces for photography, acts on a mixture of α and β in such a way as to darken the β and to leave the α bright; this effect is well seen in figs. 15, 16, and 31 (Plates 2 and 3). But there are cases, especially where β and α occur together, in which the β has undergone, during and after the chill, a change into an apparently fibrous condition which gives it a structure like that of asbestos, except that in the β there are several intersecting systems of fibres. This is well seen in fig. 21. When this change has become very pronounced in the β, ferric chloride does not produce so marked a contrast between the shade of the two materials, though, as the α is never striated, we have in this peculiarity another distinction between the two. In the chills of Sn 16 and Sn 17, chilled between the liquidus and the solidus, in which case α is absent and the β combs are embedded in a tin-rich mother-substance, the β is darkened by etching or ignition, and is rarely striated, while the tin-rich mother-substance remains a pure white.

The γ Mixed Crystals.—These occur as the primary crystallisation in all the DEFG alloys, provided they are chilled above the line *cdef*G. The γ combs are distinguished from the preceding by a well marked obliquity; instead of gridirons, they resemble sprays of foliage with rounded leaves. Heat-oxidation fails in this region, but HCl, with or without an oxidising agent, darkens the ground and leaves the γ combs pure ivory white (see Sn 38, fig. 79). The γ material is never found in unchilled alloys, for in cooling below the G temperature it breaks up into η and liquid.

The δ Material.—This substance, which we are strongly disposed to regard as the compound Cu_4Sn, occurs as the white tin-rich ingredient of the eutectic in all the BLCD alloys, provided they are unchilled or chilled below 500° (fig. 19). It also occurs in larger masses as a rosette or fern-leaf and in bars in the CD alloys, provided they were not chilled above the line C′D′ (fig. 49A). In all these alloys heat-oxidation leaves the substance δ white when the copper-rich α present has turned to a deep brown, but a better contrast is obtained by etching with HCl, when the α is blackened and eaten away and the δ left untouched in the purest white. Ammonia has no action on this substance.

The η Material.—This occurs mixed with δ in the DE alloys when they have been chilled below the line D′E′. We believe it to be in general the compound Cu_3Sn. When in presence of δ the η can be distinguished by heat-oxidation, under which treatment the invariable rule holds good that the copper-rich δ oxidises and darkens faster than the tin-rich η, we thus get a pattern in which the η is white and the δ dark brown. But for photography a sharper result is obtained by etching with a mixture of HCl and $FeCl_3$, when the η is blackened and the δ remains white (fig. 56).

In alloys containing more than 25 atomic per cents. of tin, at all events those chilled above 400°, the η is unattacked by etching re-agents, while the more tin-rich matter surrounding the η is eaten away and darkened. The η rarely forms crystal skeletons, but occurs in plates which are crystals bounded by plane faces; this is particularly well seen in the GH alloys, as in these the η has crystallised out of a liquid. If, however, these alloys are unchilled, or chilled below 400°, the η crystals are coated with H, as a result of the imperfectly accomplished transformation

η + liquid = H. Etching with HCl leaves such an alloy at first with the η and H both pure white and the mother-substance dark, but in time the η darkens through oxidation, while the border of H remains of the purest white. There is thus no difficulty in distinguishing the two substances (fig. 92).

The H *Material.*—This substance appears to resist completely the action of even the strongest HCl, or of mixtures of the acid with ferric chloride. It also resists the slow oxidising action of the air much better than η, remaining a very pure white for days or months. We find it bordering the η, as in the lower chills of Sn 29, in round or oval spots, as in the prolonged mercury-boiled ingots of Sn 50, and in definite crystalline shape in chills of Sn 90 (fig. 89).

The Evidence from the Microscopic Structure of the Chilled Alloys.

The AB *Alloys.*—As will be seen in the cooling curve of Sn 4, these alloys present but one halt in their cooling curves, so that, as far as such evidence can be trusted, they appear to solidify in one continuous process; we hope that the micro-photographs will be found to confirm this view. It is evident that if Sn 2 and Sn 4 both solidify in this manner, then the solid in these alloys cannot be a pure body, but must be a solid solution.

Sn 1. 1·85 *per cent. by weight of tin* (Plate 1, fig 1).

In unchilled and moderately slowly cooled ingots polishing, even without etching or ignition, brings out a pattern of long slender combs well seen with a power of 10 diameters. This pattern is probably due to the more rapid oxidation of the first formed α, which was very rich in copper. Heat-oxidation develops the same combs, which do not fill more than three-quarters of the area. The lobes of a comb are not isolated, but form a continuous skeleton. In every case a higher magnification makes it evident that these combs are not sharply divided from the material round them, but fade softly into it. In fact, the margin of a comb does not mark an abrupt change in the process of crystallisation. This important point became very evident in a section etched electrolytically by being made the anode in a cell containing dilute sulphuric acid. This method of etching revealed the margins of the real skeleton crystals. They have sharp edges, and occupy at least 99 per cent. of the area. It is thus evident that the combs brought out by polishing or ignition, as seen in fig. 1, are cores to the real skeletons of α, these latter being so closely packed that it is only here and there that we can detect their boundaries. Thus, in spite of the fact that the cores are somewhat richer in copper than the outside layers, we feel justified in stating that the alloy solidified in one continuous process. Moreover, the cavities between the real margins of the combs show that these combs, which so nearly fill the field, are primary, that is to say, were formed *during* the process of solidification, the small cavities being caused by the presence of gas or by the retirement of the mother-liquid during the contraction accompanying solidification. The coreing is evidently due to imperfect adjustment of the α to the liquid, a result likely to occur during the solidification of a solid solution, and is a strong confirmation of the view that the α crystals vary in composition.

The chills of Sn 2. 3·67 *per cent. by weight of tin.*

Chills were taken at the following temperatures:—1025°, 982°, 957°, 932°, 907°, 882°, 800°, 770°; all but the first of these were very slowly cooled before the chill.

The upper chill was not cooled with any precautions to ensure slow cooling, being allowed to cool in the furnace after the gas had been extinguished, but the others were very slowly cooled from the freezing-point down to the moment of chilling. The total time required for an ingot to cool from the freezing-point down to 770° was eight or ten hours, and for the upper chills the times were proportionately less.

Sn 2. *Chilled at* 1025° (Plate 1, fig. 2).

The ingot was compact, but showed some signs of granulation, on account of its semi-liquid state at the moment of chilling. It was cut in two, polished and etched with ferric chloride, but the pattern was well seen after the polish. It consists of copper-rich α combs, dark in the figure. These sometimes stretch half across the face of the ingot and are well seen under a magnification of 5 diameters. They fill about one-third of the area, and their margins are sharply divided from the mother-substance round them. They are primary crystals, the matter which was already solid at the time of chilling. The material of these combs appears to be uniform throughout, it being impossible to develop cores in them. The magnification of the photograph is too high to show the great symmetry and length of the combs, but it makes it just possible to distinguish the network of much smaller combs in the ground. These are rectangular, and in all respects except size resemble the large combs. They are evidently chill primary, that is, α which crystallised *during* the rapid cooling of the chill. In the interstices between both sets of combs there is a small amount of a quite different material. This is the true mother-substance, a white tin-rich body that solidified last of all.

Sn 2. *Chill at* 982° (not reproduced).

This was cooled very slowly down to the moment of chilling. Like all which follow, it was a compact ingot completely covered externally with a rectangular network of α combs in relief. It was cut and polished. Prolonged polishing develops an oxidation pattern of large plump copper-rich α combs, filling at least nine-tenths of the area. These show no cores. They are surrounded by a network of a white tin-rich mother-substance, containing minute copper-rich chill primary.

The growth of the large combs, which now so nearly fill the field, shows that the process of solidification has made great progress since the previous chill, but the minute combs of chill primary are an evidence that the crystallisation of the α was not quite complete.

Sn 2. *Chilled at* 957° (fig. 3A and fig. 3).

The surface, when examined under the usual normal illumination, was full of uniformly dark α combs in a slender network of pure white. It is evident that before the moment of chilling the solid α had grown until it almost filled the ingot. No cores can be detected (fig. 3A). The photograph we reproduce, in fig. 3, was taken with oblique illumination in order to show the differences in orientation that exist in the different grains, or filled-out skeletons, that make up the ingot. A change in the direction of the incident light would have completely altered the disposition of light and shade. By this method of illumination the mother-substance, which does not scatter much light, is less evident. The three figures, 2, 3, and 3A, taken together, illustrate excellently the growth of a granular solid from skeletons. Figs. 3 and 3A are photographs of the same portion of the surface of the ingot.

Sn 2. *Chilled at* 932° (not reproduced).

As usual in this group of alloys, the white substance between the combs becomes visible by polishing alone. HCl turns the combs a rich copper colour and leaves the mother-substance white. It is now present in smaller amount, not in a continuous network, but as rows of isolated dots and short lines, and in the three-branched patches to be found where three lobes of α meet. The amount of mother-substance was estimated by counting the squares of a ruled grating. Several independent determinations gave values between 2 and 3 per cent. for the fraction of the whole area occupied by this white mother-substance. A higher power still shows the merest trace of chill primary. The α combs must be very uniform, for a prolonged polish leaves them a uniform purple, and by no method of etching can cores be developed in them. It may be mentioned here that a slowly cooled chill at 940° was heat-oxidised to the second series of tints, but at no tint did any trace of cores appear. This is the most severe test of homogeneity in the α that we know of.

Sn 2. *Chill at* 907° (not reproduced).

The whole section of the ingot is similarly oriented, and it evidently consists of one crystal. We can now see cores in the α.

Sn 2. *Chill at* 882° (fig. 4).

In this ingot the specks of tin-rich mother-substance are reduced to much less than half a per cent. of the whole area. Our photograph shows a very uniform surface almost free from cores, but some weeks after etching, large faint cores were found to have developed, so that the α is not absolutely uniform.

However, it appears evident that, with a very little allowance for lag in the transformations due to too rapid a cooling, we are entitled to say that from a chemical point of view the alloy Sn 2 solidifies to a completely uniform solid at a temperature near 900°. The resulting solid must therefore be a solid solution, or, what is the same thing, an isomorphous crystalline mixture of copper and tin, or of copper and some compound of the two metals. The process of solidification revealed by these chills, in which the solid phase differs considerably in tin content from the liquid phase, but gradually absorbs it, is an exact verification of ROOZEBOOM'S theory; we must infer that the α combs seen at the various stages of the solidification are all solid solutions.

The absence of cores in the higher chills must be interpreted as indicating that the adjustment between the successive solid and liquid phases was, at these high temperatures, a fairly perfect one, but it is not improbable that, with still slower cooling, the mother-substance would have disappeared at a somewhat higher temperature. It is obvious that while each α crystal is bathed on all sides by mother-substance, it will be favourably situated for maintaining its uniformity by diffusion from the margin to the centre; but when the solidification has so far progressed that the crystals touch each other over a great part of their surface, the remaining drops of mother-liquid will be very liable to react with the margins only of the large combs, and to leave the cores of the crystals unduly rich in copper. This retardation will also have as a result that the complete solidification of the alloy will occur at an unduly low temperature. We shall find examples of this later on in spite of all our efforts to attain perfect equilibrium by slow cooling.

Sn 2. *V.s.c. chill at* 800° (not reproduced).

This is a beautifully uniform alloy. There is no mother-substance. The polished and etched surface contains two patches belonging to two crystals, distinguished by reflecting light differently. These two touch along a continuous line without a trace of mother-substance between them. We have here a very good proof of the solid solution theory, for otherwise, what has become of the tin-rich matter? However, when freshly etched with HCl, a lens shows large cores differing very little from the rest of the matter round them, so that the process referred to above has occurred. These cores are lost under the microscope.

Sn 2. *V.s.c. chill at* 770° (fig. 5).

This consists of two or three homogeneous grains of α, fitting closely together without mother-substance. There is a trace of vague coreing.* We do not reproduce

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* The striations visible in the lighter grains of α in fig. 5 are due to scratches, which are almost inevitable in polishing this very soft material.

the chills at 800° and those below 770°, as the characters of a uniform solid solution are more conclusively exhibited by Sn 4.

The unchilled very slowly cooled ingot (not reproduced).

This ingot was examined to ascertain if Sn 2 underwent any changes in the solid when cooled below the *b*C line. The polished surface, after etching, consists of several irregular rounded polygons, dovetailing into each other without a trace of mother-substance. These show the rotation effect. There is little or no indication of cores.

Sn 4. 7·2 *per cent. of tin by weight.*

This alloy, containing about 7 per cent. of tin, affords a more striking example of solid solution than the preceding.

Sn 4. *Chilled at* 990° (not reproduced).

The ingot was granulated by the operation of chilling, but it was possible to polish a good face on it. It contained the same pattern as the highest chill of Sn 2, that is, large primary combs of α, filling perhaps a quarter of the area, a good deal of chill primary, and a small amount of white mother-substance. It is clear that the large α combs were the only parts solid before the chill. As this closely resembles the upper chill of Sn 2, we do not reproduce it.

Very slow-cooled chills were made at the following temperatures:—900°, 835°, 775°, 700°, and one ingot was slowly cooled down to the melting-point of tin. All these proved to be compact ingots, and were completely covered with a raised network of rectangular α combs. Besides these, other ingots were chilled after a somewhat more rapid, but still a slow cooling.

Sn. 4. *The chill at* 900° (fig. 6).

This contained large almost coreless α combs, filling about 90 per cent. of the area; in the interstices between the large combs there is a very beautiful crop of chill primary embedded in a little of a tin-rich mother-substance, but a higher magnification is needed to show the chill primary. At the time the photograph was taken the α, though much more oxidised than the ground, was blue and hence actinically active. Consequently the contrast between the two materials is weak and reversed in the photograph.

Sn. 4. *Chill at* 835° (not reproduced).

This contains very little, not more than 1 per cent., of mother-substance, and the α combs are so fused together that their margins cannot in general be distinguished, except by the different grains reflecting light differently. The α is not, however, homogeneous, for after a time a pattern develops on the etched surface consisting of dark copper-rich combs. These are similarly oriented throughout a grain and are not separated from the α outside them by a sharp margin. They are evidently cores produced by the imperfect assimilation of the last drops of liquid. The appearance of this chill leads us to think that Sn 4 is completely solid at all temperatures below 830°. Thus the microscopic examination of chills of Sn 2 and 4 gives us, at all events approximately, two points on the solidus Ab.

V.s.c. chill at 800° (fig. 7).

This contains no tin-rich mother-substance (an estimate made the amount less than one-tenth per cent.), but no ingot was obtained free from cores, although in the most perfectly slowly cooled ingot, which we reproduce in fig. 7, these cores can barely be detected. In order to show the character of the coreing in the α combs, we give in fig. 5A a photograph of an ingot, also chilled at 800°, after a cooling that was slow, but not quite so slow as that of fig. 7. The combs have grown so as to form three grains reflecting light differently, but in two of the grains there are well-marked copper-rich cores. The difference between the soft indefinite boundaries of the cores and the sharp margins of the combs is characteristic. The very dark angular spaces between the combs were cavities from which the mother-substance had receded during the cooling.

Sn 4. *Chill at* 775° (fig. 8).

In the best slowly cooled chills there is no mother-substance, the patches that represent separate α crystals dovetailing into each other with no interstitial matter. But even in the most slowly cooled ingots there are cores in the α, and in ingots rather more rapidly cooled there is a complete pattern of such cores. Even in the presence of cores, if the cooling before the chill has been at all slow, there is extremely little of the tin-rich mother-substance. The photograph we give closely corresponds to the above description.

Sn. 4. *Unchilled* (fig. 9).

The ingot fig. 9, cooled slowly down to the melting-point of tin, is important, as it is quite free from the brilliant white tin-rich patches of the C′ complex that form such a well marked feature in the Sn 6 similarly treated. This slow-cooled Sn 4 shows no cores, and consists of several patches fitting closely together and only distinguishable by the different angles at which they reflect light. The small black spots, a millimetre or two across, seen in the photograph are holes in the alloy. This photograph closely resembles photographs of pure platinum and pure gold that have been published by Mr. ANDREWS and others. We thus see that the whole of the 7 per cent. of tin has been absorbed into the α.

We think that we have demonstrated that the condition of this solid alloy, provided that it has been cooled so slowly that the solid and liquid phases have always remained in equilibrium, is finally that of a uniform solid solution. This uniformity is no doubt rarely attained in practice, a not specially slow-cooled chill at 740° (not reproduced) more nearly representing the usual state of an ingot soon after solidification. In this there is a complete pattern of cores forming combs about the size of those on the outside of the ingot, and evidently coincident with them. These merge into another material, which is later formed, α. Finally, sharply divided from all the α, there is a very perceptible amount of mother-substance, which, however, was solid at the moment of chilling. Owing to the action of the ferric chloride etch this mother-substance, which is β, has become black. It has, strictly speaking, no right to be present in an alloy of the AB group, but is the result of imperfect transformations. Thus we see that the soft bronzes of the AB group, unless very slowly cooled, are likely to be non-homogeneous in two complementary ways—the α grains may be cored with a material richer in copper than the mean of the alloy, and between the grains there may be a little of a hard, brittle tin-rich substance.

Repeated rolling and annealing at a sufficiently high temperature ought to bring about a re-action between the cores and the tin-rich substance, and so promote a real chemical homogeneity which would be impossible in the alloys with more tin. The indication of the cooling curve that these alloys solidify by one continuous process is, as we have shown, confirmed by the microscope.

The BL *Alloys.*—These alloys show at least two halts in their cooling curves, the first at the freezing-point, the second at 790°, the temperature of the line *bl*C, a halt common to all the group.

We now observe a different final structure, however slow the cooling may have been. In the slowly cooled and unchilled alloys the α combs no longer fill the whole area, but are surrounded by a new type of mother-substance, the complex C′. This is well seen in the photograph of the slow-cooled Sn 6 (fig. 12), where the angular patches of pure white are derived from a tin-rich material that was left liquid at the termination of the α crystallisation.

Ingots of Sn 6, chilled above the C temperature, that is, above 790°, resemble the corresponding chills of Sn 4 in containing large primary combs of α surrounded by chill primary, the whole being imbedded in a tin-rich matrix. The chill at 966°, fig. 10, is a fine example of this structure. Here the large α combs are remarkable for a great rectangular symmetry, and are quite free from cores. The ingot was not specially slow-cooled.

Sn 6. *V.s.c. chill at* 805° (fig. 11).

This has large combs of primary α and at least 10 per cent. of mother-substance containing chill primary, the whole of this 10 per cent. having been liquid at the moment of the chill. This should be compared with the chill of Sn 4 at 800°, in which there is practically no mother-substance. The α in the chill of Sn 6 is remarkable for the deep cores that appear in the combs some time after etching, although in the figure we reproduce, which was put for a moment on the polishing wheel after etching for the purpose of simplifying the pattern, no cores are visible, and the combs are, on the whole, lighter than the mother-substance.

Sn 6. *S.c. chill at* 775° (not reproduced).

This shows about as much mother-substance as the preceding, but this mother-substance is now β, which had solidified at the C temperature and is consequently darkened by the $FeCl_3$ etch.

Sn 6. *Unchilled, v.s.c.* (fig. 12).

This ingot affords the most striking evidence that Sn 6, when solid, is a complex. Here, in the slow cooling through the C′ temperature of 500°, the small amount of β between the α crystals has broken up into the C′ complex of $\alpha + \delta$. As the white δ is predominant in these patches, they appear after the ferric chloride etch as a very brilliant white, while the α is darkened. The plate shows two large crystals of α differently oriented, and, therefore, reflecting light differently. Inclosed in them, in the form of the usual very angular patches of a scanty matrix, are several per cent. of the white body. (The striations in the lighter grain of α are due to imperfect polishing.)

In order to show the character of the C′ complex, we give a more highly magnified patch of this mother-substance taken from the same ingot (fig. 13). Here it is evident that the patch is margined by a homogeneous band of the white δ, but that inside this border the δ is mixed with lines and spots of a darker substance, which proves on examination with an immersion lens to be identical with the α surrounding the patch. *As the slow-cooled* Sn 4 *contains only* α, *while* Sn 6 *has several per cent. of this complex, we have placed the boundary between the two groups at* Sn 5.

Sn 6 may be regarded as the first of the BL group of alloys, the harder gun-metals, which when solid are a complex of two phases; but with increasing content of tin, as in Sn 9, the characteristic features of the group show themselves more plainly, the α decreasing in amount, and there being a corresponding growth of β or, in the lower chills, of the C′ complex, and therefore of δ.

Sn 9. 15·6 *per cent. of tin. Chill at* 880° (fig. 14).

This was a very much granulated ingot, the result of throwing the semi-liquid alloy into water being to blow away the still liquid part and to leave the skeleton crystals of α as a mass of little fir trees. A portion solid enough to grind down and polish was found with difficulty. A section etched with $FeCl_3$ is reproduced. The magnification is too high to show the large α combs well, but individual lobes are seen lighter than the ground. The section contains rounded α combs filling rather less than half the area, and immersed in the mother-substance are the minute combs, also of α, that were formed during the chill. On heat-oxidation the large combs turn red more rapidly than the minute ones, presumably because the large ones are richer in copper. It can be seen that the minute combs sometimes grow out from the margin of the large ones. We have here a very good example of the result of chilling a semi-liquid alloy.

Sn 9. *Slow-cooled chill at* 805° (not reproduced).

This chill shows very large and symmetrical primary combs of α, but their area is much less than in the corresponding chill of Sn 6. A ferric chloride etch leaves the α combs bright and darkens the mother-substance, but in the heart of each patch of mother-substance there is often an irregular line of pure white, which a high power shows to be a final tin-rich residue, the last matter to solidify. The alloy gives one the impression of having been chilled rather below the intended temperature. The rounded character of the lobes or teeth of the combs is noticeable.

Sn 9. *Slow-cooled chill at* 775° (not reproduced).

In the interval of several hours that elapsed between this chill and the preceding the re-action α + liquid = β has been going on, the original α combs have been much modified and somewhat diminished in amount, and the surrounding β shows the characteristic striation pattern. We do not give photographs of these two ingots, because the important change produced in the alloys by the C re-action is better seen in such an alloy as Sn 12.

We give, however, in fig. 15, a ferric chloride etch of an alloy not quite so slowly cooled and chilled at 777°. This is a typical example of a ferric chloride etch of an α and β complex, the α combs being light and the β dark. In the heart of the β one can see threads of a white tin-rich material that must have been liquid at the moment of chilling. The presence even of this minute amount of liquid at 777° is a result of a somewhat too rapid passage through the C temperature. Polishing this and similar alloys without etching leaves the α a bright copper colour and the β a pure tin white, and a strong ammonia etch has the same effect, but for photographic purposes we prefer the effect of ferric chloride. The β in this ingot does not show striation, it is apparently uniform.

Sn 9. *V.s.c. chill at* 546° (figs. 16 and 18).

All the chills down to above 500°, for example that at 546° (fig. 16), are like the above, and if there is any growth of α in the solid alloys, it is not enough to be detected, except, perhaps, by an increasing angularity in the margins of the combs. Moreover, the action of ferric chloride on all these alloys is the same, the α remains bright and the β is turned dark, but seems to remain homogeneous. But at 500° the β breaks up into the C′ complex of $\alpha + \delta$, and the action of the ferric chloride is reversed, as it now darkens the α and leaves the δ a pure white.

Sn 9. *V.s.c. chill at* 470° (figs. 17 and 19).

We here see the transformation, the α has become dark and the β has broken up into a pearlite or solid eutectic. As this transformation is common to all alloys containing β when they cool slowly through the C′ temperature of 500°, we give in fig. 18 a more highly magnified patch of β from an ingot of Sn 9, very slowly cooled to 546° and then chilled. It will be seen that although there is a narrow line of white, probably δ, separating the α and the enclosed patch of β, yet the latter is patternless and, as usual with a ferric chloride etch, darker than the α surrounding it. This should be contrasted with the patch of the C′ complex taken from the alloy chilled at 470° and also etched with ferric chloride, fig. 19. Here we see that the border of δ has become very wide and that the interior of what was the patch of β has broken up into a complex of δ and a copper-rich body which so closely resembles α that we give it the same name. These two photographs were both taken at a magnification of 280 diameters.

This transformation $\beta = \alpha + \delta$ is an exothermic one, and gives rise to the halt in the cooling curve that we first see in our cooling curve of Sn 10 at 500°, though, as we have shown (fig. 13), the same transformation can be detected by the microscope even in Sn 6. In fact, this change of solid β into a complex occurs at or a little below 500° in all alloys from Sn 6 to Sn 20. It is marked in our diagram (Plate 11) by the broken line $b'C'XD_2$. It must be borne in mind that at this temperature the alloys are rigid solids.

Sn 12. 20·3 *per cent. by weight of tin.*

The solidification of this alloy begins, as in the cases already discussed, by the crystallisation of α combs, but when these cease to form, on account of the residual liquid having reached the C composition, there is much more of the liquid than in the case of Sn 9, and hence the *re-solution* of the α during the transformation at the C temperature is more marked. This is well seen in the cooling curve of Sn 12, in which the C halt is a prolonged one, but it is made evident in another way by an examination of the ferric chloride etch of the v.s.c. chills at 805° and 775° (figs. 20 and 21). The first of these shows us the maximum possible amount for this alloy, of primary α, and also a minute dark chill primary which is probably β. The lower chill, made after a very slow cooling of several hours through the intervening 30°, shows much less α, and what is left has a disjointed look, as if the combs had been subjected to the action of a solvent (fig. 21). Moreover, the ground has entirely changed, being now full of the striation characteristic of β. We may regard the s.c. chill at 775° as giving the minimum proportion of α to be found in this alloy, for as the temperature falls from C to C′, that is, from 790° to 500°, the α grows in amount at the expense of the solid β. The alloy chilled at 550° and etched with ferric chloride, fig. 22, illustrates this growth of the α out of a solid solution. This particular ingot was not cooled before the chill so slowly as were the preceding, and therefore the detail is somewhat smaller, but the ratio of the white α to the darker β has evidently increased enormously, being greater than in the chill at 805°. The peculiarly pointed and flamboyant character of the α which has grown out of the solid β should be compared with the rounded lobes of the α combs in the chill at 805°. The general character of the pattern in the chill at 550° resembles that in an unchilled alloy, except that the unchilled alloy, or one chilled below 500°, would, with the same etch, have the α dark and the ground a brilliant white. The ground, moreover, in the chill at 550° is uniform β, but in the unchilled alloy it would be the C′ complex.

Sn 13·5. 22·5 *per cent. by weight.*

This alloy is important, because it fixes the point l at which the amount of α formed above the C temperature is just enough to re-act with the whole of the residual C liquid in order to form β; in fact, the re-action $\alpha_l + \text{liquid}_C = \beta_l$ can complete itself in this alloy.

Sn 13·5. *S.c. chill at* 805°.

This has less α than the chill at the same temperature of Sn 12, but otherwise it closely resembles it; hence we do not give a photograph.

Sn 13·5. *Chills at* 775°.

If an ingot of Sn 13·5 be cooled very slowly through the C temperature, so as to be maintained for several hours at or very near 790°, the α is entirely dissolved and we obtain an ingot composed wholly of β. In the photograph (fig. 23) one can see a single minute spot of α that has survived, and is paler than the β. But this β, after chilling and etching with ferric chloride, has the well marked striation pattern. Considerable light is thrown on the transformation of the α into β by the examination of some ingots which were cooled somewhat too rapidly through the transformation point to allow of a complete solution of the α. A chill at 765°, etched with ferric chloride (fig. 24), shows the effect well—there is still a little α in slender combs and crosses, and these, though isolated from each other, are so symmetrically arranged as to make it evident that they once belonged to larger skeletons. Round these, and enveloping them symmetrically, is a complete system of fat rounded combs of β, which sometimes stretch right across the surface. Outside this β there is matter that we must suppose was not solid at the moment of chilling. The photograph does not show striation in the β, but a somewhat deeper etch and a higher power brings out the striation perfectly. A photograph (fig. 25) at 45 diameters shows the striated β round the lobes of α, as well as the tin-rich material outside the β, material that was liquid at the moment of chilling. One can also see in one corner something which looks very like chill primary of β. The enormous growth of the α out of the solid β at lower temperatures can be best illustrated by the two following photographs, both at the same magnification. The first is a chill at 740° (fig. 26), that was not slowly cooled enough to dissolve quite all the α, a very little of which can still be seen in slender lines and rows of dots. It must be remembered that even this could have been dissolved by a slower passage through the C temperature. Contrast this with the other, a chill at 558°. In this (fig. 27) the enormous increase in the α and the jagged appearance of the crystals are well marked. There is no doubt that this growth of α took place in a rigid solid.

It will be noticed that in the chill at 558° there is no residue of the striation effect so marked in the very slow-cooled chill at 775°. This is one reason why we think that the striation does not exist in the β until it has cooled below 500°. We think that as the chilling alloy cools rapidly through 500° a partial breaking up of the β sometimes occurs and shows itself in the striation pattern. The two phases into which the β breaks up through the imperfection of the chill may not, however, differ so much in composition from each other as do the α and δ of the slowly cooled C′ complex, for ignition which readily distinguishes between α and δ does not readily bring out the striation even when we know it to be on a large scale. Another point is that the striation does not show itself in the chilled β of Sn 16 or 17, which has never been in contact with a nucleus of α. Under such circumstances we suppose that the state of supersaturation is more easily maintained. This view that the striation does not appear in the β until it has cooled down to 500° is of some importance, as otherwise we are hardly entitled to speak of β as a uniform solid solution. Another argument is that now and then we find a chill containing unstriated β, for example the patch of β of Sn 9 chilled at 546° and shown magnified 280 diameters. This is quite free from striation, as are all the other patches in the section (fig. 18).

The very symmetrical way in which the β grows round the α (see fig. 24) during the α + liquid = β reaction, suggests the view that the two bodies may be isomorphous. Moreover, the primary combs of β seen in the chills of Sn 16 and Sn 17, taken between the solidus and liquidus, are indistinguishable in form from α combs, although they have never been in contact with that body. The facts already known with regard to solid solutions of saline mixtures would not have led us to expect such a case of isomorphism in what may be called two conjugate solid solutions, but the great frequency of the regular system in the crystallisation of metals renders it more probable than it would otherwise be.

The LC *Alloys.*—This small group, covering the atomic percentages from Sn 13·5 to Sn 15·5, consists of alloys which polish to a yellowish-white. The unchilled alloys are compact, hard, and tough.

We detect three well marked halts in the cooling curves of this group, one due to the latent heat of crystallisation at the freezing-point, the second to the heat evolved at the C temperature by the reaction α + liquid = β, the third at the C′ temperature, due to the breaking up of solid β into the C′ complex, a reaction which we think is represented by the equation $\beta = \alpha + \delta$.

There must also, both in these and in the preceding group, be heat evolved when the temperature of the cooling alloy crosses the *l*C′ line and the crystallisation of new α in large crystals out of the solid β commences; but this is a gradual process, and the heat evolved at any one temperature is apparently not enough to produce a perceptible effect on the line of the cooling curve.

Like the preceding group, these alloys commence their solidification by the formation of α combs, but when the temperature has fallen to that of the point C and the α combs cease to form, there is more than enough liquid to transform all the α into β; hence, with sufficiently slow cooling, ingots chilled between *l*C and the solidus *lc* will be found to consist of β combs immersed in a tin-rich mother-substance, while, when the temperature has fallen to a point on the solidus, the ingot will be a uniform mass of β. The ingot will then remain uniform until the line *l*C′ is reached, when the solid β will have cooled to a point at which it is saturated with α, and that body will separate out in large crystals; the amount of these increases until the C′ temperature is reached, at which temperature the β becomes also saturated with δ, and the eutectic separation commences. The two bodies, α and δ, will now crystallise simultaneously and form the pearlite eutectic, similar to that in fig. 19. The chills of Sn 14 afford good illustrations of these changes.

Sn 14. *Chilled at* 800°. *V.s.c.* (fig. 28).

These ingots are much distorted by granulation, but are compact enough for polishing. The simplest pattern is that developed by strong ammonia. This re-agent dissolves and darkens the α combs, and leaves the ground a very uniform dead white. One sees about 10 per cent. of α, arranged in very rectangular combs. The lobes are very rounded and often separated from each other, forming rows of rounded dots. A ferric chloride etch, fig. 28, shows the same combs light on a dark ground, and the ground is now seen to contain a good deal of dark chill primary, which is probably β. In essentials, the pattern resembles that of Sn 12 chilled at 805°, with the exception that in the chill of Sn 14 there is less α.

Sn 14. *Chills at* 780° *and* 772° (not reproduced).

These were not very slowly cooled chills, consequently the alloy cooled too rapidly through the C temperature to allow of the complete absorption of the α. As a result, the ammonia etch shows a few very isolated dots of α on a white ground, and the $FeCl_3$ etch shows large combs of β symmetrically including the dots of α, the β being surrounded by a bluish-white tin-rich mother substance that was liquid at the moment of chilling. In the 772° ingot the imperfect transformation had the effect of depressing the temperature of complete solidification, for a v.s.c. chill at 775° shows the alloy completely solid at that temperature. The effect of the survival of α, through too rapid cooling, is so well shown in the photograph of Sn 13·5 at 765° (fig. 24), that we do not reproduce the Sn 14.

Sn 14. *V.s.c. chill at* 775° (not reproduced).

This, like all the chills of Sn 14, except granulated ones, is coated externally with a raised rectangular network of α or β combs, but the etched surface of the interior of the ingot shows no trace of combs. It is a compact mass of β, probably one crystal, containing no α. The striation in the β did not come at all readily, several etchings and polishings having been made before it was noticed. This is quite free from α, and closely resembles fig. 23.

Sn 14. *S.c. chill at* 766°, $FeCl_3$ *etch* (not reproduced).

A compact surface of striated β. No combs visible and no α. The chill at 740° is exactly similar.

Sn 14. *Chills at* 715° *and* 705°.

Consist of β striated as before, with polygonal boundaries beginning to show, though they are not a marked feature and have to be searched for. The direction of striation changes abruptly at a boundary.

Sn 14. *Chills at* 675° (fig. 29).

We have two; one a very slow cool (fig. 29). This contains only β, striated, but otherwise uniform, without polygonal boundaries or a trace of α. The other ingot is similar, except that there are a few specks of α, which is probably a commencement of the new crystallisation out of the solid that is so well marked in the next chill.

Sn 14. *Chill at* 647°. NH_3 *etch* (not reproduced).

This, at one end of the ingot, contains a few per cent. of the new α, but most of the surface is quite blank. No doubt, if etched with $FeCl_3$, this ingot would have shown striation in the β. The ingot appears to have been chilled almost exactly on the curve lC'.

Sn 14. *Chill at* 600°. *V.s.c. chill* (fig. 30).

We give a photograph of this ingot (fig. 30). The new α is seen as a pure white crystallisation, larger than the striation pattern and quite different in character from it In this ingot we are evidently below the lC' line, but not far below it, as one end of the ingot, the larger half, is quite free from α. This portion is not shown in the photograph. The photograph brings out a very important point, namely, that in the immediate neighbourhood of an α crystal the β is dark and unstriated. We shall return to this point.

The chills at 675° and 600°, together with the chill of Sn 15 at 600°, determine a point on the lC' line with considerable accuracy, for this line separates the region in which the β is free from α from that containing the new α which has crystallised out of the solid β.

Sn 14. *The chill at* 530°, *v.s.c. chill* (fig. 31).

Here we have, as might have been expected, a much more abundant and large α crystallisation. Moreover, the β, except in one spot far removed from α, has not broken up into the striation. This phenomenon, seen also in the preceding chill, is one reason, perhaps the most conclusive, for the truth of our view that the striation did not exist in the β at temperatures above 500°, but is a change produced during and sometimes after the chill, and due to the fact that the β of Sn 14 is so rich in copper that at low temperatures it is in a very unstable state and readily breaks up into a copper-rich and a tin-rich phase, thereby producing the striation. It is clear that β slowly cooled below the lC' line, out of which α has already crystallised, will be less supersaturated and therefore more likely to bear a low temperature unchanged than the β chilled above the lC' line. For the same reason Sn 9 chilled at 546° contains a mother-substance of β unstriated. We shall see that the β of Sn 16 and 17, necessarily poorer in copper, is much more stable and rarely striates. We are not disposed to think that the two phases forming the striated β are identical with the α and δ of an unchilled alloy.

Sn 14. *The chill at* 470°, *v.s.c. chill* (fig. 32).

Here, as usual, the residual β has broken up into the C' complex of α and δ; there is no β left in the ingot, consequently the α is darkened and the δ remains a pure white; a good example of the complete reversal in the etching that occurs when we pass below 500°. A close inspection of this eutectic shows that it differs very much from striated β, and could hardly have arisen out of it. This is another argument for the view that striation did not exist in the β at temperatures above 500°.

Sn 15.

The higher chills resemble those of Sn 14.

Sn 15. *Chill at* 775°, *s.c.* (not reproduced).

The ingot contained no α, but consisted of large β combs in a white tin-rich mother-substance. A glance at the diagram shows that this is what we should expect. The β was at first not striated, but an ignition to a temperature of about 300° developed striation when the surface was again etched.

Sn 15. *Chill at* 600°, *v.s.c. chill* (fig. 33).

This is important. It consists of several large polygons differing, on account of orientation, very much in brightness. There are also fainter polygonal boundaries, but these which do not separate regions of different brightness, may be cracks. There is no α, and the β is not striated. The ingot is undeniably a uniform solid solution. We have no other chills of Sn 15.

The fact that in this group of alloys all the primary α is absorbed at 790°, and that only at lower temperatures does α again crystallise, accounts for the singularly disjointed appearance of the combs seen in the unchilled alloys. The photograph of Sn 12, published in our paper in the 'Proceedings,' vol. 68, shows this peculiarity, but in slowly cooled ingots of Sn 14 it is much more marked. For in Sn 12 a little of the primary α has persisted, and so decided the orientation of the new α, while in Sn 14 there were no such nuclei, and the character of the primary α combs is not in the least reproduced in the later crystallisation. The chills of Sn 14 at 530° and 470° illustrate this when compared with the chill at 800° (fig. 28).

Sn 15·5. 25·5 *per cent. by weight.*

The alloy is important, because at this composition occurs the angle C in the liquidus, and also, apparently, the eutectic angle C′ of the curve lC′XD′E′, which is to the solid solutions β and γ what the liquidus is to a liquid. The cooling curves of Sn 15 and Sn 16 enable us to see what the cooling curve of Sn 15·5 would be like. The short upper flat of 15 would be absent and also the long flat at C, because there is neither crystallisation of α at the freezing-point nor an isothermal transformation of α into β. Instead, the commencement of solidification is marked, as in Sn 16, by a very gradual slope due to the heat evolved in the continuous reaction between the solid β and the remaining liquid, a reaction determined by the solidus lc and the liquidus CD, the process of solidification being quite similar to that of the AB group. The solidification having completed itself at about 740°, the cooling curve becomes steeper and corresponds to the cooling of a solid with no evolution of latent heat ;

but at 500°, or thereabouts, the cooling curve has a flat corresponding to the formation of the solid eutectic C′. Thus the cooling curve has only two singularities.

Sn 15·5 *chilled at* 767°, 760°, 759° (not reproduced; see fig. 34).

These, when etched with $FeCl_3$, show a pattern of β combs on a lighter tin-rich ground, the pattern resembling that of Sn 17 chilled at 731°, though not quite so regular. The β combs in shape and arrangement closely resemble α combs, indeed, we think the two bodies are isomorphous. But these combs of β are distinguished from α in two ways, they etch out in polishing much more readily and deeply than do α combs, and in Sn 15·5 they can be made to show the striation pattern, though when originally examined they did not show it. After the first examination they were ignited, a process which brings out the combs dark brown on a white ground. A repolish and an etch with $FeCl_3$ now shows that many of the lobes have developed a large striation pattern identical with that in the β previously discussed. We give a photograph (fig. 34) of this effect at 750°, because it links up the β previously described to the unstriated β combs we shall find in the succeeding alloys. The photograph also shows chill primary of β immersed in the white tin-rich mother-substance. In the chill at 750°, which was not specially slowly cooled, the combs fill about three-fourths of the area. Had the cooling been slower, we think the alloy would have been entirely solid at this temperature.

Sn 15·5. *Chill at* 705° (not reproduced).

This, unlike the previous chills, does not develop a pattern by polishing, for the large primaries have disappeared from the interior, though they are still visible on the outside. Ignition to orange brings out a few large softly rounded patches, differing a little in tint, but nothing that could be called a pattern. Chemical etching also fails to develop anything except a few large polygons. The alloy is a very uniform body with no striation or other pattern. We infer that, before the chilling, the primaries had grown, assimilating the mother-substance as they grew, until their margins met. Thus at the moment of complete solidification the alloy consisted of crystal grains of the solid solution β, each grain having its own orientation no doubt, but being, from a chemical point of view, approximately uniform and identical with the other grains around it.

Sn 15·5. *Chills at* 600° *and at* 552° (fig. 35).

These resemble the preceding. They show a few polygonal divisions, but otherwise are uniform; they show no striation and no pearlite effect. We give a photograph of the chill at 552° (fig. 35), taken with oblique illumination, for comparison with the next alloy.

Sn 15·5. *The chill at* 452° (figs. 36 and 37).

Polish alone leaves this a perfect mirror with no pattern, but ignition or a slight etch with either ammonia or very dilute $FeCl_3$ brings out a fine mother-of-pearl effect, the surface being now full of iridescent reflections, especially under oblique illumination (fig. 36). These are in patches oriented in many different directions, so that the effect varies with tilt and rotation. It requires a power of 500 to resolve these striations, when we see that the material consists of two substances, one darkened by the etch, the other a pure white (fig. 37). These sometimes lie side by side in groups of very narrow lines, an arrangement which accounts for the iridescent effect. In other places the darker copper-rich α (as we think it) is in dots surrounded by the white δ. This is the solid eutectic of all the alloys up to Sn 20, but in Sn 15·5 *alone* it occurs free from large crystals either of α or of the white δ; in Sn 16 we shall find such large crystals.

The CD *Alloys.*—All these, when chilled between the liquidus and solidus, or more exactly when chilled above *lcm*D, contain large copper-rich combs of β. These combs invariably etch out deeply in the process of polishing, and are then visible as a pale copper colour, while the mother-substance surrounding them is pure white. They etch with either ammonia or ferric chloride to a dark copper or black, and do not show any tendency to break up into the striation pattern. At the *cm*D transition temperature there is some difference between Sn 16 and the alloys containing more tin, but below the solidus all the alloys of the group, if they have been slowly cooled down to the moment of chilling, appear to be uniform solid solutions, a condition which persists with little or no change until the line C′XD′ is reached, when a crystallisation of δ out of the solid solution commences.

Sn 16.

The upper chills of this alloy throw a very clear light on the process of solidification. The ingots are all coated externally with a raised pattern of rectangular combs.

Sn 16. *Chill at* 773°.

When the ingot is cut and polished one finds that the polishing has etched out large combs exactly similar to those on the outside. A gentle ignition oxidises these combs more rapidly than the mother-substance, but on further heating the lobes of the combs develop margins, and changes evidently take place in them; the combs are β, very rich in copper, and therefore somewhat unstable.

Sn 16. *Chill at* 752°, *v.s.c. chill* (fig. 38).

The β combs are large and rounded, filling by far the larger part of the area, but there is still a considerable amount of the tin-rich mother-substance, thus the ingot was not altogether solid at the moment of chilling. The β has a fine uniform grain, with no trace of striation or other change, and the margins of the combs are quite sharp. There was evidently a considerable difference between the composition of the solid and the liquid at the moment of chilling.

Sn 16. *V.s.c. chill at* 738° (fig. 39).

The ingot was allowed an hour and a-half to cool from 752° to 738°, in addition to the time given to the slow cooling of the preceding alloy. The ingot was quite solid, showing no trace of granulation. The bold regular gridiron of the more rapidly cooled alloys has disappeared from the outside. A polished and etched section makes it evident that the primary combs have now grown so as to touch each other nearly everywhere, but there are two small interspaces, covering together less than 1 per cent. of the area, and full of the white tin-rich mother-substance; here we can detect the rounded form of the lobes of primary. One also begins to see polygonal boundaries, meeting three together in angles of 120°. There are not many examples of this, and the boundaries are rather geometrical lines than ribands of perceptible width, but these lines run out of the two or three little pools of white, and it is clear that the boundaries are where the primaries met.

Here we observe a process of solidification that can only be explained by the theory of solid solution; the copper-rich solid grows and at the same time assimilates the tin-rich liquid, while the unabsorbed liquid down to the last drop remains quite different from the solid phase; the process we observe is exactly predicted by Roozeboom's theory. It is clear that the alloy does not solidify by the same steps as those that a pure or nearly pure body would follow, for in the case of such a substance the solid first forming would differ very little from the remaining liquid, while we find that in the case of Sn 16, however little solid has formed, it is considerably richer in copper than the mother-substance. If a pure body differing from the liquid in composition crystallised, it could never grow so as to absorb the whole of the liquid, and the resulting solid would be a complex of two kinds of crystals, a condition which does not exist in Sn 16 immediately below the solidus. The alloy is very uniform, showing no iridescence or striation.

These two chills would lead us to fix the temperature of complete solidification of Sn 16 at a point not higher than 740°, but we had some reason for suspecting that the pyrometer had altered a little between its last standardisation and the moment when these two chills were taken. We therefore made two independent chills at 750°. These were cooled very slowly before the chill, and on each occasion the pyrometer was carefully standardised before the experiment. Each of these ingots shows the alloy as completely solid, no mother-substance being visible, and the combs of β having disappeared and been replaced by the characteristic polygons bounded by very slender white lines. The grain of the material of the polygons is very uniform; it is presumably the solid solution β. We therefore place the solidus at 750°. We do not give photographs of these, as, beyond fixing the position of the solidus more exactly, they do not add to the information supplied by the preceding photographs.

Sn. 16. *Chill at* 725°. *S.c.c.* (not reproduced).

This had all the slow cool of the alloy chilled at 738°, and, in addition, was allowed an hour and a-half to cool from 738° to 725°. There is now on the outside only a trace of a very coarse, rounded network. The cut and polished section is very uniform, with no polygonal boundaries—probably because the ingot has become all one crystal—no striation, indeed no pattern of any kind. The slow-cooled chill at 650° is similar, there is no sign of the solid solution breaking up. The chills at 546° and 500° were not slow-cooled, and therefore the number of polygonal divisions is larger, but the dividing lines are very fine, and the ground of the polgyons is uniform. The sections do not show the pearlite effect when the polished and etched surface is obliquely illuminated.

Sn. 16. *Chill at* 477°.

This chill, which must be very close to, if not below, the curve $lC'X$, does not yet show the typical pattern of an unchilled alloy. There is no iridescence, the ground not having broken up into the C' eutectic. But there are some broad irregular bands of a tin-rich substance having an asbestos-like growth. There are also stars of true δ in the copper-rich ground. Ingots chilled a little lower, or unchilled alloys, are very different. In these, after polishing and etching the surface, the pearlite effect is very well shown; indeed, with oblique illumination, a lens, or even the unaided eye, shows the surface as made up of iridescent patches. The whole alloy has broken up into the C' eutectic, exactly like the photographs we give of the same phenomenon in the Sn 15·5; but, in addition, there is in Sn 16 a new feature; this consists in sprays of δ, which began to crystallise as soon as the temperature fell to a point on the curve $C'XD'$. We give a photograph (fig. 40) of an unchilled ingot showing this, because it proves that Sn 16 lies to the right of the solid-eutectic point C', and consequently when the solid solution begins to break up, it is a tin-rich and not, as with Sn 14, a copper-rich phase which crystallises.

The Transformation at the Point D.

Sn 16, as we have seen, appears to solidify homogeneously to a uniform mass of β combs, but the alloys of the group with a larger percentage of tin do not do so. Although they all contain β combs when partially solid and chilled in the area $lcDC$, yet at the temperature of the cD line (740°) the β becomes unstable, and at this and lower temperatures suffers a change into what we must suppose is γ. We give (fig. 41) a photograph of a v.s.c. chill of Sn 17, chilled at 745°, which, as it contains no chill primaries, may be taken to indicate the maximum amount of β that can exist in this alloy. The chills of Sn 18, Sn 19, and even Sn 19·5, at this temperature are exactly similar to that given of Sn 17, except that they contain less β. We also give a photograph (fig. 42) of Sn 17, chilled at 731°, as it emphasises the symmetry of the β combs and their great resemblance to α in form. The ingot was not especially slowly cooled before the chill, so that the detail is small. The ingot must have cooled too rapidly through the D temperature for the β combs to suffer much change, though a higher power makes it evident that their margins are softened by a commencement of solution. Other experiments show that if the ingot had not been chilled, the β combs would have disappeared at lower temperatures. The transformation at the D temperature is a slow one, though it probably goes on more rapidly a few degrees below that point, so that it is possible to find β combs, more or less recognisable, in alloys somewhat slowly cooled and chilled a little below D. Sn 18 chilled at 735° shows the partial solution of the β, which is recognisable in darker irregular patches. These retain, in a distorted form, some semblance of the shape of the β combs. This ingot was slowly cooled through the D temperature, but enough time was not allowed for the completion of the change. We do not give a photograph of this ingot. The same process of solution of the β is seen in the photograph (fig. 43) of Sn 18 chilled at 734°. Here the β combs must have been originally very symmetrical, but as the ingot was not slowly cooled before the chill, they are easily recognisable in spite of the lower chilling temperature. We have ingots of Sn 17 and Sn 19 which show the same partial solution of the β. One of these, a chill of Sn 19 at 733°, is reproduced in fig. 44.

When a patch of β undergoing this change is examined with a higher power, one sees that the grain of the material, originally fine and uniform, becomes coarser and develops into a flaky pattern of grey and white, and sometimes spherulitic crystals of a tin-rich material develop in the heart of what were uniform β crystals. All these obscure changes, however, result in the complete disappearance of the β, and the formation of a very uniform material, provided the alloy is cooled slowly to the solidus *cd* and then chilled. We give a photograph (fig. 45) of Sn 18 very slowly cooled to 728° and then chilled, in which the disappearance of the β is practically complete. The fine straight polygonal boundaries are present, but they have little or nothing to do with the original β.

This apparent uniformity in the CD alloys, when chilled below the solidus, has been confirmed in instances too numerous to mention in detail. For example, a very slow-cooled chill of Sn 18 at 728° was uniform, also one at 650°, and that at 550°, of which we give a photograph (fig. 48), is very nearly so. Again, very slow-cooled chills of Sn 19 at 719° and 710° are uniform except for polygonal boundaries; and the chills at 680° and 629° show, even after repeated ignitions to orange, no pattern except a faint mottle and the polygons of slightly different tint, so common in the region of chemically uniform solid solutions. This observation, and others like it, do not, perhaps, exclude the possibility that some of the alloys below the solidus may be a *minute* complex of two materials. In accordance with the information supplied jointly by the microscope and the pyrometer as to the temperature of complete solidification, we have, therefore, ventured to draw the solidus *lcmd* with a flat between *c* and *m*. The position of *c* is, we think, correct, but that of *m* is very uncertain. The break is, however, useful as a reminder that *lc* and *md* are the solidi of two different substances. If the gap *cm* really exists, the solid alloys below it ought to be complexes of two bodies.

Although we have not been able to detect the fact, it is quite possible, from the way in which the β disintegrates, that there may be such finely grained complexes. For, unlike the C transformation, which is an obvious solution of α in a liquid followed by the crystallisation of the very different β, the D change is one of disintegration throughout each β crystal, a change that might conceivably be a separation into two phases. An alternative supposition is that the points *c* and *m* are coincident, and that the change at D is a case of dimorphism, the β and γ having, at their transformation temperature, the same composition. But the evidence we have for the position of the solidus makes it difficult to bring *m* up to *c*. We fear we must leave the question undecided. *It is certain, however, that there is a transformation at the* D *temperature, that the cooling curves of the* Sn 18 *and* Sn 19 *show heat evolution there, and that during this transformation the* β *combs disappear without having filled the alloy.*

The Transformation of the Curve C′XD′.

Whether the solid alloys below *lcmd* are all uniform or not, it is certain that they undergo a profound change after crossing the line C′XD′, this change being accompanied, as the cooling curves show, by an evolution of heat. In the case of the alloys to the left of CC′, the change consists in the crystallisation of copper-rich α crystals out of the solid, as we have already proved. In the case of the alloys to the right of C′, it consists in the crystallisation of white tin-rich δ, which appears in the form of rosettes, bars and fern-leaf. The unchilled Sn 16, of which we give a photograph (fig. 40), shows these new crystals, but with more tin the new material grows in amount until at Sn 20 it practically fills the whole alloy. The changes are well shown in Sn 17. Chills at 668° and 616° were uniform. The chill at 547° is uniform so far as much more than 99 per cent. of the surface is concerned, but dilute $FeCl_3$ brings out a few large polygons bounded by extremely thin lines of δ, and in one place the lines have thickened a little by a moss-like growth of a similar white tin-rich body. There are also a few short lines of minute rosettes of white δ. This is the beginning of the pattern that develops at a slightly lower temperature, but the traces of separation are as yet so slight that they have to be very carefully searched for. We do not reproduce this, because there is so little to see, and because what pattern there is closely resembles that of Sn 18 chilled at 550° (fig. 48), with this difference only, that the white is much more abundant in the Sn 18.

The chill of Sn 17 chilled at 495°, when etched as usual with dilute $FeCl_3$, is still largely blank (fig. 46), but the white bands bordering the polygons are now much broader, and near some of the borders and angles there is a delicate but perfect growth of the white δ in sprays that we are in the habit of calling the "fern-leaf crystallisation." The central and much the larger part of each polygon is, however, blank, so that we have in this ingot a transition from the uniform solid solution to the two-phase state proper to the region below the curve XD′. According to the diagram, this ingot was chilled a little below the line. It is important to notice that the dark ground is uniform even to a high power, and that when examined by oblique light it shows no iridescence; the ground has not yet broken up into the C′ eutectic. But the chill at 450° (fig. 47) shows the ground broken up into a minute complex,* and also the fern-leaf scattered uniformly over the whole surface. This ingot etches with very weak $FeCl_3$ and has the patchy iridescent effect of the low chill of Sn 15·5 due to the formation of the C′ eutectic. These lower chills of Sn 17 were not slowly cooled before the chill, and hence the detail is small, but two ingots of Sn 18 (fig. 48) and Sn 19 (figs. 49 and 49A), both chilled at 550° after a very slow cooling, show the nature of the change of the XD′ curve even better, and fix a point on it accurately. In the chill of Sn 18 at 550° (fig. 48), prolonged etching with $FeCl_3$ brings out very little pattern. There are, as the photograph shows, only a few small specks and threads of δ. This ingot was evidently chilled when in the triangle *l*XE′ of uniform solid solutions. On the other hand, the chill of Sn 19 at the same temperature, even when lightly etched with $FeCl_3$, develops a splendid pattern of white tin-rich δ in the form of bands, fern-leaf, and bars. Hence the ingot must have been chilled below the transformation curve. We also give a chill of Sn 18 at 501° (fig. 50), in which the D′ crystallisation has taken place. It must be remembered that the curve XD′E′ has been determined from the halts in the cooling curves and not from the chilled alloys, but we see that the latter confirm its position.

The copper-rich ground in the chill of Sn 19 at 550° is uniform, but unchilled ingots, or those chilled below X′, show the ground to be the C′ complex, fig. 53. It must also be remembered that in the chill of Sn 19 at 550° the crystallisation of the δ was arrested by the chilling before it was complete, hence this ingot does not show the δ fern-leaf so closely packed together as would be the case in an unchilled ingot.

Sn 20. 31·8 *per cent. by weight of tin.*

This alloy, the "speculum metal" of Lord ROSSE, has the formula Cu_4Sn, and the

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* This feature requires a higher magnification than that of fig. 47.

slowly cooled unchilled alloy may at ordinary temperatures consist of this compound. Occurring as it does at a singularity both in the liquidus and in the solid transformation curve, the alloy is a border-line one, separating two groups. Its cooling curve shows two well marked evolutions of heat, the first due to the latent heat of solidification, the second to the re-crystallisation that takes place in the solid at temperatures below the point D′.

As the diagram indicates, solidification is complete at a temperature not more than 30° below the freezing-point. Ingots chilled in the region of temperature between the liquidus and solidus contain copper-rich primary combs embedded in tin-rich mother-substance. These are well seen in a chill at a little below 740°, in which they are comparatively scanty, and in a chill at 726°, in which they fill more than half the ingot (fig. 51). These combs of primary are evidently β which has begun to disintegrate. The important point to notice is that this alloy, although it has a formula, does not solidify after the fashion of a pure body, but by the formation of crystals considerably richer in copper than the liquid. A little above 710°, however, these combs have disappeared, and from here down to 650° no pattern can by any means be developed in the chilled ingots, except sometimes the pattern of large polygons, or counties, so common in pure metals and solid solutions. The chill at 605°, only just above the point D′, requires very prolonged exposure to strong ferric chloride to bring out anything except the polygons, but by this means one sees that the polygons are bordered by broad but vague white bands. A high power makes it evident that these bands are of the angular patchiness seen in some previous ingots. This is evidently a growth of tin-rich material in places where broad ribands of compact δ would be seen in an unchilled ingot. It is quite doubtful whether these markings have any right to appear in this ingot, or whether they are not a result of imperfect chilling or a change that has taken place subsequently to the chill.

The chill at 558°, about 25° below D′, is full of a splendid pattern of the δ bands and rosettes. The only difference between this pattern and that of an unchilled alloy is that in the former there is rather more mother-substance, and that this is uniform, instead of being, as in the unchilled ingots, a complex. The photograph of an unchilled ingot that we give (fig. 52) shows how very little of this mother-substance (dark in the photograph) is to be found in the alloy. Moreover, this mother-substance is itself mainly composed of the same material as that of the bands and rosettes, its dark colour after etching or ignition being due to a small admixture of spots and lines of a copper-rich material, which we think is α. We give a higher-power photograph (fig. 53A) of a patch of this eutectic, taken from an unchilled and somewhat slowly cooled ingot of Sn 20; the darker straggling patch in fig. 53A corresponds to one of the minute specks of black in the preceding figure. We also give in fig. 53 a high-power photograph of the eutectic in unchilled Sn 19. The resemblance to the eutectic, also formed at the same temperature, of Sn 14 is very great, and we have little doubt that this eutectic complex, formed in the solid alloys at a temperature of, or a little below, 500°, contains the same two phases, α and δ, in all the alloys from Sn 6 to Sn 20. Beyond Sn 20, *even with a mere trace more tin*, the eutectic vanishes, and there is so little of it in Sn 20 that we are disposed to regard it as an accident in that alloy, or as due to the fact that the alloys that we call Sn 20 may have a slight deficit of tin in them. If so, there is considerable reason to regard the δ substance of Sn 20 and of all the previous C′ eutectics as being the compound Cu_4Sn. In this case the compound is not present, at all events in crystalline form, above the transformation curve, and is finally produced by crystallisation out of a solid solution. On this view the transition from the condition of the alloy just above the point D′ to that just below it must be compared to the conversion of a pure substance from the liquid to the solid state, only that in the case of the alloy we are considering both states are solid. The change, like that from a liquid to a solid, is an exothermic one.

It is, of course, possible that the δ material found in all the alloys from Sn 6 to Sn 20 may be a series of solid solutions varying in composition throughout this range of alloys, but the great similarity in the appearance of the δ, from its first appearance in the scanty eutectic of Sn 6 to the moment when it fills the whole alloy in Sn 20, makes us think it far more probable that it is a pure compound of constant composition. Up to the present we have not been successful, by means of a chemical solvent, in removing the α from such an alloy as Sn 16 in order to analyse the δ.

The character of the pattern of riband, bar and rosette, or fern-leaf, seen in the CD alloys when cold and unchilled, is partly, we think, dependent on the greater or less perfection of the transformations that take place *during solidification*. Too rapid cooling during solidification will leave the grains somewhat copper-rich with some tin-rich mother-substance round them; in fact, the D transformation will not be complete. This will lead, when the δ crystallises, to its doing so in broad ribands, enclosing areas in which it is more sparingly distributed as rosette or fern-leaf. In the chill at 558°, and the same is seen in the unchilled alloy of fig. 52, the δ forms many straight pointed bars. This peculiarity, which is first seen in Sn 20, suggests the bars of Sn 21 and succeeding alloys.

The DE *Alloys*.—All slowly cooled ingots of the DE alloys, but especially the higher chills, are more or less covered, particularly on the top, with a raised primary crystallisation. This suggests bunches of grapes packed closely together, but sometimes, as in the upper chills of Sn 24 and Sn 25, there are suggestions of combs in the form of long bars with rounded serrations. In the lower chills the grape pattern alternates with patches of linear ruling, showing iridescence.

We have examined an unchilled ingot of Sn 20·5. This alloy seems to consist of masses of δ in close juxtaposition, the trace of the C′ eutectic visible in the Sn 20 having disappeared. The bar pattern noticeable in some of the ingots of Sn 20 is now more marked, the bars having pointed ends, so that they resemble elongated willow leaves. But the bars now seem to differ a little in composition from the rest of the alloy; they oxidise more slowly than the ground, so that they probably contain more tin. They are also blackened by $FeCl_3$, a feature that becomes very marked in the succeeding alloys.

Sn 21. *S.c. chill at* 725° (fig. 54).

This ingot was very much distorted by granulation in the chill, a proof that it was far from solid at that moment. Polishing etches out the surface into a pattern of primaries, leaving these faintly copper-coloured on a dead white ground, and heat-oxidation darkens the primaries more rapidly than the ground, a proof that they are richer in copper. $FeCl_3$ is rather variable in its action on them, but, on the whole, it darkens them as compared with the ground. These primaries (fig. 54) consist of rounded blobs, often isolated, but sometimes grouped in oblique sprays, unlike the rectangular β. The lobes of primary, when examined with a higher power, are uniform, not showing any tendency to break up into the bar pattern of the lower chills, but in the chill primary, or in the mother-substance, one can see the beginning of the bar pattern.*

Sn 21. *S.c. chill at* 710° (not reproduced).

This is a smooth solid-looking lump, but cutting and polishing develop large cracks; polishing reveals no pattern. $FeCl_3$ acts very slowly, but finally brings out polygonal patches and some rotation effect, but no bars or other pattern. The ingot is a good example of a uniform solid solution, and shows that the solidus lies above 710°. The chill at 700° was uniform. That at 650° was a pattern of large patches (fig. 55), but each of these patches had a uniform surface, with no bars or other pattern. There is, therefore, a region of temperature in which the alloy is a uniform solid solution. Probably on account of fragments breaking off from the edges of the cracks, we found it impossible to avoid scratches in polishing this ingot.

Sn 21. *S.c. chill at* 590° (fig. 56).

Here we are a little below the transformation curve D′E′, and several per cent. of the new η body has crystallised out of the solid solution in curved bands which coincide with the previous polygonal boundaries, and in groups of parallel bars which generally start from a boundary. In the photograph (fig. 56), which is taken from a $FeCl_3$ etch, these are black, but they are richer in tin than the ground, for if the surface is heated, these η bars oxidise more slowly than the ground, remaining white while the ground turns a rich brown. The photograph tends to give a false impression as to the amount of the new material, as it was taken from a patch of the surface where it was abundant; really, there is less than 10 per cent. of it.

As the chill was made a little above the D′ temperature of 580°, we should not have

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* The striation visible in fig. 54 on the lobes of primary is due to imperfect polishing.

expected to find evidence of the ground having been transformed into δ, but this has occurred, and here and there are copper-rich gaps in the massive δ of the ground, in which the δ fern-leaf is seen growing out from the edge of the more massive δ. One of these gaps is visible in the figure. This ingot of Sn 21 would therefore appear to show the real nature of the ground as δ. In addition to the quite black bands of η, there are, in places, paler bands. These may owe their paleness either to a different orientation or to a somewhat smaller content of tin.

Sn 21. *Chill at* 588°, *not specially slowly cooled* (not reproduced).

This shows, perhaps, a little less of the bars, but it has some paler patches in addition to the black bars, also one or two small spots of δ granulation or fern-leaf. The bars are well seen to have the orientation of the grain of solid solution from which they were formed. There are also places where white δ bars crystallised on a darker ground.

Sn 21. *Chill at* 580° (fig. 57).

This ingot, chilled on the D′ line, was not a slow-cooled ingot before chilling. When etched with $FeCl_3$, it has a larger fraction of the surface covered with bands than fig. 56, but these vary in tint from black to the palest grey. The bars can, in some cases, be made to alter a little in shade by tilting and rotation, but not enough to make it possible to explain their very varied appearance as due to differences in orientation of a pure material such as $SnCu_3$. Moreover, considering the percentage of tin in the alloy, the bars are far too abundant for such a hypothesis. It seems more probable that when the temperature of the transformation curve was reached at 600°, the solid alloy began to separate into two, or, through imperfect equilibrium, into several phases with different percentages of tin, all the more tin-rich phases re-crystallising in a form isomorphous with η, and therefore all to be classified as η. An analogy for this may, perhaps, be found in the breaking-up of a liquid into conjugates during rapid cooling. In such a case a whole series of liquid phases must through imperfect transformation exist together, and if a process analogous to chilling could be effected they would be stereotyped as we see them here. In the whitest parts, which in the $FeCl_3$ etch are the most copper-rich, the δ crystallisation has taken place. The bars, which are really sections of plates, have definite crystalline shape, and present many good examples of twinning. As Mr. FEARNSIDES has pointed out to us, it resembles the twinning seen in soda felspars, but the fact that the bars darken at different rates when heat-oxidised, is some indication that they are not merely twins in a homogeneous substance.

Sn 21. *Slow-cooled chill at* 570° (not reproduced).

This has a decidedly smaller area of the new crystals than the chill at 590°, and the same is true of all lower chills; for example, those at 556° and 380°, that is to say, of all ingots chilled below the D′ temperature. But these ingots contain a new feature in the form of lace bars. The bars do not present the same variety of shade, and many of them are merely outlined and not completely filled in with the black, but their interior consists either of a fine ruling of black and white, or of a lace-work of the two. We are disposed to think that the lace bars are not bars imperfectly formed, but bars that have suffered a partial disintegration into two phases, which may be the final phases of δ and η. On this view we may presume that the broader uniform bands of the chill at 580° would have turned into lace bands if slowly cooled to a lower temperature before the chill. We do not reproduce the lace-bar effect in Sn 21, as it is even better shown in Sn 22.*

Sn 22. 34·45 *per cent. of tin.*

At this percentage there is a slight singularity in Roberts-Austen and Stansfield's transformation curve, and although our pyrometric determinations did not justify us in reproducing this singularity in our diagram (Plate 11), the microscopic study of the chills to some extent confirms their curve. The chill patterns resemble those of the preceding alloy, but there are certain differences.

Sn 22. *Chilled at* 733° (fig. 58).

This shows very well the characteristic clumsy γ combs, generally dark on a lighter ground. One also sees bars of η, as a rule, in the mother-substance.

Sn 22. *Chilled at* 710° (not reproduced).

The solidus appears to lie at 700°, for the alloy at 710° has abundant primary combs in it of the true γ type, with nothing rectangular about them. There is also a little chill primary. The combs are copper-rich, but the heat oxidation employed to prove this point has, in places, modified the somewhat unstable material and caused the growth of bars of η. The γ crystals will be found to be still more unstable when they contain a little more tin.

Sn 22. *Chilled at* 690° (fig. 59).

The ingot must have been quite solid at the moment of chilling, for the primaries have entirely gone and are replaced by large patches of uniform solid solution, but

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* [At a later date the ingot of fig. 57 was re-heated to a temperature between 500° and 600°, cooled without chilling, polished and etched with $FeCl_3$. The re-heating has entirely altered the pattern; the broad twinned bands of η have disappeared, by far the greater portion of the surface consists of white δ with some scanty lace bars of black η. Unfortunately, this experiment was made too late for the reproduction of the photograph.—June 29, 1903.]

the chill did not prevent the formation of a few long slender bars of η, dark in the photograph.

Sn 22. *S.c. chill at* 680°, *and chills at* 650° (not reproduced).

This is a remarkable example of the polygonal pattern produced by cutting the grains of solid solution composing the ingots at different angles, and so causing them to etch differently, though they are probably the same chemically. Tilting, or rotation under oblique illumination, does not much alter the relative shade of these patches, and they show no iridescent effect. The bars of η are much scantier than in the preceding ingot, but they can be found. The chill at 650° is very similar to the preceding, and as far as we can see it is free from bars. Another chill at 650°, very slowly cooled before the chill, has many more bars, but they are small and thin, and may, we think, be attributed to the chill not being sharp enough to arrest all further change. In fact, the bar pattern is so slight in all the above-mentioned ingots, that we think it almost certain that the alloy passes through a region of temperature in which it is really a uniform solid, as in the case of Sn 21.

Sn 22. *S.c. chill at* 600° (not reproduced).

We should have expected the bar pattern to become a real feature when the transformation curve was passed, as in the present chill, but it is, on the contrary, a very good example of a uniform solid solution consisting only of a few large patches, which turn from dark to light when tilted. There is hardly a trace of the bars. Even the chill at 588° is very similar, though here some of the polygons are bounded by straight lines and may be massive bars.

Hence, although the cooling curve of the alloy shows a considerable evolution of heat at 627° where the transformation curve is reached, yet the chills fail to show the corresponding change.

Sn 22. *Chill at* 570° (not reproduced).

The polygons, still very varied in tint, are now crossed and sometimes margined by massive bars of η, but there is no lace either in the bars or the ground.

Sn 22. *Chilled at* 565°, *a slow-cooled chill* (fig. 60).

This is certainly below the last, or D′, halt on the cooling curve, a point marked in the cooling curve of this alloy by a somewhat sloping flat. A lens now shows massive bars and curved bands of η dark on a light ground. A slightly higher power brings out the fact that this ground is full of paler bars and of lace bars, the effect being even better seen in fig. 61. Thus the crystallisation has taken place in at least two stages: at first the massive η bars formed, and, secondly, the mother-substance broke up into a copper-rich and a tin-rich phase. The lace bars are probably, as we said in discussing Sn 21, due to the similar breaking up of η bars that were too rich in copper for the final equilibrium. As in the ingot of Sn 21, chilled at 580°, the paler bars were probably intermediate phases.

A chill at 560° is very similar to that at 565°, but shows better the separate crystalline bars of the copper-rich phase.

Chills at lower temperatures show no further change, as can be seen from a not specially slowly cooled chill at 495° (fig. 61), so that the unchilled alloy must be a complex of two phases, which may be Cu_4Sn and Cu_3Sn, but are more probably conjugate solid solutions composed of these two bodies, and best described as δ and η.

An ingot that took several days to cool to ordinary temperature without a chill shows all detail on a very large scale. There is not the lace ground-work, though there are some traces of lace in the bars. Instead of the lace, the very slow cooling has allowed the white δ phase to crystallise in definite needles round the margins of the dark η bars, and sometimes in the heart of these bars.*

Sn 23. 35·8 *per cent. of tin, and* Sn 24, 37·1 *per cent. of tin.*

These alloys form copper-rich primaries of γ when chilled in the narrow region between the liquidus and the solidus, and at temperatures between the solidus and the transformation curve we believe that they form uniform solid solutions of γ, but we have never been able by chilling to obtain perfectly uniform ingots of the solid solution in this region.

Below the transformation curve a large scale crystallisation of η in bars and ribands take place. No change can be detected at the D′ temperature, so that unchilled alloys at ordinary temperatures must be regarded as consisting of two phases, a copper-rich one of the δ type and a tin-rich one of the η type, the two being, as in Sn 22, either the two compounds themselves, or solid solutions of them.

Sn 23. *S.c. chill at* 710° (not reproduced).

The ingot was very liquid at the moment of chilling, and, consequently, was badly granulated and blown into holes, but one can very well see a few broken sprays of γ primary on a darker ground. The γ is sometimes twinned, part of a spray being light and the rest dark, and it is evidently very unstable, dark η bars being visible, running across the lobes of primary. There is a great deal of chill primary, indeed the true mother-substance is shown by a high power to be a thin network of grey.

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* The flatness of the liquidus between D and E caused us to suspect at one time that the alloy, while wholly liquid, might have separated into two liquid phases; the above-mentioned extremely slow cooling was arranged in order that by difference of density two layers might be produced; there was no trace of such a separation, even the plates of η were uniformly distributed throughout the whole depth of the ingot.

Sn 23. *Slow-cooled chills at* 690°, 685°, 680°, 650° (not reproduced).

These are all very much alike; when ignited they are uniform, at all events to the eye or a lens, but $FeCl_3$ brings out a number of rather small angular and interlacing patches, which show the effect of varying brightness on tilting or rotation. A moderate magnification makes it evident that each patch is broken up into narrow bands with still narrower lines of a mother-substance between them. In fact, the separations proper to the region below the transformation curve have taken place although on a very small scale. This detail is not perceptibly larger in the chill at 650° than in that at 690°, although a long period of slow cooling was allowed between the two chills; hence we suspect that it occurred at lower temperatures during the chilling. Fig. 63, a chill at 685° of Sn 24, gives a fair idea of these ingots.

Sn 23. *S.c. chill at* 620° (fig. 62).

We are now below the transformation curve; the iridescence has increased and the patches are much larger, but, in addition, there has grown a large scale pattern of broad η bands and sprays of what may be likened to foliage. This is the true breaking-up of the solid solution into two phases, and we see that the η phase has very much increased as compared with Sn 22 and Sn 21. The chills at 590° and 570°, and indeed all lower chills, have the same pattern, so that the D′ transformation has now vanished or become unimportant. Oblique illumination shows, by the position of the shadows, that the darker ingredient has been etched out below the level of the lighter ground. Thus the darkening of the tin-rich phase is due to a real attack by the etching reagent. The pattern seen in these lower chills reminds one of the alloys from C to D when chilled below the transformation curve. In both cases there are ribands of a tin-rich material, often enclosing polygonal areas, and, branching from these ribands, a fantastic crystallisation of the tin-rich phase partly fills the enclosed areas. But in the CD alloys the ribands and fern-leaf crystallisation is left white and not attacked by the etching, while in the DE alloys it is attacked and darkened; in the CD alloys it is δ, in Sn 23 and Sn 24 it is η.

Sn 24 is similar throughout to the above, with the exception that in the chills in which the η phase appears it is more abundant; in fact, nearly filling the alloy. Primaries and chill primaries are obtained by chilling above 700°, and between the solidus and the transformation curve the chills are uniform when ignited; but when strongly etched show the iridescence and patchiness due to minute separations, while as soon as the chilling temperature falls below the transformation curve, the solid solution breaks up and the bars, or really plates of η, nearly fill the field. We give two photographs of Sn 24. The first (fig. 63) was a slow-cooled chill at 685°, that is, a little below the solidus. It shows no primary, but is full of iridescence due to minute linear separations; there are also some long slender bars of η. It may seem bold to assert that this ingot was, immediately before the chill, a uniform solid, but we are convinced that such was the case.

The other chill (fig. 64) of Sn 24 was also a slow-cooled chill at 635°, a little way below the transformation curve. It is at the same magnification as the preceding chill. We now see that the true crystallisation of η has taken place, and that the η nearly fills the ingot. Perhaps we may remind the reader that, on account of the ferric chloride etch, the tin-rich η is dark and the copper-rich mother-substance is white. Had the pattern been brought out by heat oxidation, it would have been reversed.

Sn 25. 38·4 *per cent. of tin.*

This alloy is especially interesting because it has the formula Cu_3Sn, and because of the many physical properties which reach their maximum intensity in the unchilled alloy of this composition. There has on such grounds been a consensus of opinion that it is a chemical compound. So far as the slowly cooled and unchilled alloy is concerned, this view is almost certainly correct. But we find that when a liquid of this composition begins to solidify, the crystals first formed are considerably richer in copper than the mother-substance, so that the crystals cannot be Cu_3Sn. At a lower temperature, however, the compound itself crystallises out of a solid solution. This occurs at E′, the summit of the transformation curve, a point where the cooling curve shows a large evolution of heat and a phenomenon analogous to surfusion.

Sn 25. *V.s.c. chill at* 720° (fig. 65).

The ingot was not granulated by the process of chilling, though the figure makes it evident that there was a considerable amount of matter liquid at the moment of chilling. Polishing alone shows the combs in a more brilliantly white network of mother-substance. The usual etching reagents do not give a contrast between the γ combs and the mother-substance sufficiently well marked for photography, we therefore adopted the method of heat-oxidation, the ingot being heated over a Bunsen until the first tint of orange appeared. Under this treatment the γ combs oxidised more rapidly than the mother-substance, becoming a dark orange while the latter remained almost white. This selective oxidation of the γ, which is reproduced in the photograph, proves that the γ combs are richer in copper than the liquid out of which they are crystallising, and therefore that they cannot be the compound Cu_3Sn. The heating has, however, to some extent decomposed the γ, leaving a rim of whiter material round each lobe of the combs. This and other features are better seen in fig. 65A, which is a more highly magnified photograph of the same ingot. Here we can see that not only the borders of the combs but also the whole of some of the smaller masses of γ are paler than the rest; this probably indicates that they are richer in tin than the earlier formed γ. The central parts of the γ combs have also broken up into a complex, which reminds one a good deal of Sn 23 and Sn 24. This again is evidence that the γ is not a pure chemical compound. A little of this separation could be detected in the surface when etched with ferric chloride before the alloy was repolished for the heat-oxidation. A slowly chilled ingot, very sharply chilled at 715°, was almost untouched by the strongest mixture of hydrochloric acid and ferric chloride, but heat-oxidation still reveals a little mother-substance.

The lower chills were etched in the usual manner with ferric chloride. Many of these show polygonal divisions, but very little difference in the tint of the polygons, and no pattern in them. Even the strongly exothermic change at E′ does not show itself by any pattern in the pure Sn 25, for the obvious reason that both before and after the change there are no two substances for the etching reagent to distinguish between. In quite the lowest chills, and in the unchilled ingots, the patches sometimes assume a bar-like form, especially if the polished and etched surface is exposed to the air for some days before examination. This appears to be due to the fact that the plates of η, of which the ingot is composed when the temperature is below E′, oxidise at different rates according to their position with reference to the plane of the section. This effect is seen in fig. 66, an unchilled ingot. A similar selective darkening of the η by atmospheric action was observed in a chill of Sn 28 at 725°.

The EF *Alloys*. Sn 26 *and* 27.—This region is not marked by a singularity in the liquidus, and in harmony with this fact the first steps in the solidification are very similar to those of the preceding alloys. But there is a greater difference between the composition of the first solid and that of the liquid, and consequently the γ combs of the upper chills are revealed by polishing alone through the more brilliant network of mother-substance around them. This effect is common to the upper chills of all the alloys as far as the point G of the diagram. This network is rapidly eaten out by etching re-agents, leaving the unchanged γ combs pale in a black network. Examples of the appearance are given in the photographs of the succeeding alloys. Below our solidus this network of mother-substance vanishes, and the only pattern is that typical of a chemically uniform solid made up of grains. The chills of Sn 26 at 677° and 656° are both of this character. A chill at 640°, that is, below the transformation curve, is extremely uniform, and most of the surface defies all the efforts to etch it, but a high power enables one to discover some places where a new network has grown, due, we presume, to the breaking-up of the solid solution into two phases, η and a little of a tin-rich phase. It is pretty certain that we may venture to be more precise, and say that the change is the crystallisation of the compound Cu_3Sn out of a solid solution containing rather more tin. This change is not complete at 640°, and there is very little of the new tin-rich phase. The chill at 612° shows the whole surface broken up into the characteristic bars of Cu_3Sn, and the dark lines between, where the tin-rich phase has been eaten out by the etch. We give two photographs of Sn 26, one at 656° showing the characteristic light and dark patches of the grains of a chemically uniform body, fig. 67 (this is just above the transformation line), and also a chill at 612° (fig. 68), which shows the complete crystallisation of the Cu_3Sn.

An ingot of Sn 26 was slowly cooled to 380°, and maintained at that temperature for four hours, then chilled. The lines dividing up the η into bars are visible in places, though very narrow. They contain a little of the H body, and practically none of the I eutectic.

The cooling curve of Sn 26 has a peculiarity which at first looks like an accidental defect, but which we have verified. The first long halt gradually rounding to steepness is due to the almost isothermal solidification, the latent heat of solidification ceasing to be evolved when the temperature has fallen to 700°; this gives us very roughly the position of the solidus. The singularity of the curve lies in the second halt. Here there is a sudden rise due to causes analogous to surfusion, the heat evolved being the latent heat of transformation of the solid γ into plates of Cu_3Sn. The short flat which follows the surfusion is unlike anything else in the cooling curves. It is due, we think, to a third evolution of heat rapidly following the second. We can only attribute this to the transformation of the residual γ into a mixture of Cu_3Sn and liquid, a reaction that becomes much more marked in the succeeding alloys. If this be the right explanation of the singularity, then the reaction occurs at a slightly higher temperature than in the case of alloys with more tin. This, again, may be due to the fact that when the change, $\gamma = Cu_3Sn + \text{liquid}$, takes place in Sn 26, there are already crystals of Cu_3Sn in the alloy which may serve as nuclei and precipitate the reaction. In order to verify this cooling curve we repeated it with a different pyrometer and a fresh sample of alloy, and found the same phenomenon.

Sn 27. 40·8 *per cent. of tin.*

In the cooling curve of this alloy the second and third halts are completely merged into one. In fact, the solidus and the liquidus meet very near here at the temperature of the G point, and the possibility of a uniform solid solution ceases. The meeting of these two curves at the G temperature is, as Professor ROOZEBOOM has pointed out to us, a theoretical necessity.

Sn 27. *S.c. chill at* 700° (not reproduced).

This ingot is still covered externally with large rounded rosettes of γ in relief. When cut and polished, about half the surface of the section consists of similar rounded combs, the rest consisting of chill primary immersed in a slender, bright network of the tin-rich residue of mother-substance. The $FeCl_3$ etch blackens this network. The surface of the large γ combs is quite uniform and free from inclusions of the tin-rich material; but the chill primary, when examined with a higher power, is a mass of rounded bars, and has these inclusions in it. We thus see that this chill primary was formed at lower temperatures than the large combs, and did not altogether escape the transformation of the G temperature.

Sn 27. *S.c. chill at* 675° (not reproduced).

This is similar to the preceding except that the large combs occupy a greater area and there is less of the chill primary. We do not give photographs of these upper chills, as the γ is sufficiently well seen in succeeding alloys.

Sn 27. *S.c. chill at* 647° (fig. 69).

In this the combs of large primary have almost entirely filled the ingot before the moment of chilling. It is quite possible, however, to detect here and there the gaps where three lobes of primary meet, and to see in such places a trace of chill primary which is now completely bar-shaped. The surface, when strongly etched, assumes the patchy appearance of a chemically uniform mass of grains, but in the photograph which we give this effect is barely visible.

Sn 27. *S.c. chill at* 635° (fig. 70).

This ingot proves that Sn 27 is capable of existing as a uniform solid solution of γ without mother liquid. The G transformation has not yet taken place, the state of the alloy at the moment of chilling being represented by a point, very near f, in the angle between the lines ef and E$'f$. A few dark spots represent droplets of tin-rich mother-substance still liquid at the moment of chilling, and these contain chill primary consisting of η bars; this liquid is not sufficient in amount to invalidate the above statement that the ingot is a uniform solid solution.

Sn 27. *Chill at* 625° (fig. 71).

Here we see the same alloy as that of the preceding figure but chilled ten degrees lower, *after, instead of before, the* G *transformation.* The uniform γ has broken up into bars (really plates seen edgewise) of η, and at the same time liquid, represented in the figure by dark lines and rows of spots, has been formed.

As Professor ROOZEBOOM has pointed out to us, we can calculate approximately the amount of the G liquid formed in any alloy by the reaction $\gamma_f = Cu_3Sn + liq_G$. For, assuming that f is at Sn 27 and G at Sn 42, let us consider the changes in Sn 26. As the temperature falls through the short interval between the transformation curve ef and the fG line, the following gradual change occurs:—

$$Cu_{74}Sn_{26} = 0{\cdot}5\ Cu_{75}Sn_{25} + 0{\cdot}5\ Cu_{73}Sn_{27},$$

or, more concisely, $\gamma_{26} = 0{\cdot}5\ Cu_3Sn + 0{\cdot}5\ \gamma_{27}$, where the subindices give the atomic percentage of tin in the particular kind of γ.

The change that occurs abruptly in passing through the fG temperature is represented by the equation :—

$$0{\cdot}5\ Cu_{75}Sn_{25} + 0{\cdot}5\ Cu_{73}Sn_{27} = 0{\cdot}941\ Cu_{75}Sn_{25} + 0{\cdot}059\ Cu_{58}Sn_{42},$$

or, more concisely, the final state is $0{\cdot}941\ Cu_3Sn + 0{\cdot}059\ liq_G$.

Thus, assuming that the unit of volume of each substance contains 100 atomic per cents. of copper and tin jointly, we may say that in this alloy the G reaction produces about 6 per cent. of liquid. Considering Sn 27 in the same way, we find for the final state, just below the fG line, about 12 per cent. of liquid. This liquid is represented in the photographs of Sn 26 and Sn 27 by the lines of dark and the rows of black dots in the bars of γ. The regression of the solidus from f to E_2 records this partial liquefaction ; although not unprecedented, it is not a very common phenomenon. The chills at 600° show the effect even better than that at 625°, and a chill at 565°, which was not cooled with extreme slowness before the chill, shows the rows of dots along the axis of each plate still better. We give a photograph of this (fig. 72).

The FG *Alloys.*—Sn 28. 42 *per cent. of tin.* *S.c. chills at* 650° *and* 625° (figs. 73 and 74).

In the upper of these (fig. 73), the rounded γ combs are quite uniform and free from inclusions, but the chill primary, of which there is a considerable amount, consists of bars of Cu_3Sn. In the lower chill (fig. 74), the rounded outlines of the γ combs are still visible, as they by no means fill the field, but are frequently separated by patches of chill primary. The G transformation has, however, taken place, for the combs are broken up into a delicate pattern of bars, and these have the rows of inclusions in them. It is clear that the γ combs do not, at this percentage, ever quite fill the alloy, so that the transition point f must lie to the left of Sn 28.

Sn 33. 47·9 *per cent. of tin.*

The highest chill we have of this alloy is at 676°, not more than 20° below the liquidus; it affords a good example of primary combs of characteristic γ (fig. 75), surrounded by a large excess of matter that was liquid at the moment of chilling; most of this is shown by a higher power to be chill primary, not unlike the large combs.

The chills of Sn 33 at 644° and 628° (figs. 76, 77, and 78) illustrate admirably the transformation at the G temperature. The combs of γ in the upper chill are rounded, quite smooth and free from the inclusions of liquid, while in the lower chill we see instead an angular material, ruled with lines and containing, in what were the lobes of γ, many black dots due to the liquid liberated in the reaction.

The only other example we need give of this is in the case of Sn 38. Here, in the chill at 644° (fig. 79), the rounded combs of γ, though large, are scanty, and they contrast well with the abundant chill primary which approximates to the bar type. At 628° the γ has been transformed, though the parts that were γ combs can still be distinguished from the rest of the alloy, in spite of their now angular character and the bars that run through them (fig. 80). This ingot, however, was evidently chilled before the transformation had completed itself, and the orientation of the bars is very irregular. If we allow the change to complete itself during the slow cooling, we get the beautifully regular pattern of the chill at 606°, in which the large and small crystals are of the same type (fig. 81).

As far as Sn 42 (the G point), similar features are seen in the chilled alloys, but this point marks the extreme limit of the γ type of primary. We shall refer to the lower chills of the EG alloys in discussing the succeeding groups.

Before leaving the region of chills in which γ is found, we wish to draw attention to the resemblance between the combs of γ, from their first appearance in Sn 21 to the latest we reproduce in Sn 38. It is very difficult to get good γ combs in the upper chills of the DE alloys, because the material is so unstable that it is more or less transformed and turned into η during the chill. But with normal combs of γ, such as those of Sn 33 for comparison, it is easy to trace the γ character in the primaries of Sn 21 (fig. 54), Sn 22 (fig. 58), and Sn 25 (fig. 65). Sn 27 forms normal γ combs like those of Sn 33. The maximum amount of γ found in each of the FG alloys occurs in the chill slightly above the G temperature, and this maximum decreases from the whole volume of the ingot in Sn 27 to a vanishingly small fraction in Sn 42.

The GH *Alloys.*—These alloys, ranging in composition from Sn 42 to Sn 87, deposit, when they begin to solidify, crystalline plates of the η type. We have been able to isolate these and analyse them. They appear to be the body Cu_3Sn in an almost or quite pure state. We have, therefore, drawn the solidus as a vertical line, E_2E_3 at the atomic percentage Sn 25. For a particular percentage of tin the large primary plates of η (generally seen in the figure as bars) increase in amount the lower the chilling temperature, so long as this does not fall below 400°. The chill primary is a network of slender bars or plates, that in the polished section may be described as needles. Polish alone shows the η, both primary and chill primary, as a purplish-white surrounded by a pure white tin-rich substance. If the section is kept for some days the contrast becomes greater through the gradual oxidation of the η, the mother-substance remaining a very pure white. For photography a slight ferric chloride etch is preferable, as it leaves the η unchanged and dissolves and blackens the ground. The chills of Sn 42 at 600°, and of Sn 45 at the same temperature, are of this type, but in the former (fig. 82) the large bars of η have curved lines of the tin-rich material (black in the figure) crossing them; these suggest that the very first solid may have been γ. In Sn 45 this feature is not so well marked. This peculiarity perhaps indicates that the curve FG might have been traced for some distance below GH, in a region of unstable equilibrium.

If we compare chills, taken at, or a little below, 400°, of all the alloys from Sn 27 to Sn 87, that is almost from E to H, we find the η decreasing in amount from a quantity that almost fills the alloy at Sn 27 to a vanishingly small quantity, and with the larger percentages of tin the ingots are very liquid at the moment of chilling. Figs. 83 and 84 of ingots of Sn 38 and Sn 50 that had been kept in the vapour of boiling sulphur (at 445°) for 70 hours and then sharply chilled, show the decrease in the η with increasing percentage of tin, and fig. 85 of Sn 80 chilled without a very slow cool at 433° illustrates this decrease in a more marked way.

In the sulphur-boiled ingots in which the η has been in contact with the liquid for a long time, no doubt at a slightly varying temperature, the bars are rounded, and in fig. 83 one sees a tendency for them to group themselves into families. This rounded appearance is not seen in the η except in the sulphur-boiled ingots; the more usual appearance is of great angularity in the outline of the crystals, as in fig. 86, of a slow-cooled chill of Sn 50 that was maintained at 420° for some hours and then chilled. In this ingot the plane of section coincided with the plane of the plates; an inspection of the outside of the ingot shows that a section at right angles would have cut the plates at right angles and given a pattern of bars.

If one of the FGH alloys is cooled below 400° before chilling the amount of η is not increased but the bars are margined by a new substance, and the same new body is present as chill primary between the bars. This new substance H is the primary crystallisation of the branch HI of the liquidus. H and η are both very little acted on by hydrochloric acid, especially if excess of tin is present, and etching consequently leaves them both white on a dark ground. But the η gradually oxidises in the air and darkens so that it is readily distinguished from the H. Fig. 87 of Sn 73, chilled at 373°, illustrates the effect. It will be noticed that the bars of η are true crystals bounded by plane faces. They remind one of the twinned bars of η seen in fig. 57. If we chill below 400° a little H can be detected even in Sn 26, but it is well seen in the ingot of Sn 29 that was chilled at 380°, after having been kept at this temperature for four hours (fig. 88). In this ingot, except a few holes which may have been full of tin-rich mother-substance before the etch, the η and H fill the ingot. The conversion of the η into H by reaction with liquid at the temperature of 400° requires more detailed study, but we will reserve this point until the survey of the remaining groups is complete.

The HI *Group.*—The singularity H occurs in the liquidus at Sn 87. The curve does not change its direction perceptibly here, but Roberts-Austen and Stansfield found a row of second halts in the cooling at this temperature in all alloys from about Sn 27 to Sn 87. We have not verified their results pyrometrically, but the microscope amply confirms them. The evolution of heat is due to the reaction η + liquid = H. With perfect equilibrium transformations the whole of the η in all alloys between the percentages given by the points H′ and H ought to disappear at temperatures below 400° in consequence of this transformation, but in the alloys as usually prepared the H only forms a thin coating over the crystals of η, much of the η remaining even in ingots that have not been chilled. We have however succeeded, by maintaining the ingots for a very long time at temperatures a little below 400°, in removing all η from alloys between the points H′ and H. We shall return to this point.

With more tin than that contained in Sn 87, that is, in the HI alloys, the primary crystallisation should consist of H, and, in fact, as an unchilled ingot of Sn 90 shows (fig. 89), the alloy consists of primary crystals of H in a eutectic of H and tin. The crystals of H are often hollow, as if they had grown round something that had afterwards disappeared; this again suggests the possibility that, through a surfusion of the H, the η may have formed first and been decomposed when the H began to crystallise. We are not quite confident that the above is the true explanation of the peculiar and well-known form of the H. It will be noticed that the exterior of the crystals of H is rectilinear and angular, and that in the neighbourhood of a large crystal of H the mother-liquid has been so much exhausted of that body that there are no particles of H in the eutectic, while in places remote from a large crystal of H the eutectic is full of minute specks of that body. The same feature can be detected in the long slender crystals of H in an unchilled ingot of Sn 95 (fig. 90).

The IK *Alloys.*—With more tin than corresponds to the point I, it is no longer a copper-rich body which crystallises first, but a tin-rich body which must be very nearly pure tin. A chill of Sn 99, when well polished, showed primaries of a new type in a eutectic, but etching reagents destroy the pattern of primaries and only leave the patchy appearance of a solid solution. This end of the series deserves more attention than we have as yet been able to devote to it.

The Transformation η + liquid = H.

This reaction, which commences when any alloy of a composition between Sn 25 and Sn 87 sinks below the temperature of 400°, is necessarily a slow one, for as soon as the plates of η have become covered with a coating of H, the process can only proceed by a diffusion through the thickening layer of H. The diffusion is far from rapid at temperatures near 400°, and at much lower temperatures it practically ceases. Consequently, with ordinary rates of cooling, these alloys contain when cold three phases instead of two. This is recorded in the diagram by placing a bracket round the symbol of the third phase whose presence is due to an incomplete reaction. But, although this incomplete equilibrium is the usual condition of the alloys, it can be avoided. We have succeeded in transforming all the alloys from

Sn 45 to Sn 87 into complexes of H and Sn, free from η, and although it will not be quite so evident from the photographs, we think we have also eliminated all the eutectic from the alloys between Sn 25 and Sn 45. This result was attained by maintaining the temperature of the ingots for hours, and, in some cases, for many days and nights, at a temperature near 350°. By varying the length of this period of incubation one can watch the gradual disappearance of the phase to be eliminated The constant temperature was that of a bath of boiling mercury, the little ingots being sealed in glass tubes and suspended in the vapour. The first alloy systematically examined in this way was Sn 50, and the series of photographs we publish illustrate the changes very well (figs. 84, 91, 92, 93, 94).

The Sn 50 maintained for some hours at 420° and then chilled (fig. 86), has been already described; it contained no H. Fig. 91 is that of an ingot that was not cooled very slowly, but was not chilled at all. This section cuts the plates of η so that they appear as bars. The η has oxidised a good deal before the photograph was taken, and it is seen to be margined and traversed by narrow threads of pure white H. This small amount of H is what one usually finds when no special pains have been taken to complete the reaction by slow cooling.

The next ingot (fig. 92) had been maintained for 10 hours at 380° before chilling. The η is now seen to be surrounded by a thick margin of H, and although the photograph does not perhaps make it evident, the proportion of tin-rich mother-substance has decreased considerably. The next ingot was maintained for 60 hours in the mercury bath at about 350°. It will be seen from the photograph (fig. 93), that the η is now reduced to a few spots and lines enveloped in the massive H.

In order to ascertain whether the reaction could be made complete, an ingot was boiled for 21 days and nights in the mercury bath. This operation, as fig. 94 shows, has removed every trace of η, and very much changed the character of the masses of H. The shape of the H had been hitherto dependent on that of the original η, but now the grains of H are independent of each other, and though still rounded they are beginning to change into polyhedra with plane faces. It would be interesting to study the effect of a still longer incubation on the shape of the H. We have isolated these little pellets of H and examined them under a low power; they are then seen to be crystalline.

The ingot of Sn 50 (fig. 94) contains around the masses of H a considerable amount of tin-rich eutectic, in other words the H does not fill the alloy; consequently, this H cannot be exactly CuSn. We therefore examined ingots of Sn 40, 42, 45, as well as ingots of Sn 55, 60 and 85, that had all been heated for 21 days in the mercury bath. The result showed that all the η, except mere traces, could be removed from Sn 45, but that, although large portions of the section were compact H, yet there were large gaps in the H (fig. 95). These gaps appear, however, to be cavities in the ingot, and not spaces full of the eutectic. These gaps are numerous in all the alloys, such as Sn 45 to Sn 40, when they have been boiled for a long time in mercury; we think it probable that they are due to a contraction accompanying the reaction in which the H is formed from the mixture of η and liquid.

The chill of Sn 42 (fig. 96), and in a still more marked degree the chill of Sn 40 (fig. 97), contains η uniformly scattered through the massive H. This study of the H transformation seems to point to the conclusion that the H body has at 350° a composition not far from that of Sn 45. This conclusion is confirmed by the results of analyses of the H extracted from ingots of Sn 90, which give the value of Sn 45·5. Thus neither the microscope nor the analyses allow us to regard H as pure CuSn, but it is very probably this body with a few per cent. of Cu_3Sn in solid solution.

Fig. 98 is a photograph of an ingot of Sn 60 after 21 days in mercury at 350°. Like most of the ingots boiled in mercury it was not chilled, although it was cooled rapidly at the end of the period of boiling. When compared with Sn 50 we see less of the H and more of the eutectic. The progress of the masses of H towards the condition of polyhedra is well marked.

Fig. 99 is an ingot of Sn 85 after 21 days in mercury. Some of the masses of H have the rounded form that indicates their origin from η, but there are other crystals of H which are probably idiomorphic.

Fig. 101 illustrates the facility with which the reverse change

$$H = \eta + \text{liquid}$$

takes place. It is an ingot of Sn 50 that had been heated for 10 days in mercury vapour, the η having been thus almost entirely removed; it was then heated for a few minutes to a temperature a little above 400°, with the result that all the masses of H have broken up into η and liquid. The pattern, resembling that of 93, produced by the mercury boiling, can still, however, be traced.

Fig. 100 records an early attempt to study the reaction of the H temperature. A considerable mass of the alloy Sn 90 was maintained for several hours at a temperature slightly below 400°, and it was automatically stirred by means of a massive copper stirrer made of coils of thick wire. The reaction, which produced nothing but H, was continued until the stirring was brought to an end by the large quantity of solid H that had formed. The ingot was then cut and polished as usual. A comparison with fig. 89 makes the great increase in the amount of H very evident.

The Isolation and Analysis of the Bodies η *and* H.—The fact observed during the etching of the alloys, that hydrochloric acid has no perceptible action on the crystals of η or H, can be utilised for the separation of these bodies from an alloy in which one of them is present together with tin. If we wish to get pure η, the alloy must be sharply chilled at a temperature above 400°; to obtain pure H, the alloy must have been maintained at a temperature a little below 400° for a period long enough to transform all the η. It is in the observance of these two precautions that our method of isolating the substances constitutes an advance on previous work. We find that the ingots of alloy are rapidly disintegrated by the action of strong hydrochloric acid at 30° C., and that if air is excluded there is no solution of copper until all the excess of tin has been dissolved. The alloys disintegrate to a grey or black mud, which can be elutriated, leaving as a residue well-formed plates of η or brilliant slender spearlike filaments of H. The washed H can be left for days in contact with strong cold hydrochloric acid without perceptible solution of either copper or tin. The η is more attacked when the excess of tin has been removed, but the attack is slight.

The following are the results of some analyses, the composition being expressed in percentage weights of tin. In a few cases the copper was independently determined.

COMPOSITION of η.

Alloy.	Chilled at	Percentage of tin in η.	Percentage of copper in η.
Sn 35	550°	39·09	—
Sn 35	550	38·53	61·20
Sn 35	450	39·15	—
Sn 50	450	39·10	60·89
Sn 50	450	38·5	—
Sn 50	450	38·77	—
Sn 65	450	41·71	57·88
Sn 65	450	42·20	—

The above were early experiments, and no very great care was taken to maintain the temperature constant for a considerable time before chilling. Three ingots were however, treated after three days and nights in boiling sulphur vapour and then chilling. This preparation may be expected to ensure equilibrium between the solid and the liquid phases at 450°. The results are given below.

η SULPHUR Boils 454°.

Alloy.	Sn 38.	Sn 38.	Sn 50.	Sn 70.
Per cent. of tin in the η	38·73	38·53	39·73	38·97

In theory, whatever the percentage of the alloy, the composition of the solid phase at a particular temperature should be the same, and depend on the temperature only. But the character of the ingot at the moment of chilling seriously affects the possibility of extracting the desired body free from excess of tin, as, unless each plate of η is separated from its neighbours, inclusions of tin may be unavoidable. Most of the discrepancies in the result are probably due to this cause. In view of the value obtained from Sn 70 in the sulphur-boiled series, we do not think that the earlier very high values from Sn 65 are to be trusted; if we neglect these we get an average content of slightly under 39 per cent. of tin in the η, with practically no difference between the η at 550° and 450°. It must be remembered that no method of chilling will prevent the presence of a trace of H on the plates of η.

The percentage required by the formula Cu_3Sn is 38·35, so that the analyses are consistent with the view that the η is this compound with a little of a more tin-rich body in solid solution; but the excess of tin is so small and so easily accounted for that we have drawn the solidus from E_2 to E_3 as a vertical straight line.

The samples of H were prepared in various ways and isolated from excess of tin in the manner above described. The H prepared by the use of the copper stirrer, that is the H of fig. 100, contained 61·2 and 61·4 per cent. of tin; after re-crystallisation in tin in a vacuous tube and separation from excess of tin, it contained 61·5 and 61·85 per cent. Sn 45, after 21 days in mercury vapour, gave 60·42 per cent. Sn 60, similarly treated, gave 61·15, and Sn 90, after the same treatment, gave 60·8 and 61·2 per cent. All these, with the exception of the re-crystallised H, had been maintained for a long time at 350°. The mean value, neglecting that of the re-crystallisation H, is 61·1 per cent. A sample of Sn 90 was incubated for three days and nights at 250°, after a previous period at 350°: the H extracted from it contained 61·91 and 61·73 per cent. of tin. These two values suggest, though they can hardly be said to prove, an increase in the tin content of the H at lower temperatures. The percentage of 61·1 at 350° gives to the H an atomic percentage of 45·5, and agrees extremely well with the results of the microscopic examination of the alloys boiled in mercury. We have fixed the point H′ in the diagram in accordance with these results.

There is a reasonable certainty that the H is not pure CuSn, though it may very well be that body containing a little of the higher compound in solid solution. There is very little justification from these results for the slope we have given to the branch H′H″ of the solidus, and we have therefore drawn it as a dotted line to indicate the uncertainty. We think a further examination of such alloys as Sn 47 after a prolonged heating at 250° may settle the position of H″. At present, the only argument for placing H″ at Sn 50 is to be found in the numerical value of the depression of the freezing-point of tin by small additions of copper, that is, from the slope of the branch IK of the liquidus. This appears to prove that, whatever the molecule in solution in the liquid tin, it can contain only one atom of copper.*

We hope that the experimental evidence given in the preceding pages will be considered to justify the general conclusions of Section I.

We are much indebted to Miss D. MARSHALL, B.Sc., Lecturer at Girton, and to Mr. W. FEARNSIDES, B.A., of Sidney College, for the help they have given us in the

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* 'British Association,' 1900—"Report on Alloys," by F. H. NEVILLE.

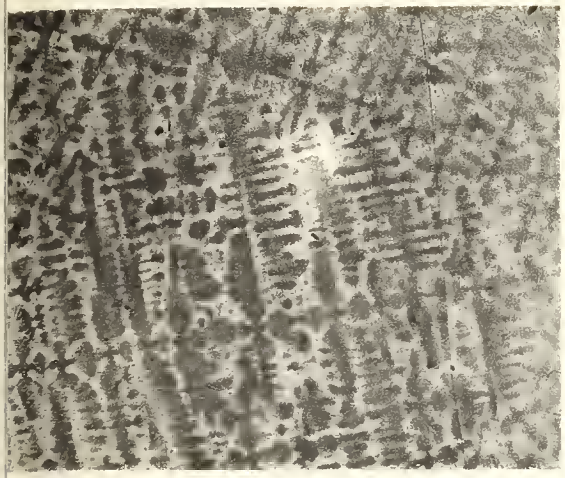
experiments. Mr. FEARNSIDES took many of the more difficult photographs, and carried out many of the tedious experiments on the slow cooling and chilling of the alloys.

During the course of the research Professor BAKHUIS ROOZEBOOM was kind enough to write to us several encouraging and instructive letters on the theory of the subject, and we wish here to express our gratitude to him.

We have also had help and encouragement from the late Sir GEORGE STOKES.

PLATE 1.

Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
1	Sn 1	1·85	× 18	Unchilled	Ignited	Dark cores in the α.
2	Sn 2	3·7	× 45	C. 1025°	HCl + FeCl$_3$	Dark α primaries.
3	"	3·7	× 10	S.c.c. 957°	"	Grains of α possessing different orientation. Oblique illumination.
3A	"	3·7	× 10	S.c.c. 957°	"	Dark α in white liquid. Vertical illumination.
4	"	3·7	× 18	S.c.c. 882°	HCl	Homogeneous α.
5	"	3·7	× 18	V.s.c.c. 770°	NH$_3$	"
5A	Sn 4	7·2	× 18	S.c.c. 800°	HCl	Cores in the α combs.
6	"	7·2	× 18	V.s.c.c. 900°	HCl + Br	α combs and liquid.
7	"	7·2	× 45	V.s.c.c. 800°	HCl	Homogeneous α.
8	"	7·2	× 18	V.s.c.c. 775°	HCl + Br	Cores in α. No matrix.
9	"	7·2	× 18	V.s.c. not chilled	HCl + FeCl$_3$	Grains of uniform α.
10	Sn 6	10·15	× 45	C. at 966°	"	Dark α in white liquid.
11	"	10·15	× 18	S.c.c. 805°	HCl and repolish	Light α and liquid.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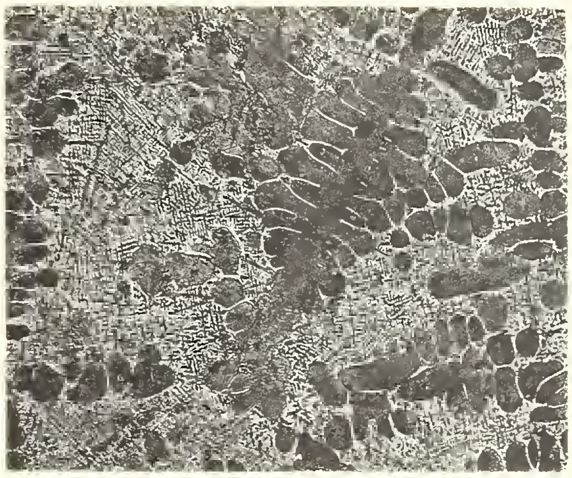
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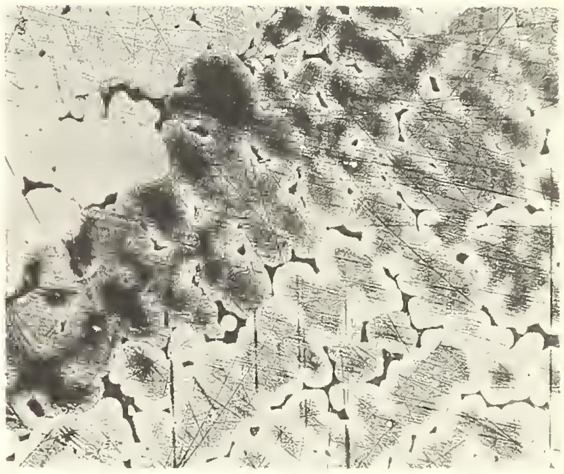
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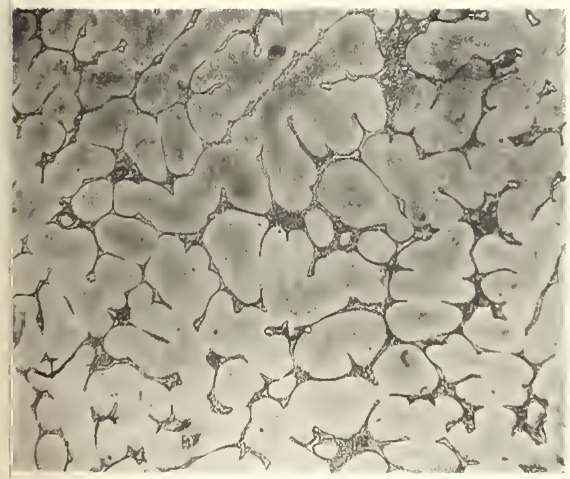
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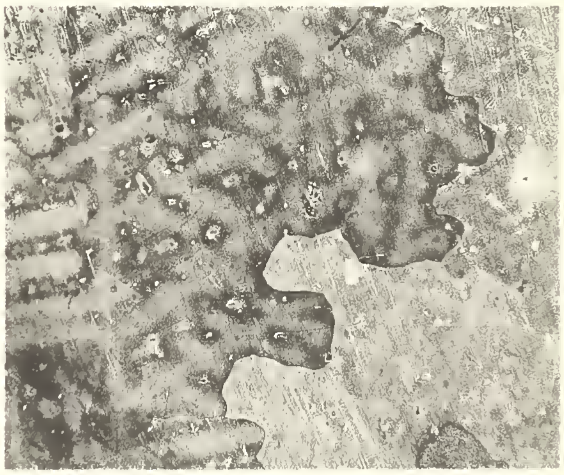
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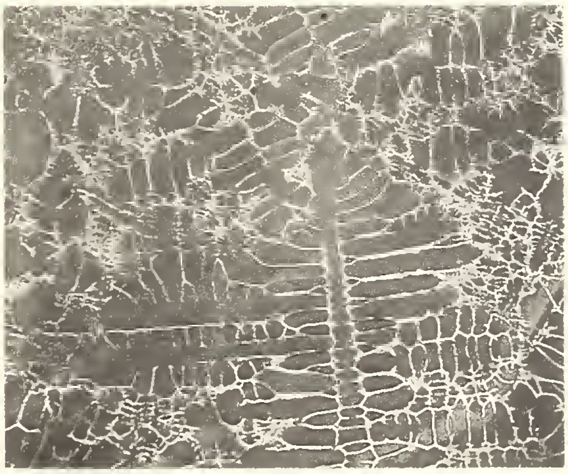
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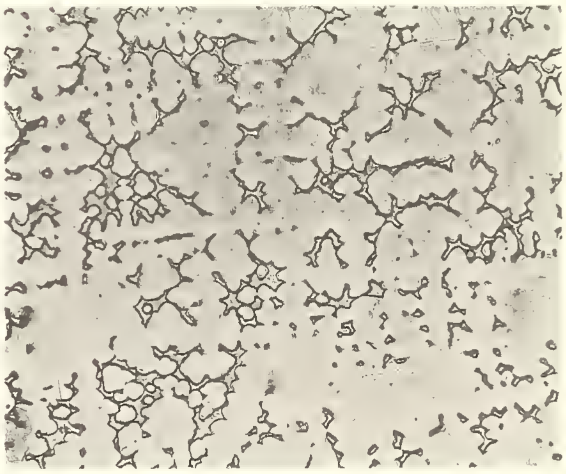
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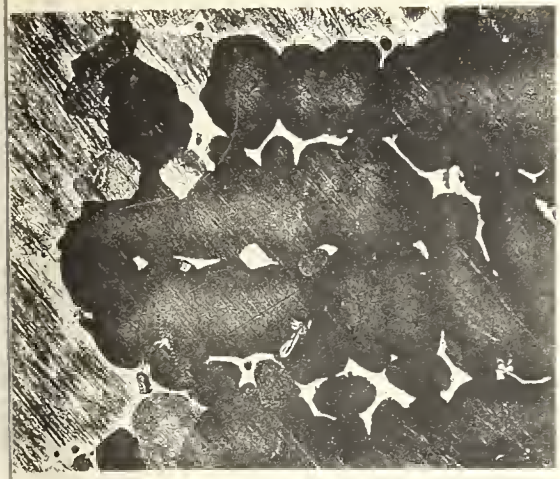
PLATE 2.

Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
12	Sn 6	10·15	× 18	V.s.c. not chilled	$HCl + FeCl_3$	α, dark. C′ complex, light.
13	,,	10·15	× 280	,, ,,	,,	Patch of C′ complex ($\alpha + \delta$).
14	Sn 9	15·6	× 120	C. 880°	,,	Primary and chill primary of α (light), in matrix that was liquid at chilling temperature.
15	,,	15·6	× 18	C. 777°	,,	α, light. β, dark.
16	,,	15·6	× 18	V.s.c.c. 546°	,,	,, ,,
17	,,	15·6	× 18	V.s.c.c. 470°	,,	α, dark. C′ complex, light.
18	,,	15·6	× 280	V.s.c.c. 546°	,,	Uniform dark β, margin of white δ. α outside.
19	,,	15·6	× 280	V.s.c.c. 470°	,,	Patch of C′ complex ($\alpha + \delta$), bordered by δ. α outside.
20	Sn 12	20·3	× 18	S.c.c. 805°	,,	Primary α, light. Liquid darker. Chill primary of β, darkest.
21	,,	20·3	× 18	V.s.c.c. 775°	,,	Partly dissolved α, light. Ground of solid striated β.
22	,,	20·3	× 18	C. 550°	,,	Light α that has crystallised out of the solid uniform β. Dark β.
23	Sn 13·5	22·5	× 18	V.s.c.c. 775°	,,	Striated β free from α.



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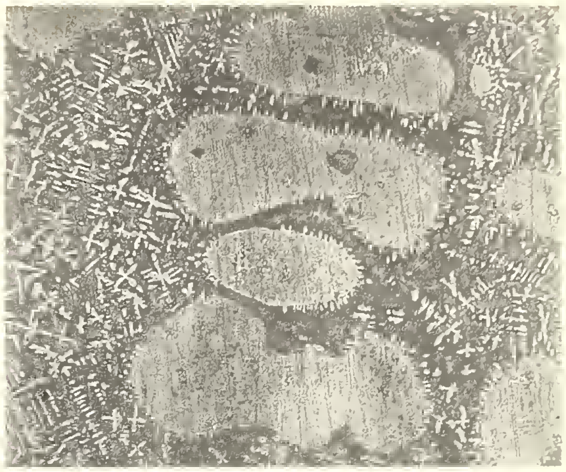

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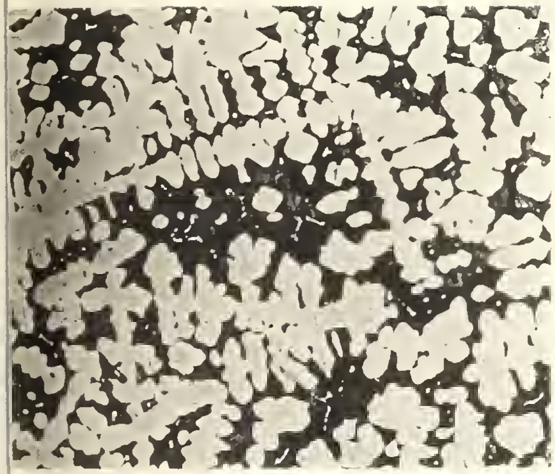

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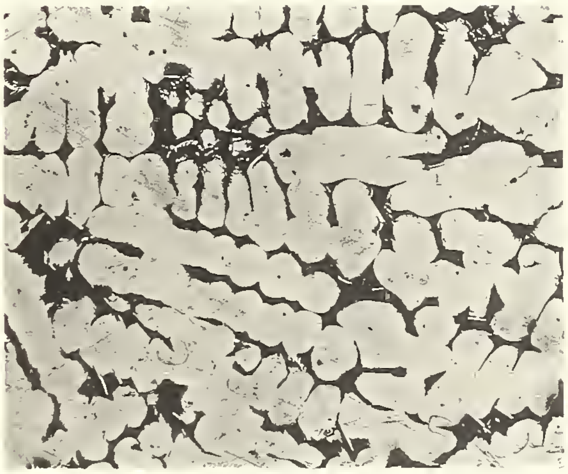

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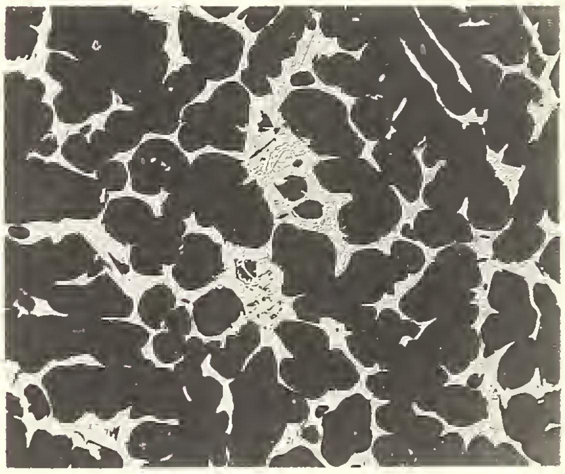

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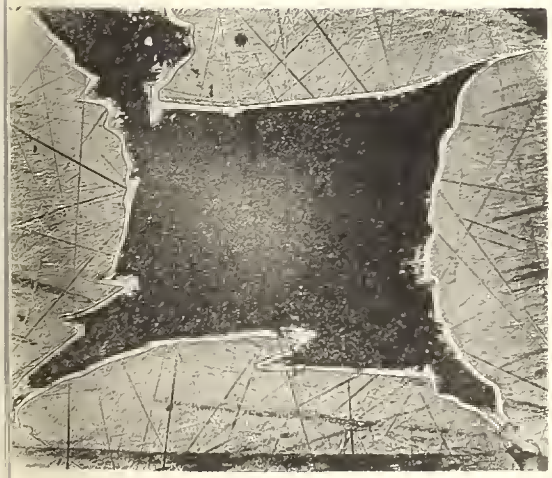

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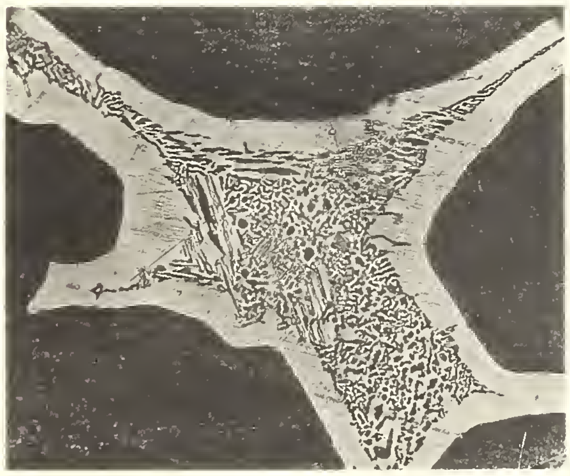

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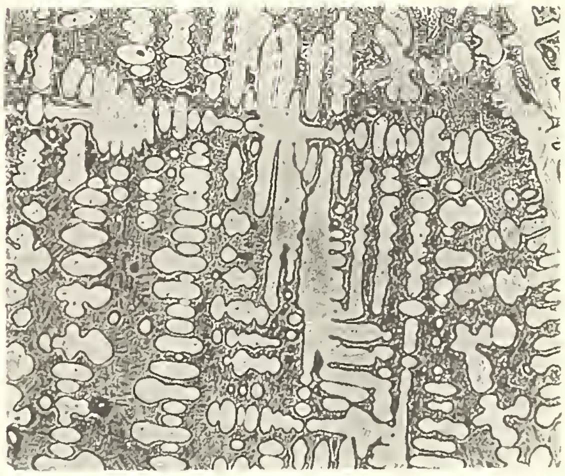

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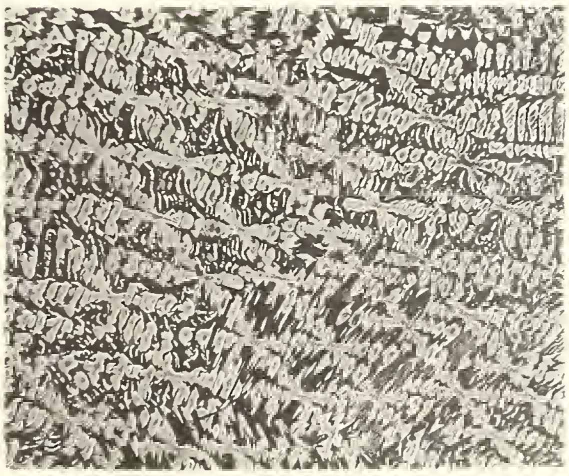

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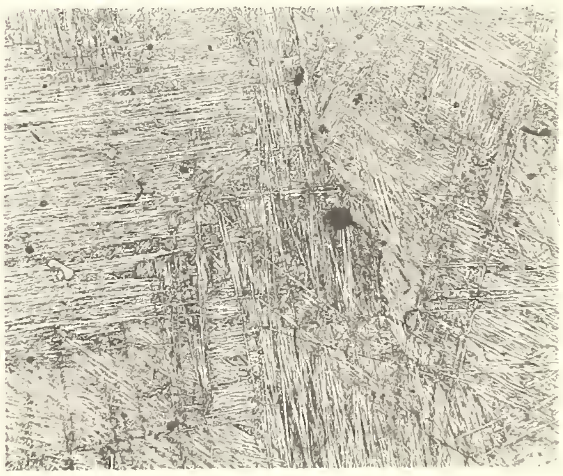

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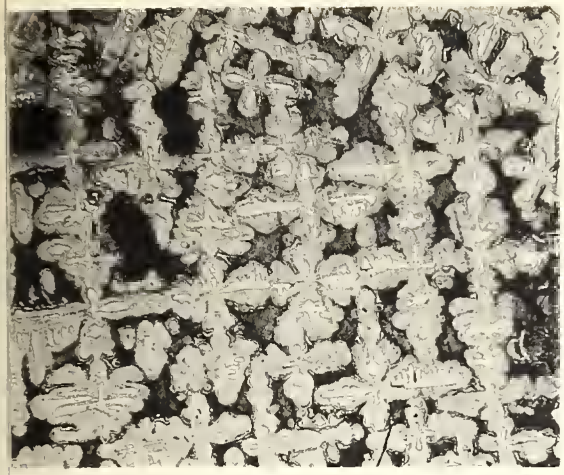
PLATE 3.

Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
24	Sn 13·5	22·5	× 18	C. 765°	$HCl + FeCl_3$	Residue of α, white, in β combs, darker. Liquid darkest.
25	,,	22·5	× 45	C. 775°	,,	Residue of α in darker striated β. Dark chill primary of β. Liquid light.
26	,,	22·5	× 18	C. 740°	NH_3 (negative)	Residual α, light. β, dark.
27	,,	22·5	× 18	C. 558°	$HCl + FeCl_3$	New α, light. Uniform β, dark.
28	Sn 14	23·3	× 18	V.s.c.c. 800°	,,	Primary α, light. Liquid and chill primary of β, dark.
29	,,	23·3	× 18	V.s.c.c. 675°	,,	Striated β only.
30	,,	23·3	× 18	V.s.c.c. 600°	,,	New α, white. Dark and striated β.
31	,,	23·3	× 18	V.s.c.c. 530°	,,	New α, white. Uniform β, dark.
32	,,	23·3	× 18	V.s.c.c. 470°	,,	α, dark. C′ complex $(\alpha + \delta)$, light.
33	Sn 15	24·75	× 18	V.s.c.c. 600	,,	Grains of uniform β.
34	Sn 15·5	25·5	× 45	C. 750°	,,	Dark primary crystals of β, chill primary of β. Tin-rich liquid, white.
35	,,	25·5	× 45	C. 552°	,,	Uniform β. *Oblique illumination.*



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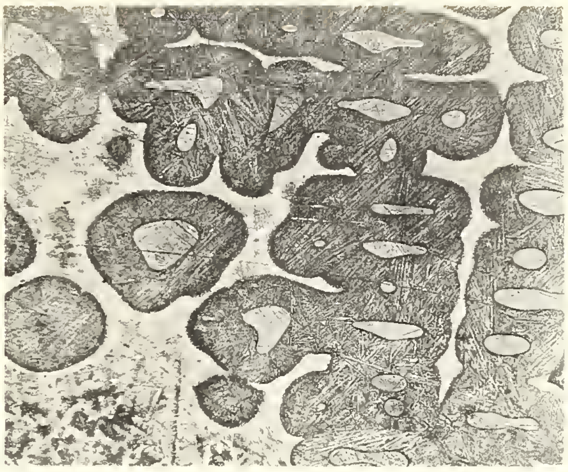

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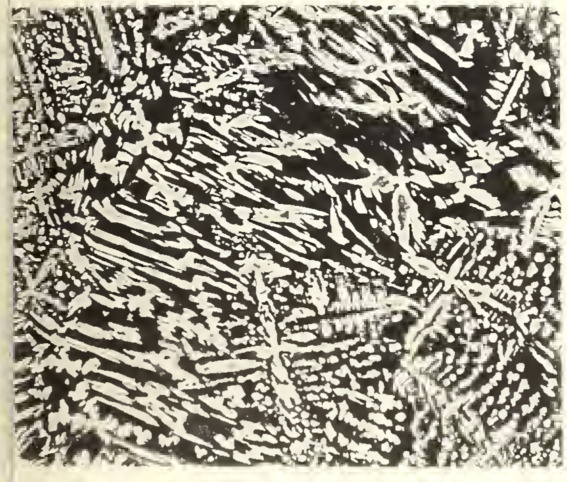

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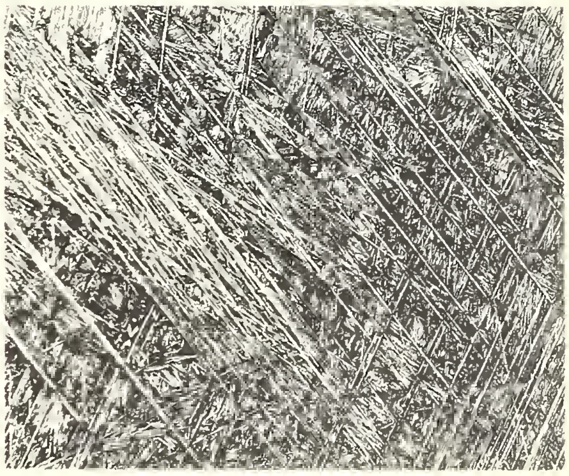

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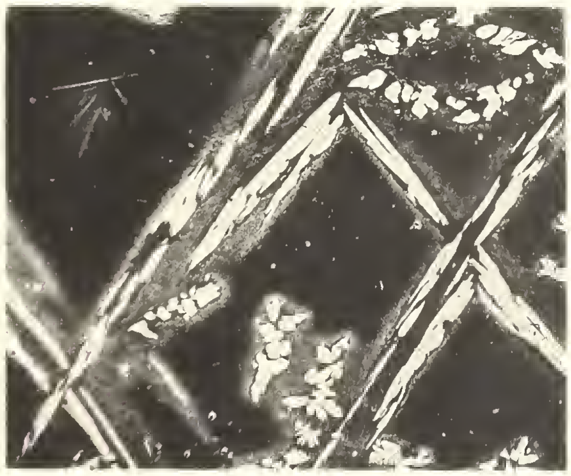

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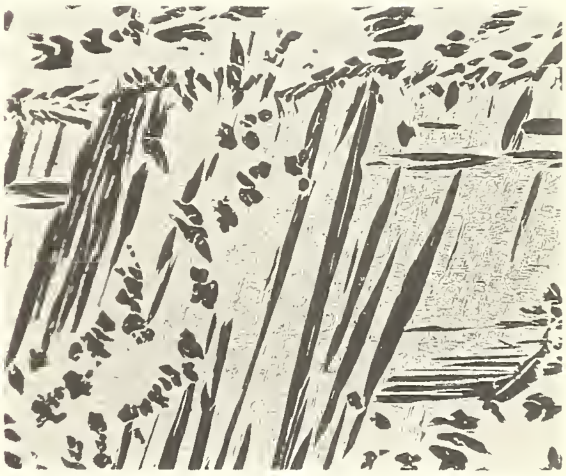

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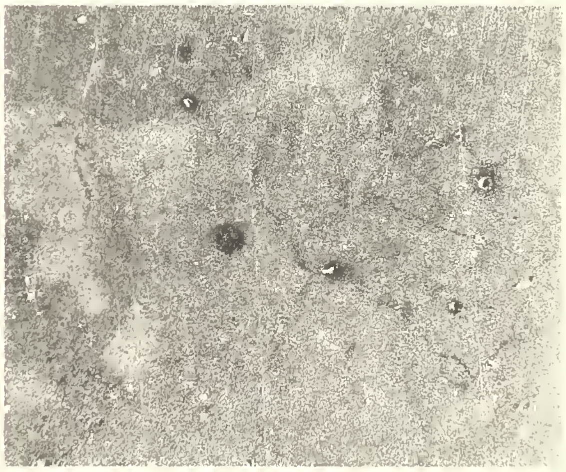

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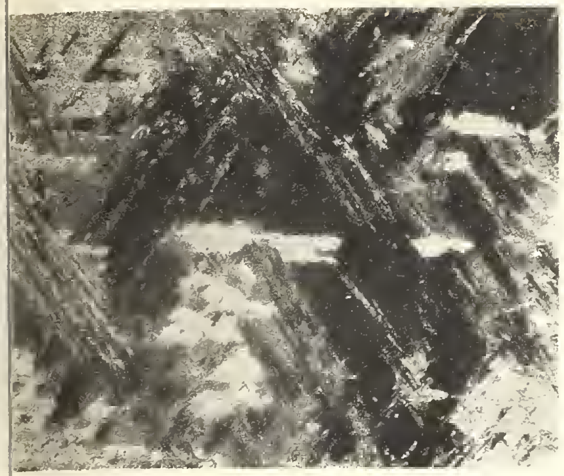
PLATE 4.

Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
36	Sn 15·5	25·5	× 45	C. 452°	$HCl + FeCl_3$	C′ complex. *Oblique illumination.*
37	,,	25·5	× 550	C. 452°	,,	C′ complex. Vertical illumination.
38	Sn 16	26·25	× 18	V.s.c.c. 752°	,,	Dark β. Tin-rich liquid white.
39	,,	26·25	× 18	V.s.c.c. 738°	,,	β filling ingot.
40	,,	26·25	× 280	Not chilled	,,	Crystals of δ in C′ complex.
41	Sn 17	27·65	× 45	V.s.c.c. 745°	,,	Maximum of β in liquid.
42	,,	27·65	× 18	C. 731°	NH_3	Dark β in tin-rich matrix.
43	Sn 18	29·05	× 18	C. 734°	$HCl + FeCl_3$	β decomposing (D. reaction).
44	Sn 19	30·4	× 125	C. 733°	,,	,, ,,
45	Sn 18	29·05	× 45	V.s.c.c. 728°	,,	Homogeneous. Probably γ.
46	Sn 17	27·65	× 45	C. 495°	,,	Commencement of δ crystals.
47	,,	27·65	× 250	C. 450°	,,	White δ in C′ complex.



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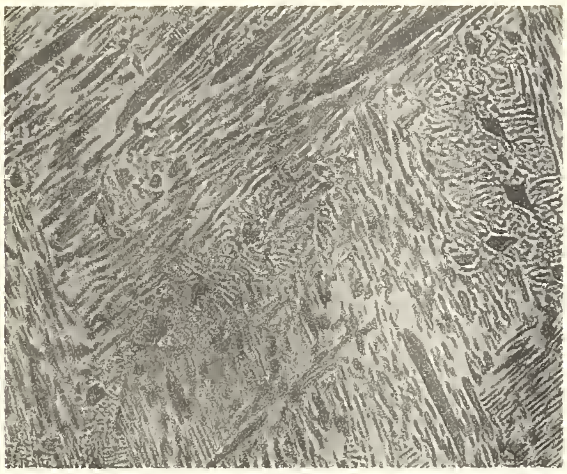

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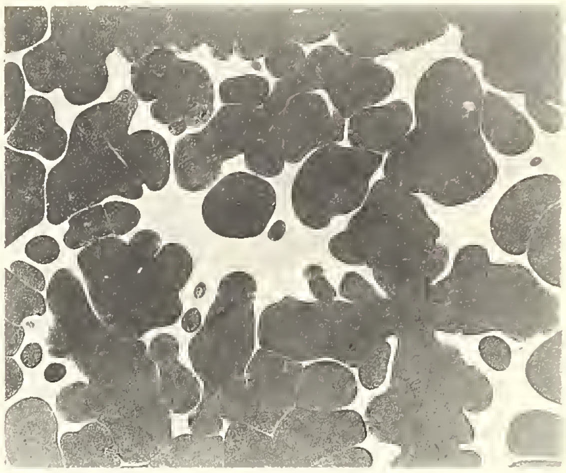

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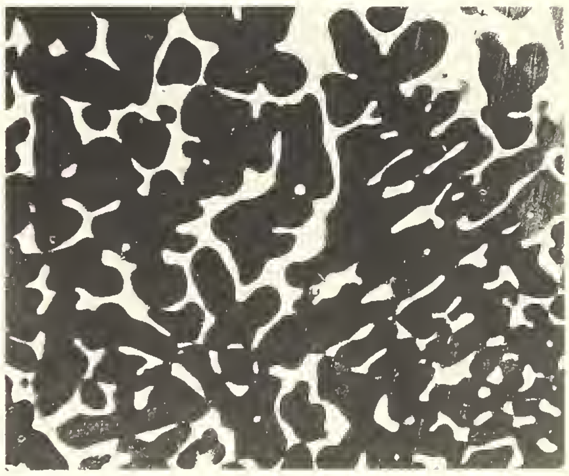

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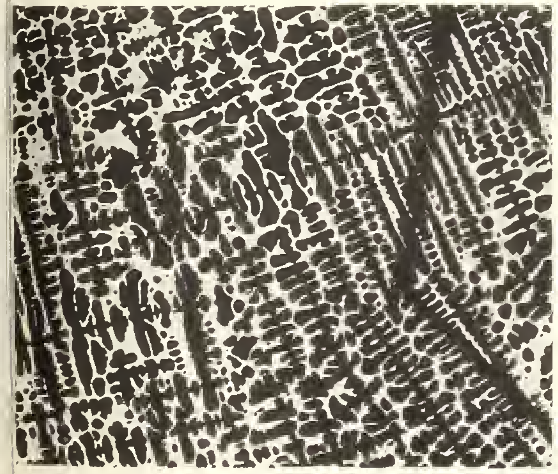

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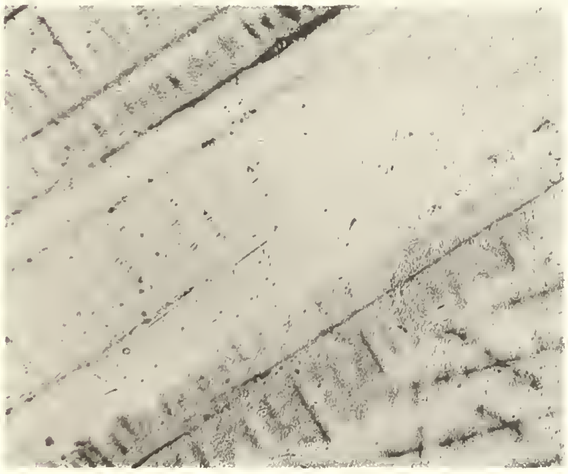

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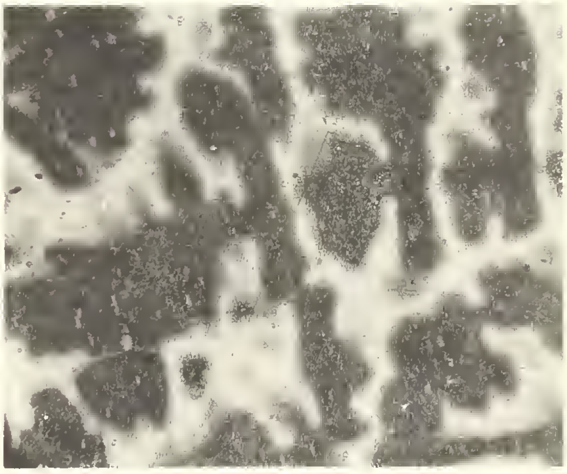

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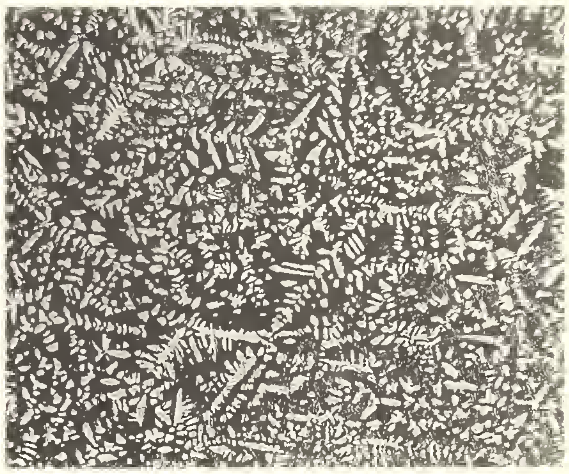

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PLATE 5.

Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
48	Sn 18	29·05	× 45	S.c.c. 550°	HCl + $FeCl_3$	Uniform solid.
49	Sn 19	30·4	× 45	S.c.c. 550°	,,	White crystallisation of δ.
49A	,,	30·4	× 45	S.c.c. 550°	,,	,, ,,
50	Sn 18	29·05	× 45	C. 501°	,,	,, ,,
51	Sn 20	31·8	× 18	C. 726°	,,	Decomposing β in a white tin-rich matrix.
52	,,	31·8	× 45	Not chilled	,,	White δ. Traces of C′ complex.
53	Sn 19	30·4	× 800	,,	,,	Patches of C′ complex in lighter α.
53A	Sn 20	31·8	× 600	,,	,,	Patches of C′ complex in lighter α.
54	Sn 21	33·15	× 45	S.c.c. 725°	,,	γ primary and chill primary.
55	,,	33·15	× 45	C. 650°	,,	Uniform γ.
56	,,	33·15	× 45	S.c.c. 590°	,,	Dark η. Light δ.
57	,,	33·15	× 45	C. 580°	,,	Twinned plates of η.
58	Sn 22	34·45	× 45	C. 733°	,,	Primary combs of γ.
59	,,	34·45	× 18	C. 690°	,,	Uniform γ and slender dark bars of η.


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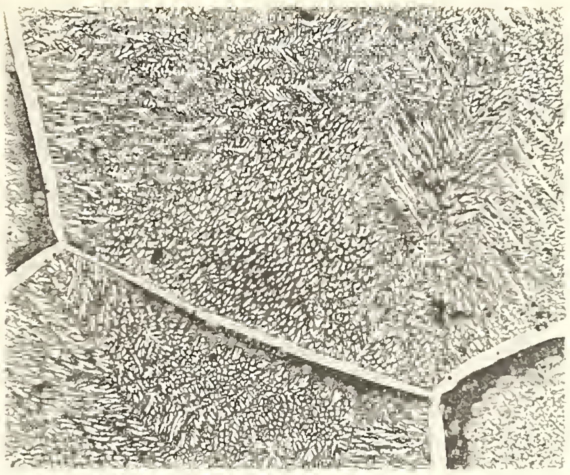
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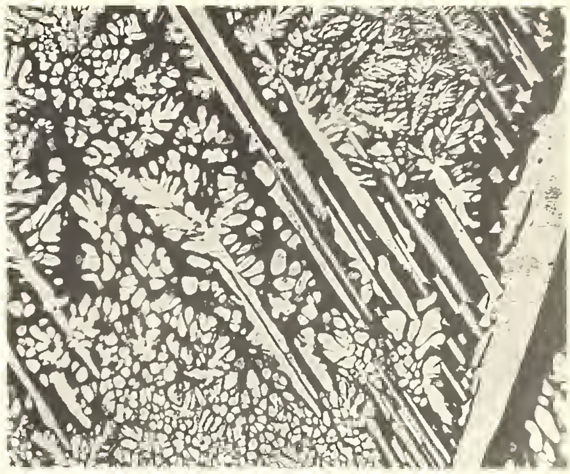
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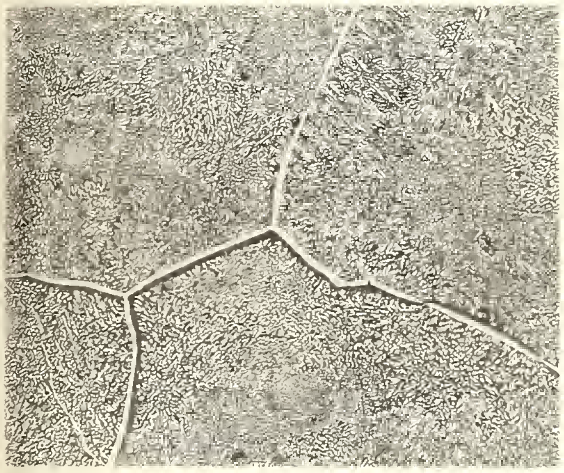
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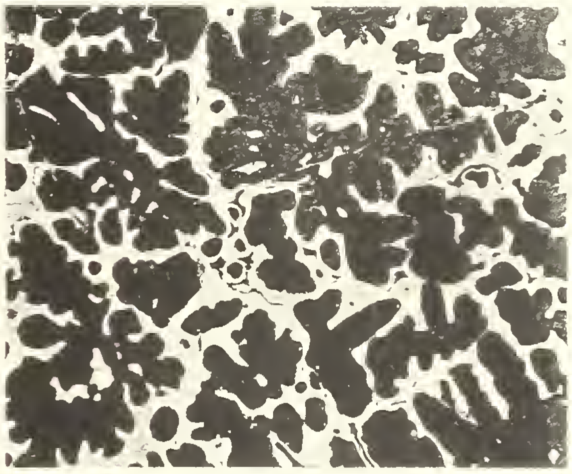
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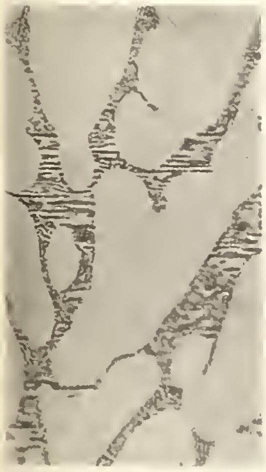
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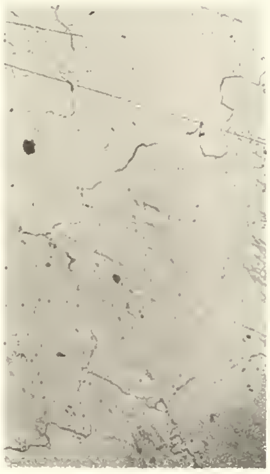
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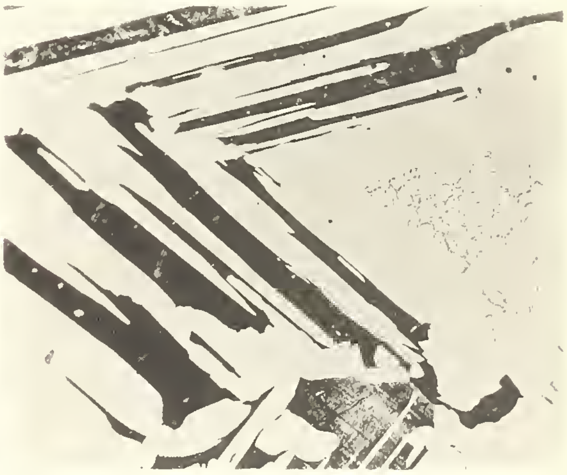
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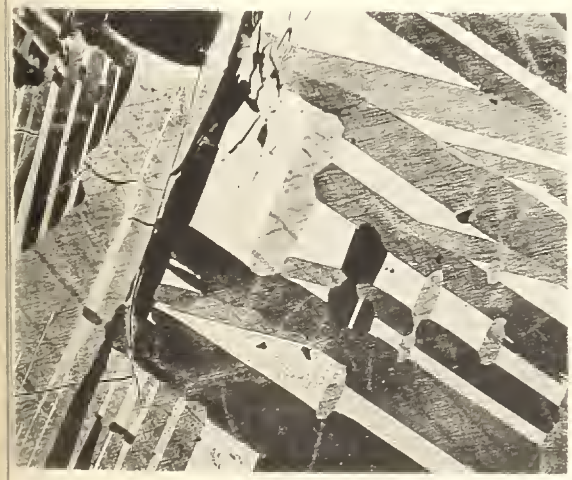
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PLATE 6.

Figure	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
60	Sn 22	34·45	× 18	S.c.c. 565°	$HCl + FeCl_3$	Dark bands of η and lace complex of $\delta + \eta$.
61	,,	34·45	× 45	C. 495°	,,	Dark bars of η and lace bars of $\delta + \eta$.
62	Sn 23	35·8	× 18	V.s.c.c. 620°	,,	Crystallisation of η increasing in amount.
63	Sn 24	37·1	× 18	S.c.c. 685°	,,	Solid γ (crystallisation of η not wholly prevented by chill).
64	,,	37·1	× 18	S.c.c. 635°	,,	Dark crystals of η nearly filling the alloy.
65	Sn 25	38·4	× 13	S.c.c. 720°	Ignited to orange	Copper-rich γ combs darker than tin-rich liquid.
65A	,,	38·4	× 45	S.c.c. 720°	,,	Shows the breaking up of the γ into complex of fig. 64.
66	,,	38·4	× 18	Not chilled	$HCl + FeCl_3$	Bars of differently oriented η.
67	Sn 26	39·65	× 45	C. 656°	,,	Solid solution of γ.
68	,,	39·65	× 45	C. 612°	,,	Plates of η.
69	Sn 27	40·8	× 18	S.c.c. 647°	,,	γ with traces of liquid and chill primary of η bars.
70	,,	40·8	× 45	S.c.c. 635°	,,	Solid solution γ.
71	,,	40·8	× 45	C. at 625°	$HCl + Br$	Plates of η with inclusions of tin-rich liquid.

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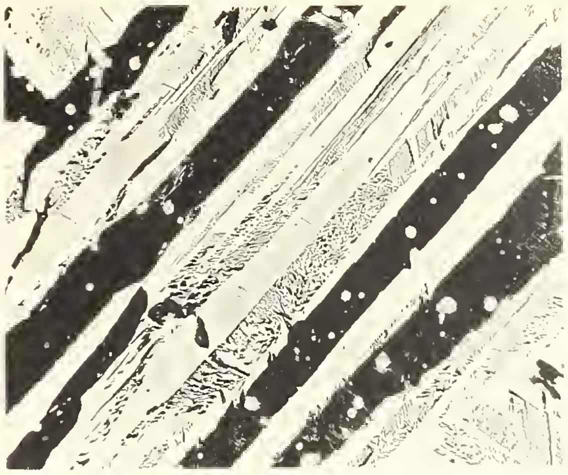

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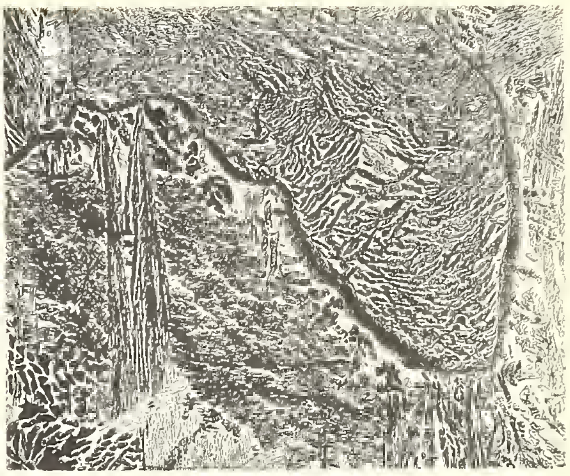

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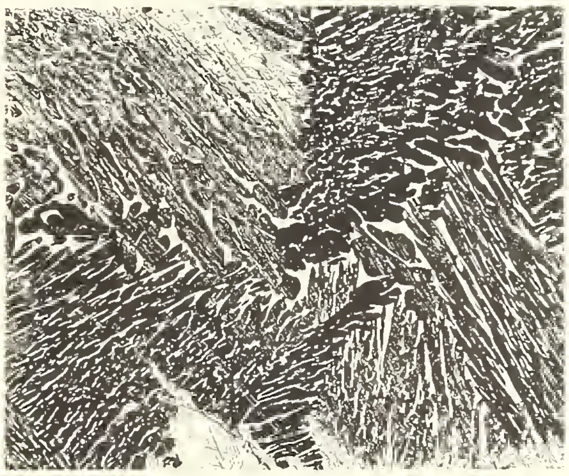

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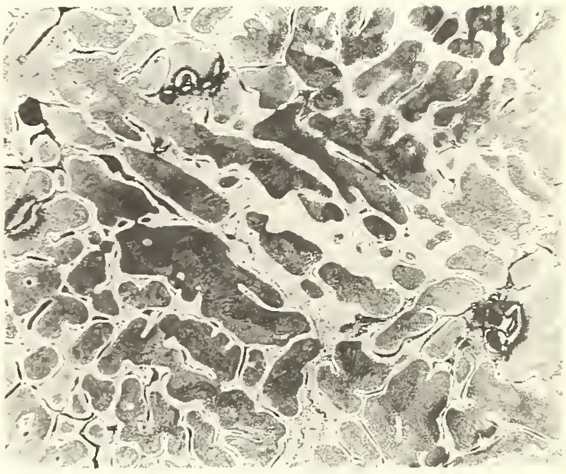

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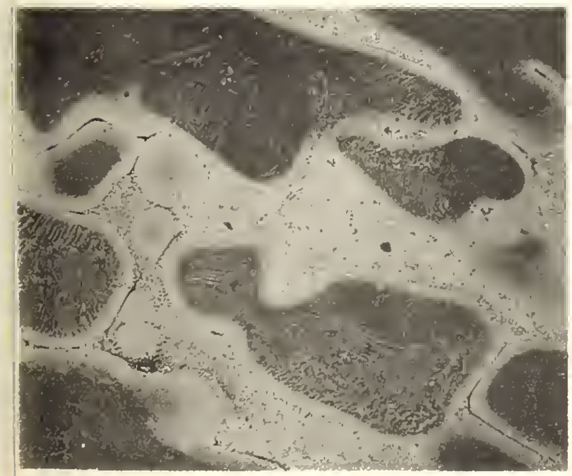

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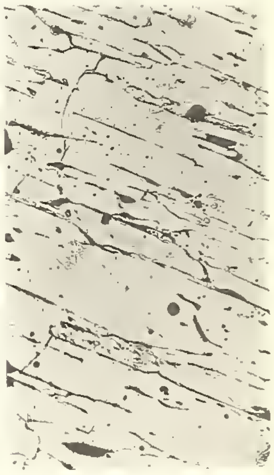

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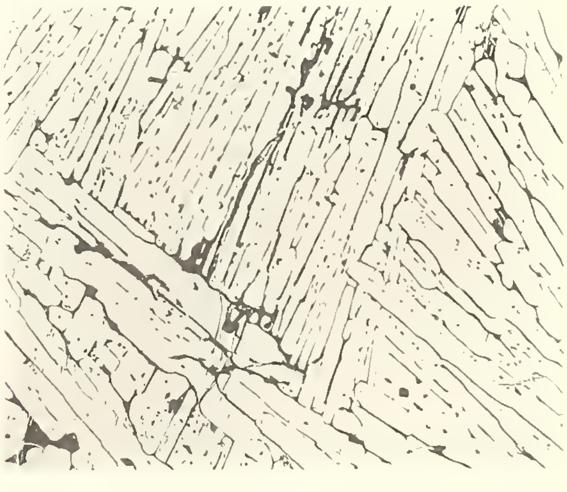

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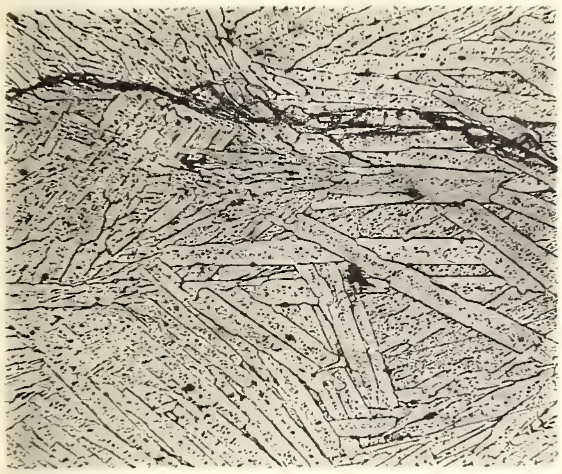
PLATE 7.

Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
72	Sn 27	40·8	× 18	C. 565°	$HCl + FeCl_3$	Plates of η with inclusions of liquid (due to G transformation).
73	Sn 28	42·05	× 45	S.c.c. 650°	„	Uniform lobes of γ. Chill primary of η. Dark tin-rich liquid.
74	„	42·05	× 45	S.c.c. 625°	„	Same as preceding, except that the G reaction has occurred.
75	Sn 33	47·9	× 45	C. 676°	„	Primary γ. γ chill primary.
76	„	47·9	× 18	C. 644°	„	Primary of γ. Chill primary of η.
77	„	47·9	× 45	C. 644°	„	Primary of γ. Chill primary of η.
78	„	47·9	× 45	C. 628°	„	Same, after the G transformation.
79	Sn 38	53·35	× 45	C. 644°	„	Primary γ. Chill primary of η.
80	„	53·35	× 45	C. 628°	„	The incomplete G transformation.
81	„	53·35	× 45	C. 606°	„	The complete G transformation.
82	Sn 42	57·5	× 18	C. 600°	„	Primary and chill primary of η.
83	Sn 38	53·35	× 45	S.c.c. 445°	„	Primary η after 70 hours in boiling sulphur.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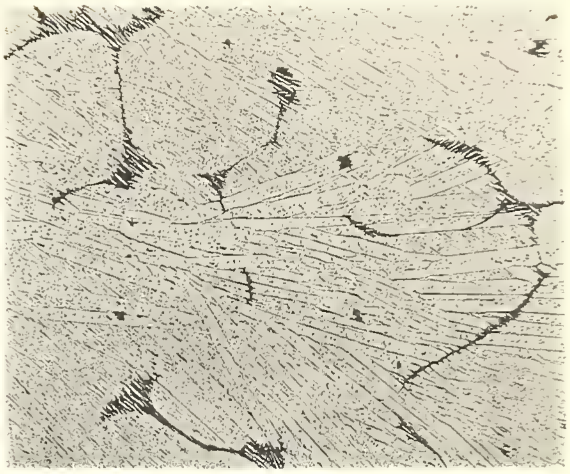
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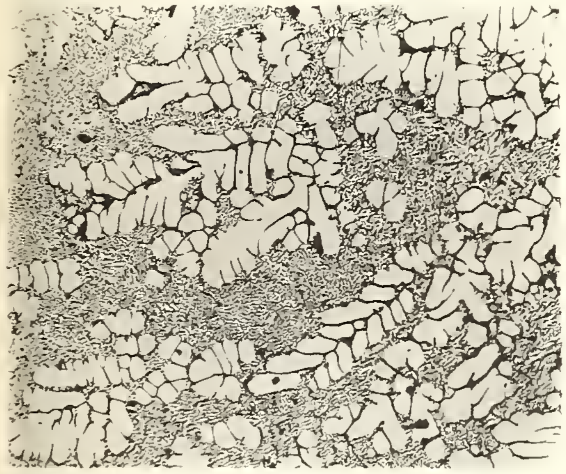
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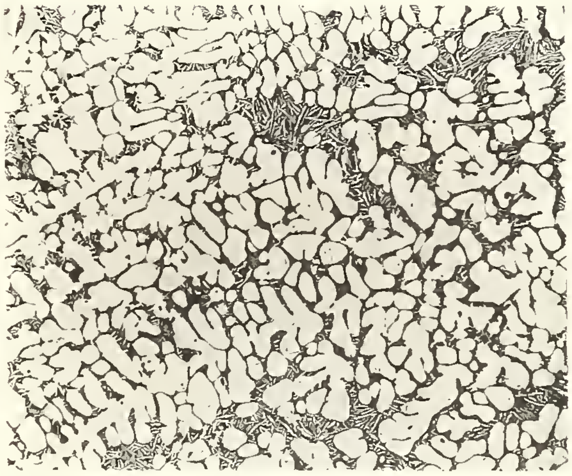
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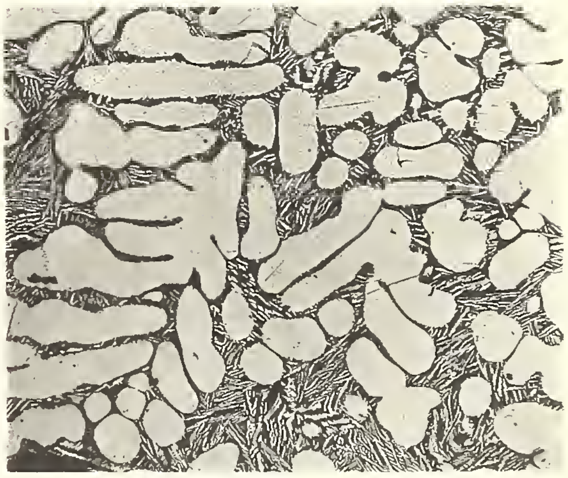
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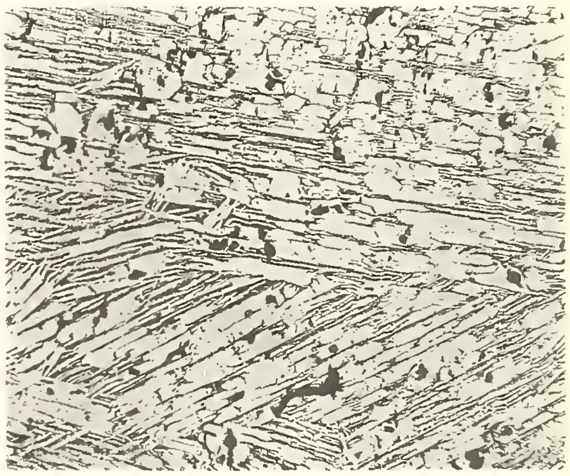
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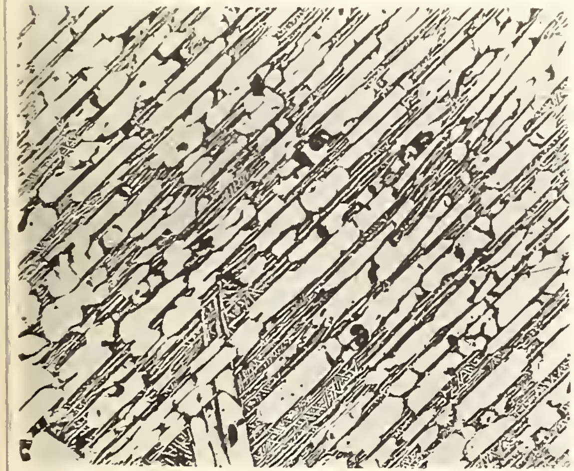
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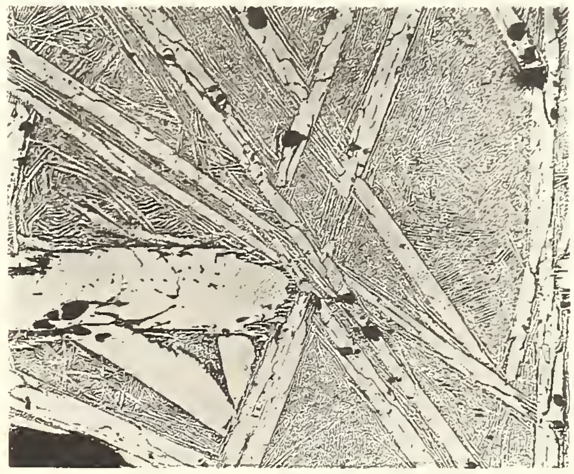
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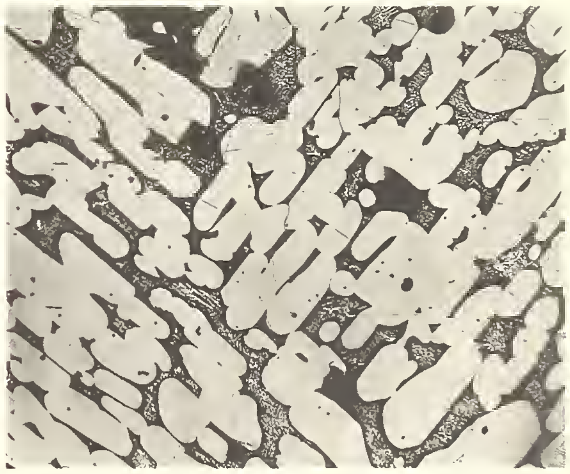
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PLATE 8.

Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
84	Sn 50	65·1	× 45	S.c.c. 445°	$HCl + FeCl_3$	Primary η after 70 hours' sulphur boil. Chill primary is H.
85	Sn 80	88·2	× 18	C. 433°	,,	Primary plates of η in tin-rich liquid.
86	Sn 50	65·1	× 45	S.c.c. 420°	,,	Primary plates of η in tin-rich liquid.
87	Sn 73	83·5	× 45	C. 373°	,,	Plates of darkened η, margined by white H. In liquid.
88	Sn 29	43·2	× 45	S.c.c. 380°	,,	Plates of darkened η, margined by H. No liquid.
89	Sn 90	94·4	× 45	Not chilled	,,	Primary of H in eutectic of H and tin.
90	Sn 95	97·25	× 45	,,	,,	Primary of H in eutectic of H and tin.
91	Sn 50	65·1	× 45	,,	,,	Bars of η with narrow margin of H, in H + tin eutectic.
92	,,	65·1	× 18	C. after 10 hours at 380°	,,	H reaction incomplete. η largely transformed.

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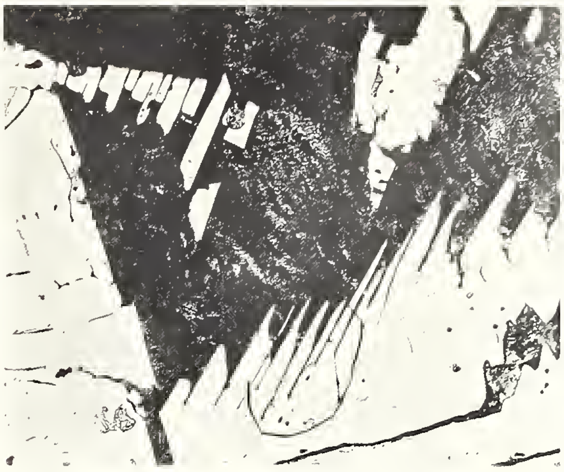

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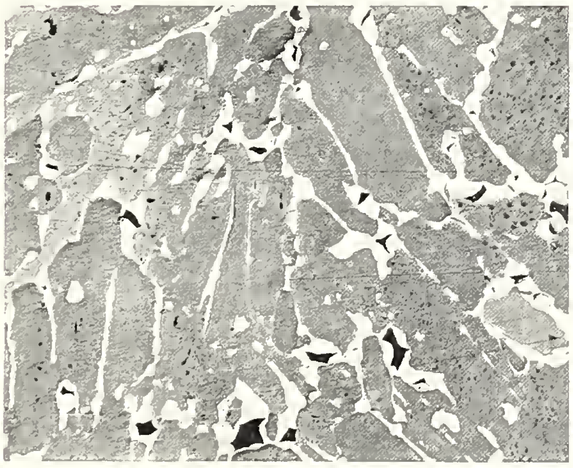

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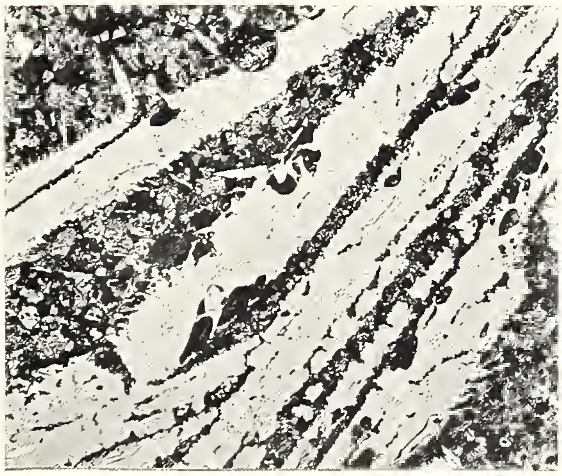

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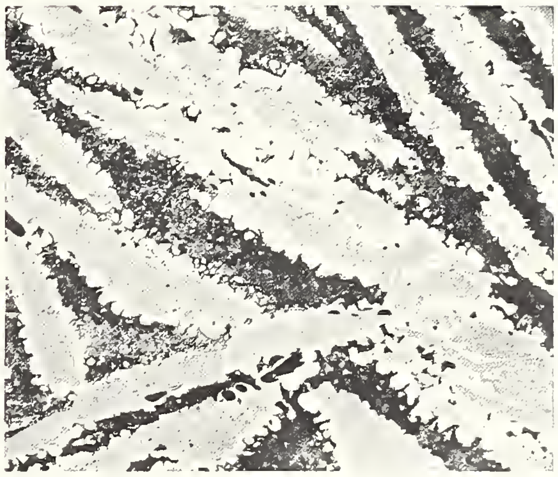

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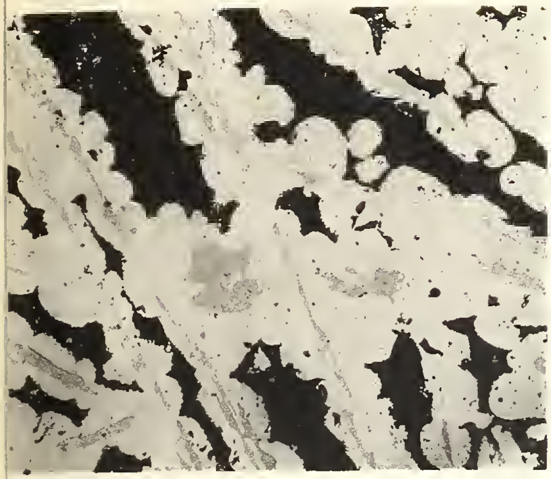
PLATE 9.

Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
93	Sn 50	65·1	× 18	After 60 hours at 350°	HCl + $FeCl_3$	Traces of η in bands of H. Tin-rich liquid dark.
94	,,	65·1	× 18	After 21 days at 350°	,,	η entirely gone. Polyhedra of H. Dark tin-rich matrix.
95	Sn 45	60·4	× 45	After 21 days at 350°	,,	Uniform H, with holes. No liquid. No η.
96	Sn 42	57·5	× 18	24 days at 350°	,,	Compact H, containing η. Many cavities (black).
97	Sn 40	55·4	× 45	21 days at 350°	,,	Compact H, containing η.
98	Sn 60	73·7	× 45	21 days at 350°	,,	Light polyhedra of H in the H + tin eutectic.
99	Sn 85	91·3	× 45	21 days at 350°	,,	Two types of H crystals in the eutectic.
100	Sn ?	?	× 45	—	,,	H made by prolonged stirring of Sn 90 at 350° by means of a copper stirrer.
101	Sn 50	65·1	× 18	10 days at 350° then heated to 400°	,,	η and liquid produced from H by heating for a short time to above 400°.



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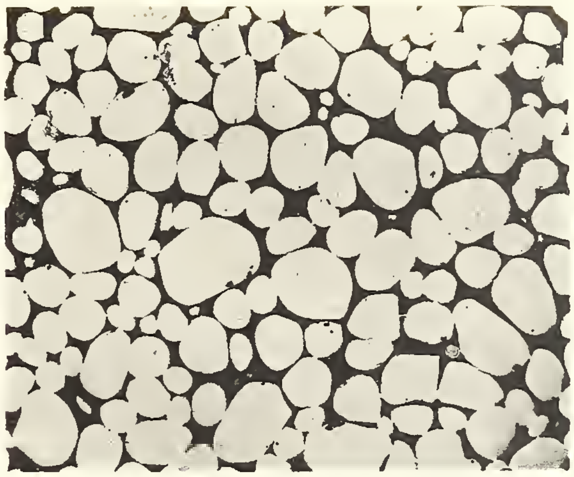

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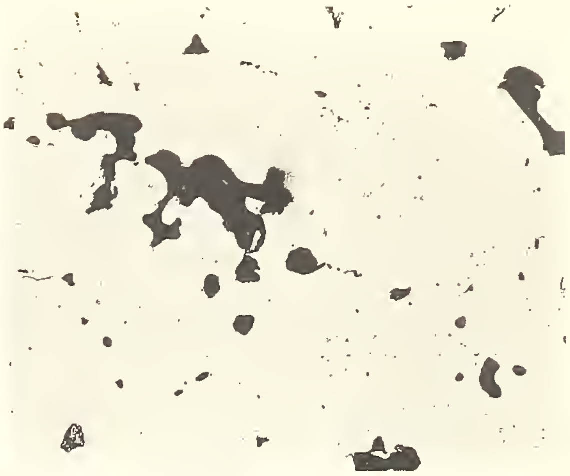

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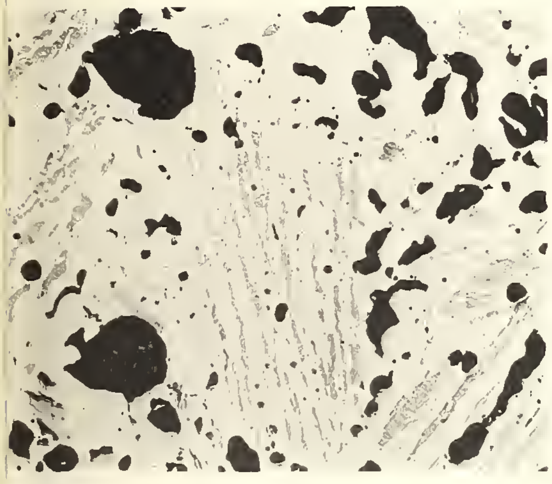

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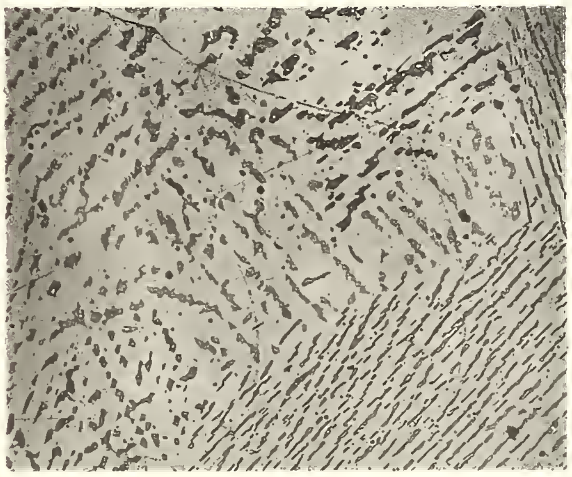

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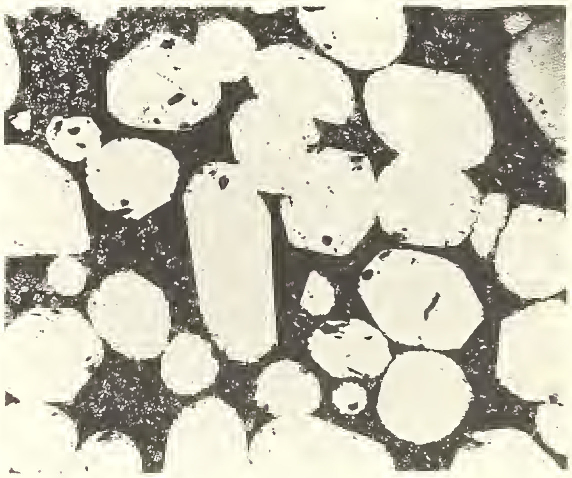

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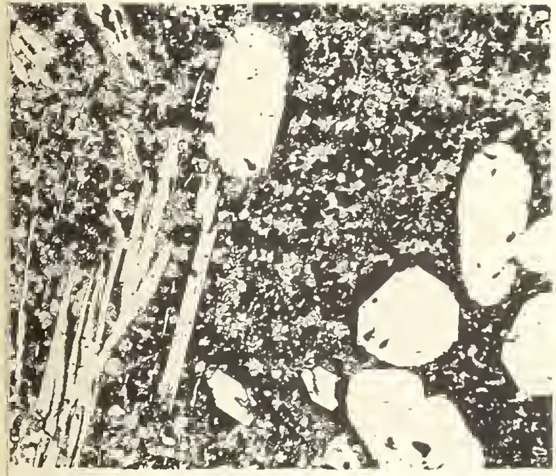

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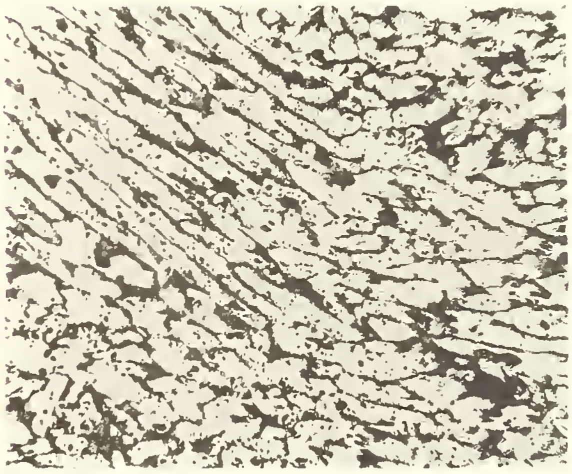

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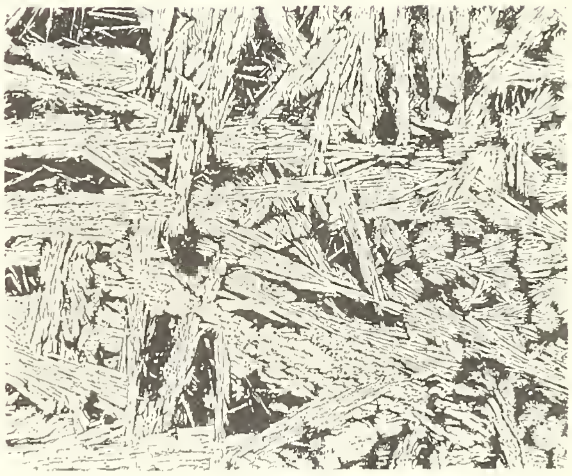

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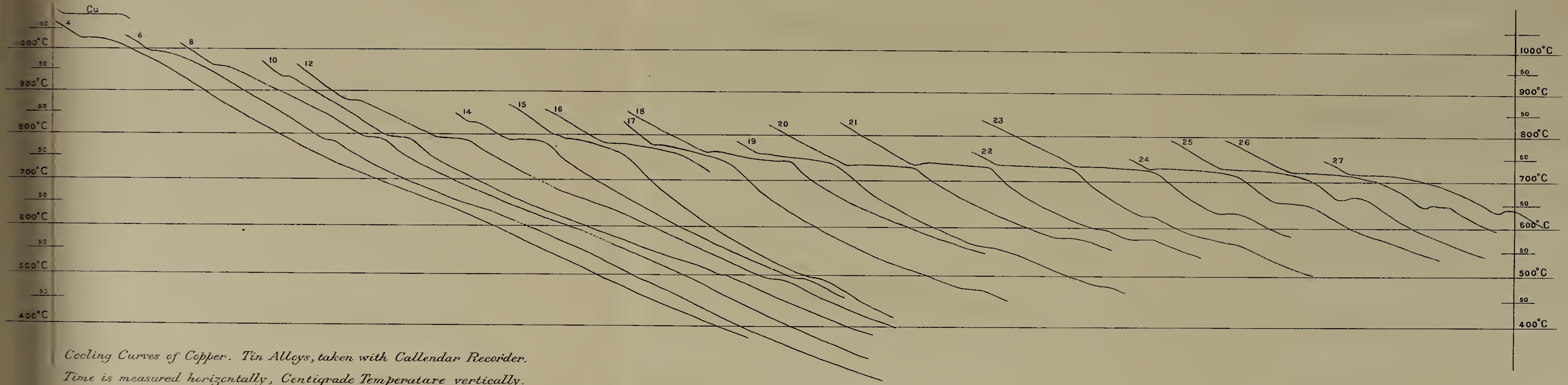
COOLING CURVES OF COPPER-TIN ALLOYS.



Cooling Curves of Copper. Tin Alloys, taken with Callendar Recorder.

Time is measured horizontally, Centigrade Temperatare vertically.

The numerals near beginning of each Cooling Curve give Atomic Percentage of Tin in the Alloy of the Curve.

Curves are given for Alloys between Sn_4 *and* Sn_{27}.

Equal vertical distances correspond to equal differences of Temperature on the Platinum Scale.

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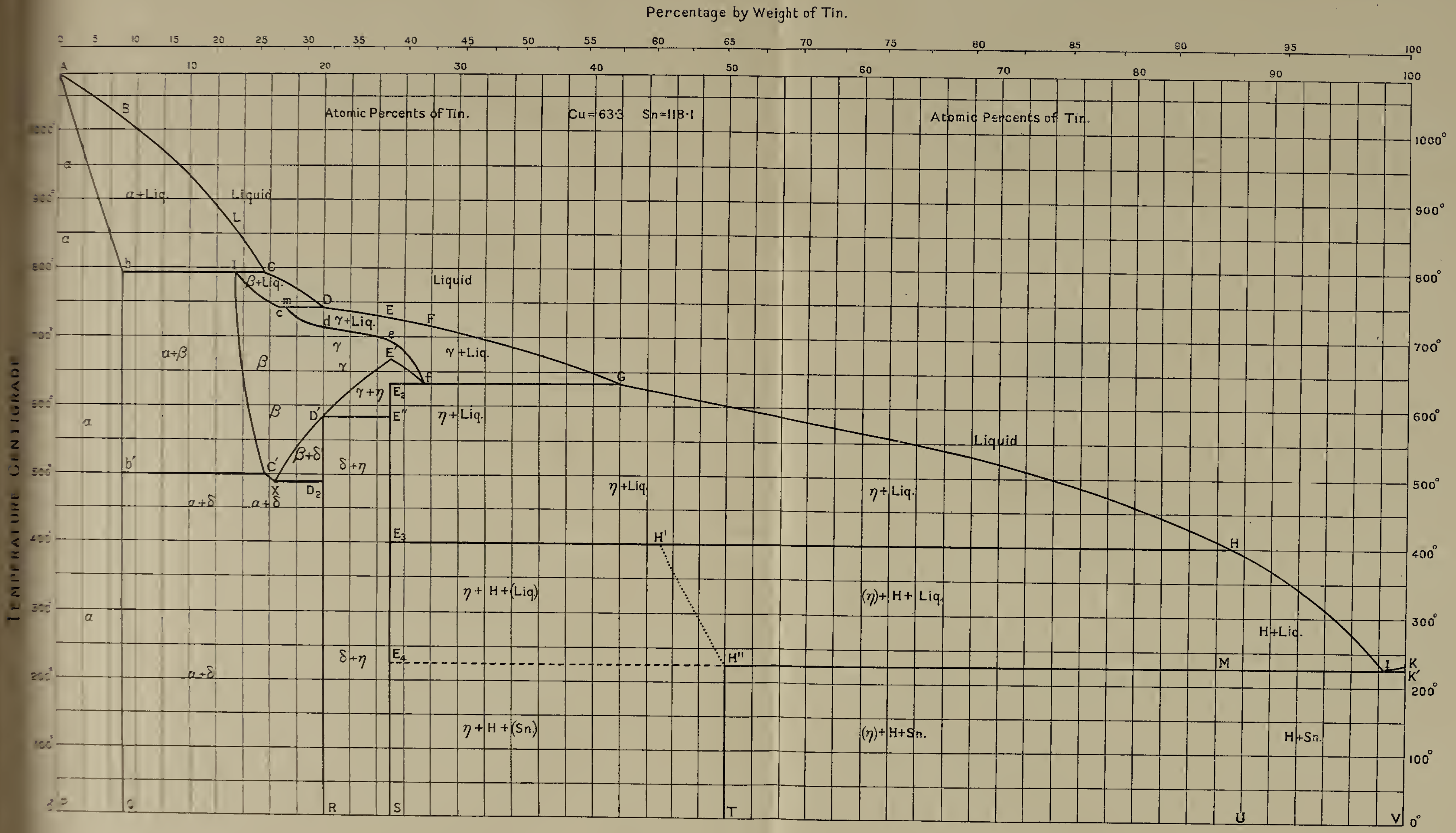
EQUILIBRIUM OF THE COPPER-TIN ALLOYS.



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THE COMBINATION OF HYDROGEN AND CHLORINE UNDER THE INFLUENCE OF LIGHT

BY

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II. *The Combination of Hydrogen and Chlorine under the Influence of Light.*

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Communicated by Professor J. J. THOMSON, *F.R.S.*

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I. HISTORICAL INTRODUCTION.*

IN the year 1801, WILLIAM CRUICKSHANK† noticed the gradual combination of a mixture of hydrogen and chlorine in diffuse daylight. GAY LUSSAC and THENARD‡ observed that the mixture of these two gases exploded on exposure to direct sunlight.

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[*] For the historical introduction I am much indebted to a paper by MELLOR in the 'Journal of the Chemical Society,' vol. 79, 1901.

[†] CRUICKSHANK, 'Nicholson's Journal,' 1801.

[‡] GAY LUSSAC and THENARD, 'Mem. Soc. Phys. d'Arcueil,' 1809.

In the same year, 1809, DALTON[*] made several experiments with direct sunlight, and with diffuse daylight, as causes of the combination. He states, "upon repeating the experiment with sundry variations it was confirmed that light is the cause of this rapid combustion of hydrogen and oxymuriatic gas; that the more powerful is the light, the more rapid is the diminution of the mixture; and that if the eudiometer be covered by an opake body, the mixture will scarcely be affected with any diminution for a day, and will not completely disappear in two or three weeks. Moreover when the diminution is going on with speed, if the hand, or any other opake body, is interposed to cut off the solar light, the diminution is instantly suspended." DALTON also, as well as CRUICKSHANK, noticed that the diminution did not begin at once under the influence of sunlight. This was the first notice of the "period of induction" of BUNSEN and ROSCOE. DALTON, in his analysis of the oxymuriatic gas, mixes hydrogen and chlorine in an eudiometer over mercury and water, and exposes the mixture to the sunlight, "when after remaining two or three minutes without any change, the water, and afterwards the mercury ascend the tube with increasing and afterwards diminishing velocity, till they nearly reach the top." SEEBECK discovered the effect of difference in the colour of the light used, observing that in a clear glass vessel explosion occurred with sunlight, in a dark blue vessel combination occurred quickly without explosion, whilst in a dark red glass vessel the action was very slow.

DRAPER took up the investigation in 1840 and made a series of careful and detailed experiments resulting in the invention of the "tithonometer," an instrument by which he endeavoured to refer the chemical action of light to a standard measure. His first paper[†] contains a description of this instrument. In 1844 he published a memoir on "tithonised" chlorine, in which he gives some of his reasons for believing that the effect of light is to produce an allotropic form of chlorine. This view is further dealt with in a paper published in 1845. The allotropic modification is, according to DRAPER, more active than chlorine which has not been illuminated, as it combines readily with hydrogen even in the dark.[‡] This conclusion was contradicted by BUNSEN and ROSCOE,[§] who exposed the gases evolved by the electrolysis of hydrochloric acid separately to sunlight, and led them then into their "insolation" vessel. On exposing the mixture to light, they found no greater difference between the duration of the induction period of this pre-illuminated mixture and that of gases which had not been previously illuminated than is to be accounted for by unavoidable errors of experiment.[||] This contradiction is explained by the fact that, in DRAPER's experiment, the gases were mixed in the vessel where they were submitted to the

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[*] DALTON, 'A New System of Chemical Philosophy,' I., p. 300.

[†] 'Phil. Mag.,' vol. 23, 1843.

[‡] 'Phil. Mag.,' vol. 27, 1849, p. 339.

[§] 'Phil. Trans.,' 1857, p. 382.

[||] 'Phil. Trans.,' 1857, p. 398.

action of the light, while in BUNSEN and ROSCOE'S experiments the gases were bubbled through water into the "insolation" vessel after the preliminary exposure to light. (See later, p. 101).

FREMY and BECQUEREL[*] confirmed DRAPER'S result, finding that the effect of light on a damp mixture of hydrogen and chlorine is much greater if the chlorine has been previously illuminated than otherwise.

DRAPER[†] further discovered that if an intense light, such as that of a spark from a Leyden jar, be flashed on the mixture, a rapid expansion takes place, followed by a return to, or near to, the original volume. This expansion was also noticed and studied by PRINGSHEIM.[‡] Curiously enough, no mention of this effect is made by BUNSEN and ROSCOE.

BUNSEN and ROSCOE'S classical work on this action, as a means of measuring the chemical effect of light, appeared in 1855 and after. They investigated the phenomena from the beginning of illumination to the stage when the velocity of the action is constant. This interval of time they called the "Period of Induction." At the beginning of this period they observed the "period of inertness" noticed by CRUICKSHANK and DRAPER, after this inert period a period of acceleration, and finally a time when the velocity reached a constant maximum. On stopping the illumination they noticed also a further set of phenomena: a period of retardation followed by the complete cessation of the action. BUNSEN and ROSCOE introduced the words "insolation" and "insolated," the gas mixture being insolated when it has been exposed to light, and the gas being in a state of insolation as long as the effect of illumination persists.

The most important work after that of BUNSEN and ROSCOE is that of PRINGSHEIM.[§] The subject of PRINGSHEIM'S investigation was the expansion noted by DRAPER at the moment of illumination with a bright light. He considered the effect of the heat liberated in the formation of hydrochloric acid molecules. From the known heat of formation of hydrochloric acid we should expect that if hydrochloric acid is formed immediately on the incidence of light, an expansion of 10·5 times the volume of hydrochloric acid formed would occur. The expansion, therefore, should be proportional to the hydrochloric acid formed. PRINGSHEIM concluded that this was not the case. With an instantaneous illumination, obtained by means of a spark, he observed a very small expansion followed by a return to the original volume; but no decrease of volume afterwards, showing the formation and absorption of hydrochloric acid. He concluded, therefore, that the heat liberated by the action is not the cause of the expansion.

PRINGSHEIM supposed that the first action of the light is to cause a dissociation of

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[*] FREMY and BECQUEREL, 'WURTZ., Dict. de Chimie.,' 1879, II., p. 255.

[†] 'Phil. Mag.,' vol. 23, 1843, p. 415.

[‡] PRINGSHEIM, 'Wied. Ann.,' 1887, vol. 32, p. 384.

[§] 'Wied. Ann.,' 1887, vol. 32.

H_2 and Cl_2 molecules into atoms, which, giving rise to a larger number of systems in the gas mixture, causes an expansion. But the immediate effect of such a dissociation would not be to increase the volume at constant pressure. For the volume at constant pressure is proportional to the sum of the kinetic energies of all the molecules; and by a mere dissociation this total kinetic energy cannot be increased, so that the volume would at any rate not increase. In fact, we have

$$pv = \tfrac{1}{3}\Sigma mnC^2,$$

where n is the number of molecules per unit volume of molecular weight m, and C is their mean velocity. Then, in dissociation, Σmn is unaltered, and in the most favourable case, where no energy is needed for the dissociation, C is unaltered. But now the total number of molecular systems is increased and the average kinetic energy of the molecules is diminished, as in place of certain molecules m with velocity C we have molecules $\tfrac{1}{2}m$ with velocity C. The effect of this diminution of average kinetic energy is a fall in temperature. We have yet to consider whether energy is obtained from the light. BUNSEN and ROSCOE* have shown that the photochemical extinction—the light absorbed associated with the chemical action—is very considerably less than the optical extinction due to chlorine alone, and the amount of energy absorbed by chlorine alone from light is exceedingly small and not capable of producing an expansion at all comparable with that occurring with the mixture of gases. (See PRINGSHEIM, *loc. cit.*, p. 413, and below, p. 90.) The energy absorbed from the light is thus very much too small in quantity to have any appreciable effect in the initial expansion. The effect of dissociation would, therefore, be a fall in temperature of the mixture; and an expansion would only follow owing to heat being supplied from the walls of the containing vessel. Experiments described below (p. 88), however, show that associated with the expansion there is a rise in temperature; and that for very short illuminations, where there is not time for equalization of temperature between the gas and the vessel containing it, the rise in temperature is proportional to the amount of hydrochloric acid formed; and in all cases the expansion is fully accounted for by the rise in temperature observed. Under favourable conditions the ratio of expansion to the subsequent contraction, measuring the amount of hydrochloric acid formed, may be as much as 7 or 8, so that in PRINGSHEIM'S experiments, where the expansions were 2 millims. on his scale, the hydrochloric acid formed may have escaped detection. PRINGSHEIM† further concluded that the expansion due to a given quantity of light was independent of the amount of hydrochloric acid formed—independent of the state of the induction. This conclusion, however, is not borne out by more careful experiments—in fact, a corresponding phenomenon to the period of induction appears in the case of the initial expansion (see below, p. 83).

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* 'Phil. Trans.,' "Photochemical Researches," Part III.

† PRINGSHEIM, *loc. cit.*, p. 413.

In 1897 GAUTIER and HÉLIER* investigated the action of light on dry chlorine and hydrogen. They noticed that the gas they prepared, by electrolysis of aqueous hydrochloric acid, did not consist of a mixture of the pure gases, but that there was present in addition oxygen, free, and combined with chlorine. This has also been shown by several observers; but the proof of the presence of oxygen when aqueous acid saturated with hydrochloric acid gas is used is not complete. MELLOR† concluded that the lower chlorine oxides formed in the process of electrolysis are all removed by washing, but that some free oxygen remains in the gas mixture. It remains, however, somewhat doubtful whether the oxygen found by MELLOR was not produced by decomposition of water vapour by chlorine, under the influence of light. In his method hydrochloric acid was electrolysed and the gases continually acted on by light in the upper part of the vessel used for the electrolysis, so that recombination took place as rapidly as the gases were formed. In this way a residue of oxygen was found in the electrolysis. But it seems more reasonable to attribute the formation of this oxygen to the decomposition of water vapour by the chlorine under the intense light used.

Because of this supposed impurity, GAUTIER and HÉLIER used hydrogen and chlorine prepared separately. But the difficulties pointed out by BUNSEN and ROSCOE, in obtaining molecular quantities of the gases, introduce very much more uncertainty in the results, when this method is used, than occurs with the exceedingly small quantity of oxygen, if any, evolved in the electrolysis.

The method of GAUTIER and HÉLIER was different from that of BUNSEN and ROSCOE and PRINGSHEIM, in that in their experiments the hydrochloric acid formed remained in the gas mixture, and so modified the action. The period of induction was not studied by them, and in their hands the problem was simply one of mass action.

With the dried gases they find that the rate of action is not proportional to the density of the free hydrogen and chlorine. If M is the quantity of hydrochloric acid at time t, D the density of hydrogen and chlorine, then, if the rate of combination were proportional to the density of hydrogen, we should have

$$\frac{\mathrm{M}}{t} = c\mathrm{D}\,; \quad c \text{ being a constant.}$$

From their experiments, GAUTIER and HÉLIER deduce the following values for C :—

For the 1st period,	2·5	hours	. . .	C = ·0217,
,, 2nd ,,	3	,,	. . .	C = ·0310,
,, 3rd ,,	41	,,	. . .	C = ·0130,
,, 4th ,,	191	,,	. . .	C = ·0070.

---

* GAUTIER and HÉLIER, 'Comptes Rendus,' vol. 124, p. 1128.

† MELLOR, 'Journal of the Chem. Soc.,' Feb., 1901.

But from the law of mass action we should expect that the rate of combination would be proportional to the square of D or to the product of the densities of hydrogen and chlorine, so that we should have

$$\frac{dD}{dt} = -cD^2, \text{ whence } \frac{1}{D_{t_1}} - \frac{1}{D_{t_0}} = -c(t_1 - t_0).$$

And this gives for C for the same periods as before

·00023, ·00038, ·00024, ·00045.

These numbers are not constant enough for any definite conclusion as to the action in this case following the mass action law; but remembering the great effect of impurities, and noticing that in the bulbs used in these experiments from 4·2 to 6 per cent. of air was present, it is surprising that the values of C are so nearly equal.

GAUTIER and HÉLIER also tried the effect of increase in the proportion of one or other of the gases in the mixture, and found that the rate of action was increased, thus contradicting a result of BUNSEN and ROSCOE. The principle of mass action would lead us to expect a decrease in the rate of combination from this cause. For suppose D, D′ the concentrations of hydrogen and chlorine in the mixture, x the concentration of hydrochloric acid gas, then

$$\frac{dx}{dt} = CDD', \qquad x + D + D' = 1,$$

and

$$D' - D = A, \text{ a constant,}$$

and therefore

$$\frac{dx}{dt} = \frac{c}{4}\{(1-x)^2 - A^2\},$$

which is obviously a maximum when A = 0, or when hydrogen and chlorine are present in molecular proportions.

We must accept BUNSEN and ROSCOE's result in preference to that of GAUTIER and HÉLIER, from the very much better conditions of the experiments of the former observers. In GAUTIER and HÉLIER's experiments different bulbs were used for each observation, and, further, the amount of impurity present was very indefinite. It is very doubtful if experiments made in different vessels can ever be more than very roughly comparable, as the determination of the factor required to allow for loss of light by reflexion and by absorption by the glass of the bulb is impossible. The absorption of ultra-violet light by the glass makes a large difference in the rate of combination. With bulbs filled with the mixture and exposed, side by side, to diffuse daylight, very different proportions are combined after the same exposure.

GAUTIER and HÉLIER believe the action to take place in more than one stage, oxides of chlorine being formed which are reduced by the action of the hydrogen present. The oxidation of the chlorine is effected by the water vapour present in the mixture.

They suppose, for example, an action of the following type

$$Cl_2 + H_2O = HClO + HCl, \qquad HClO + H_2 = H_2O + HCl.$$

The presence of moisture was found by these observers, as well as by many others, to increase the rate of the action. The question arises, do hydrogen and chlorine combine at all under the influence of light when no water vapour is present? BAKER[*] found that complete combination did not take place after exposure to bright sunshine for two days. According to PRINGSHEIM, action does occur slowly in the most carefully dried gases.

The catalytic action of water vapour is of great importance in other actions besides the one under consideration. There have been several theories proposed for the explanation of this action, but none of them are very satisfactory. DIXON supposes that the molecules of water undergo decomposition; for example, in the oxidation of carbon monoxide he assumes two stages

$$CO + H_2O = CO_2 + H_2 \quad \text{and} \quad 2H_2 + O_2 = 2H_2O.$$

PRINGSHEIM'S theory is that, in addition to this type of action, we have the preliminary dissociation into atoms, which then act with the water molecules

$$2H + 2Cl + H_2O = Cl_2O + 2H_2,$$

and finally

$$Cl_2O + 2H_2 = 2HCl + H_2O.$$

This explanation has been criticised[†] from the point of view of BERTHELOT'S principle of maximum work. This criticism does seem to be applicable to PRINGSHEIM'S scheme when we are dealing with free atoms of hydrogen and chlorine; but the principle does not necessarily hold when the rates of action between molecules come into consideration. If the action

$$2CO + O_2 = 2CO_2$$

takes place slowly compared with the actions

$$CO + H_2O = CO_2 + H_2 \quad \text{and} \quad 2H_2 + O_2 = 2H_2O,$$

the course of the oxidation of carbon monoxide to carbon dioxide may be as DIXON suggests. And the view in this case is more probable, as it appears from DIXON'S experiments that if the action

$$2CO + O_2 = 2CO_2$$

can occur at all it occurs extremely slowly.

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[*] 'Phil. Trans.,' A, 1894.

[†] 'Brit. Ass. Rep.,' 1894.

PRINGSHEIM'S explanation, however, of the hydrogen and chlorine reaction is not tenable, as when we have free atoms it is hardly conceivable that the complicated action, requiring the meeting of five molecular systems, should occur, and not the direct combination of hydrogen and chlorine atoms.

Another explanation* of the action of water vapour is that hydrogen peroxide is formed by direct oxidation of the water molecule, and that this gives up some oxygen to the other substance taking part in the action. This view is only applicable to oxidation and not to such actions as the combination of sodium and chlorine, which does not occur in the absence of moisture.

This view may, however, be extended, and we may suppose that intermediate compounds, which are purely additive, are formed, and which break down into more stable forms, giving the final result of the action. This hypothesis will be further developed after we have discussed the experimental investigation of the combination of hydrogen and chlorine.

II. EXPERIMENTAL INVESTIGATION.

For the experimental part of this investigation the method of BUNSEN and ROSCOE was in main followed for the study of the initial expansion, or Draper effect, and the period of induction. The mixture of gases was prepared by electrolysis of ordinary pure hydrochloric acid saturated with hydrochloric acid gas. It has already been remarked that oxygen has been supposed to occur in the gases prepared in this way, but this quantity of oxygen is, at any rate, extremely small and seems to be without effect ; otherwise it seems impossible to explain the constancy of the results obtained by this method, when we remember the large effect produced by the addition of a very small quantity of oxygen. At any rate, the difficulty of preparing a pure mixture of separately formed gases in the right proportions is so great, that the electrolytic method is far superior to any other.

Several forms of cell for electrolysis were tried. Platinum electrodes are dissolved after some time, so that carbon rods were used, as it was found that they lasted for a long period. The form of vessel adopted consisted of an ordinary lamp chimney sealed to a three-way tap leading to a thistle tube and to the insolation apparatus. The carbon electrodes were fitted through an indiarubber stopper, through which also passed a tube connected with a tap through which the spent acid could be removed while fresh acid was introduced through the thistle tube. In this way there was no fear of introducing air into the apparatus when recharging the cell. Above the stopper a layer of paraffin wax was melted so as to form a paraffin bottom to the cell. This paraffin, after the cell had been in use for several weeks, was apparently unaffected by the acid itself or the chlorine in solution. The cell was continually

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* MENDELÉEFF, 'Principles of Chemistry,' I., p. 305.

kept in the dark and was found to work extremely well. Fig. 1 is a diagram of the cell.

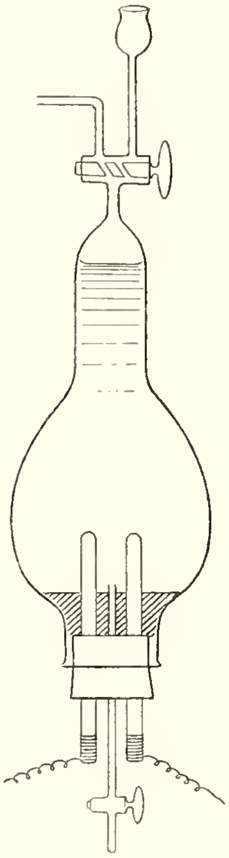

Fig. 1.

The insolation apparatus (fig. 2) was essentially the same as that of Bunsen and Roscoe. Considerably larger bulbs were sometimes used to make the Draper effect more evident. The gases from the generating vessel pass through the washing bulbs (*b*) to the tube (*c*) leading to the insolation bulb (*d*). At (*e*) a side tube is sealed, so as to allow the gases when the tap C is closed to pass through the water in (*f*) and so out through (*g*) into (*h*), an earthenware pot filled with lime to absorb the chlorine. The clip in (*g*) serves to close this outlet. With (*c*) open, all the gas evolved passes into the bulb (*d*), which contains some water in its lowest part, thence through the capillary tube (*i*) to the bulb (*j*), and thence to the absorbing vessel (*k*), which is similar to (*h*). The bulbs (*d*) used were from 3 to about 8 centims. in diameter. The capillary tubes (*i*) were from 50 centims. to 200 centims. long. The bulb (*j*) has water in it to just above the level of the capillary tube, so that when (*c*) is open the gases bubble through the water in (*j*), and when (*c*) is closed the water runs a few centimetres into the capillary and forms the index defining the volume of the gas in the insolation bulb (*d*). With large insolation vessels it is very necessary that the capillary tube (*i*) should be level along its whole length, as it is easy to see that the water in the capillary may produce changes of pressure in the bulb (*d*), causing corresponding changes of volume which are greater than the effects to be observed unless the tube is horizontal. This tube was usually supported along its whole length on a wooden table. The bulb (*j*) also must be large enough for the alteration of level of the water in it, due to motion of the index, to be negligible. When practicable, the whole apparatus from the generating vessel to the outlet tube had only glass joints, as indiarubber is soon destroyed by chlorine, and, also, with only glass joints there is no danger of contamination of the gases. The glass joints at the ends of the

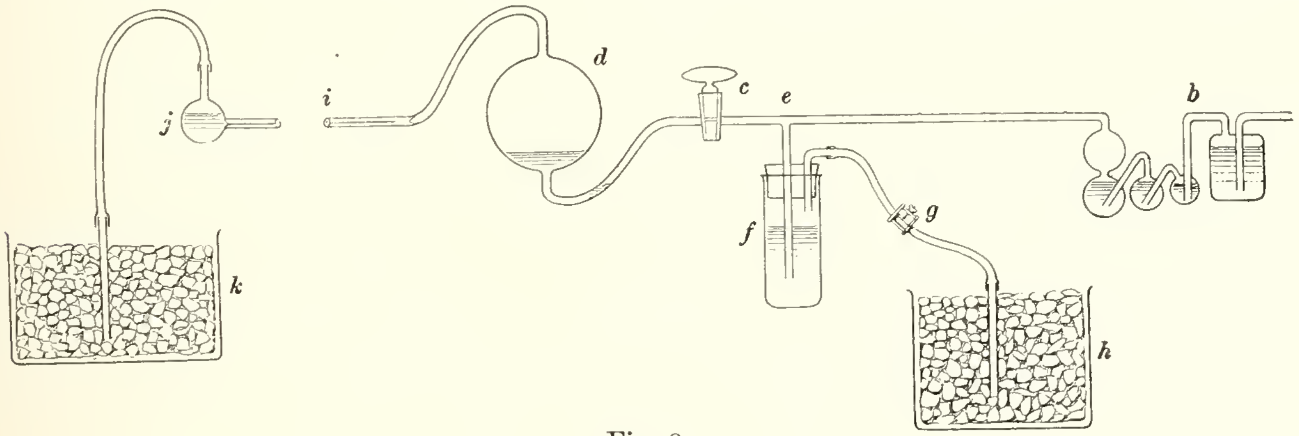

Fig. 2.

capillary had to be carefully made, as slight irregularities occasion the stoppage of the tube by a drop of water at one end or a bubble of gas at the other.

The insolation vessel from the tap (*c*) to the beginning of the capillary tube was enclosed in a wooden box packed with cotton waste to keep the bulb from light and from temperature changes. In the side of the box was a tube of diameter about two-thirds that of the bulb, so that light could be thrown on the upper part of the bulb, the part with water in it being blackened and remaining in the dark. On this tube was fitted a Thornton-Pickard photographic shutter, so that an exposure of the bulb to the light of a given time could be made. With some practice, by counting the ticks of a watch, exposures of one-fifth of a second and upwards could be given with fair accuracy. For the illumination of the bulb a Welsbach incandescent burner was usually used as a source of light. The lamp was enclosed in a box with a hole in it placed opposite to the shutter. The light was passed through a water trough to cut off heat rays, and through a convex lens to be sent down the tube to the insolation vessel in as nearly as possible parallel rays. Other screens were arranged to cut off extraneous light and accidental heating effects from the burner. With these precautions, working in a cellar, the temperature of the insolation vessel could be kept constant for a considerable time. Fig. 3 shows a diagrammatic representation of the arrangements for illumination.

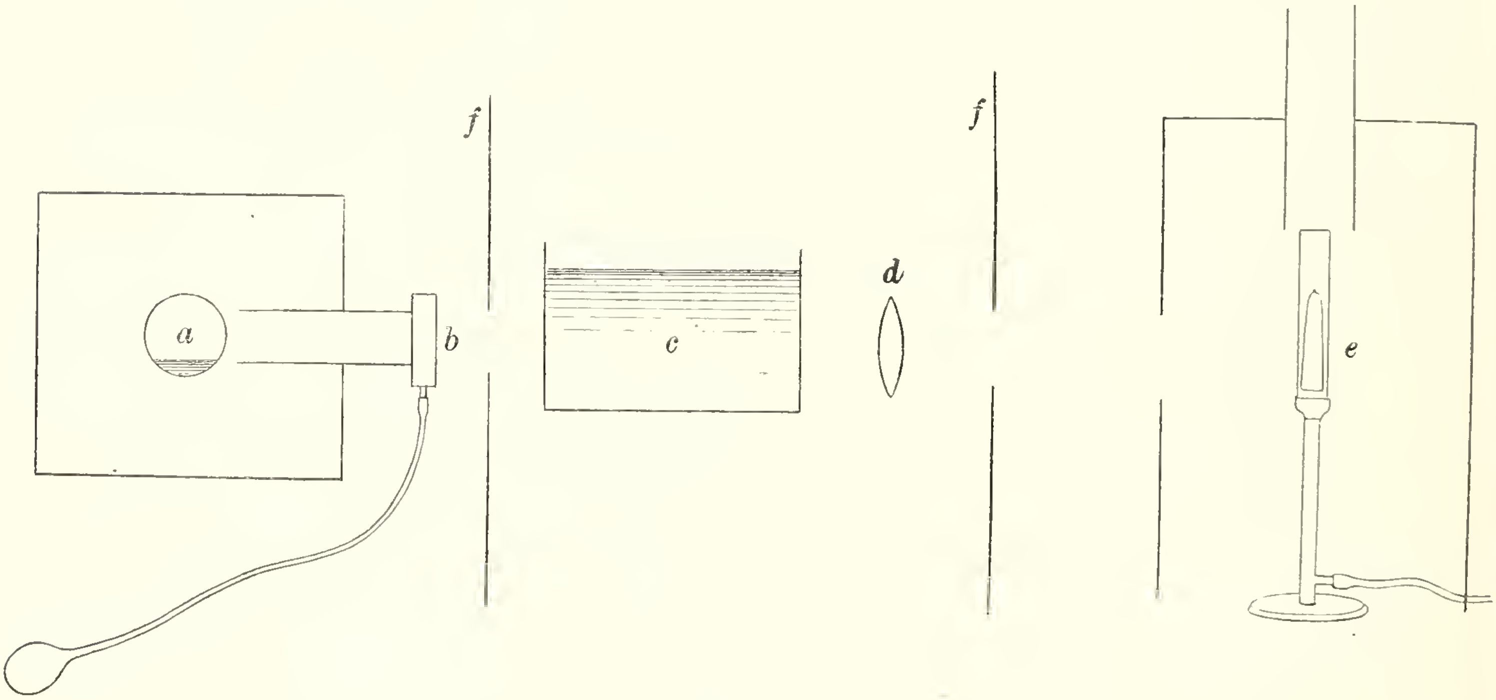

Fig. 3.

It is necessary that the electrolytic gas should be continuously passed through the apparatus for nine or ten days, to thoroughly drive out all air, and to saturate the water in the various parts of the apparatus with chlorine. It was found necessary to run a certain quantity of gas through the apparatus before each experiment, especially if the gases had been standing for some time, as slight changes in temperature of the whole apparatus alter the solubility of the chlorine, and produce slight changes in the relative amounts of chlorine and hydrogen in the insolation bulb. It was found also necessary not to alter greatly the rate of evolution of the gases. Such alteration produces effects which are probably to be attributed to the alteration of concentration of the solution round the electrodes in the generating vessel, which causes the gases for a time not to be given off in the right proportions. If the rate of evolution is not fast, however, this difficulty gives rise to no trouble. Following Bunsen and Roscoe, a small current was kept decomposing the acid continually during a series of experiments, so that there was always a slight excess of pressure inside the apparatus above that outside; in this way all danger of small quantities of air being drawn into the apparatus was avoided.

In the first experiments performed the light of the sky was used, but this proved to be much too variable, so the Welsbach burner was employed. In some of the later experiments an incandescent electric lamp was used, and, for instantaneous illumination, a spark from a Ruhmkorff coil with several Leyden jars in circuit.

If a not too powerful source of light be used, the phenomena observed when the light falls on the mixture are as follows:—For some time the water index remains stationary; but after a certain time, depending on the intensity of the light, the water index begins slowly to move towards the insolation bulb, indicating a decrease in the volume of the gas under observation caused by the absorption in the water at the bottom of the bulb of the hydrochloric acid formed. The rate of this motion increases at first slowly, that is, the acceleration is at first small. The acceleration increases to a maximum and then decreases to zero, when a maximum rate of action is reached which remains constant. The curves (fig. 4) represent the results of an experiment of this kind, showing the general phenomena of the "Period of Induction." The curve I has for abscissæ the time in minutes from the beginning of illumination, and for ordinates the observed contraction from the beginning of the experiment, measuring the amount of hydrochloric acid formed. The curve II is the velocity curve for the same experiment.

If the light be more intense the phenomenon known as the Draper effect appears. Instead of the period of inertness when the water index does not move, the index, immediately on illuminating the gases, moves away from the insolation bulb, showing an increase in the volume of the gas mixture. With very intense light this expansion can be made to increase in magnitude practically without limit, until the point is reached when explosion takes place. And this suggests at once that the phenomenon is a heat effect. The expansion may continue for as long as half-a-minute (there seems no reason why it should not continue for a longer period, the only difficulty being that with more intense light the whole apparatus is likely to explode). But after a time the expansion stops and at once the gas begins to contract; and then the general phenomena are the same as when no expansion occurs. If the illumination is stopped before the expansion is complete, contraction immediately follows, and the final volume is one which is less than the original volume.

When the light is cut off, after or before the steady velocity of contraction has been reached, the rate of contraction at first increases, reaches a maximum, and then decreases until the index comes to rest.

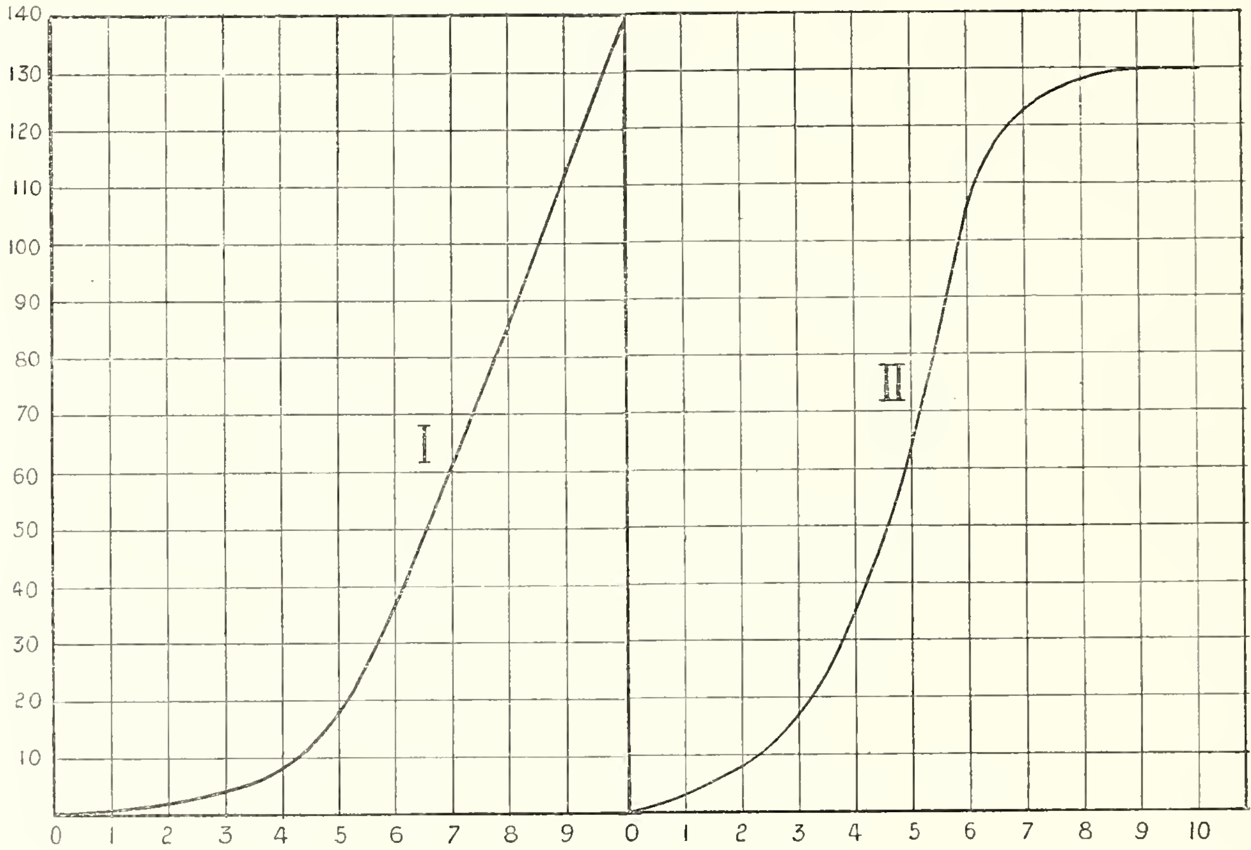

Fig. 4.

The phenomena to be investigated thus fall under three heads :—1. The initial expansion. 2. The final contraction (when light has been cut off). 3. The period of induction proper.

1. *The Initial Expansion.*[*]

This expansion can, as we have seen, be made exceedingly large. But with light of suitable intensity it can be kept within manageable limits.

Pringsheim has worked at this phenomenon, but his conclusions have not been confirmed in this investigation. The following experiments were therefore made very carefully and in considerable detail.

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[*] The results of this section were published in the 'Proceedings of the Cambridge Philosophical Society,' vol. 11, Part IV., 1902. J. W. Mellor published almost simultaneously the fact that hydrogen chloride is formed during the momentary illumination producing the initial expansion. He also afterwards arrived at the conclusion of § 5 with regard to the expansion of damp chlorine alone under the influence of light. Mellor's investigations are in the 'Journal of the Chemical Society,' 1901, 1902.

§ 1. *The Relation of the Initial Expansion to the Time of Insolation.*

The first point considered was the relation of the expansion to the time of illumination, the intensity of the illumination remaining constant.

The influence of very small quantities of impurity was found to be merely to diminish the quantity of effect observed, not to alter the quality of the effects, so that impure gas and more intense light give the same effects as pure gas and less intense light. This is useful practically, as there is no need to take so much time for preparing the purest mixture obtainable in order to observe the qualitative effects in the initial expansion.

In fig. 5 are plotted the results of four series of experiments. In each series the light was of constant intensity. For any single observation the illumination was for the time represented as abscissa and the expansion observed was that represented as ordinate.

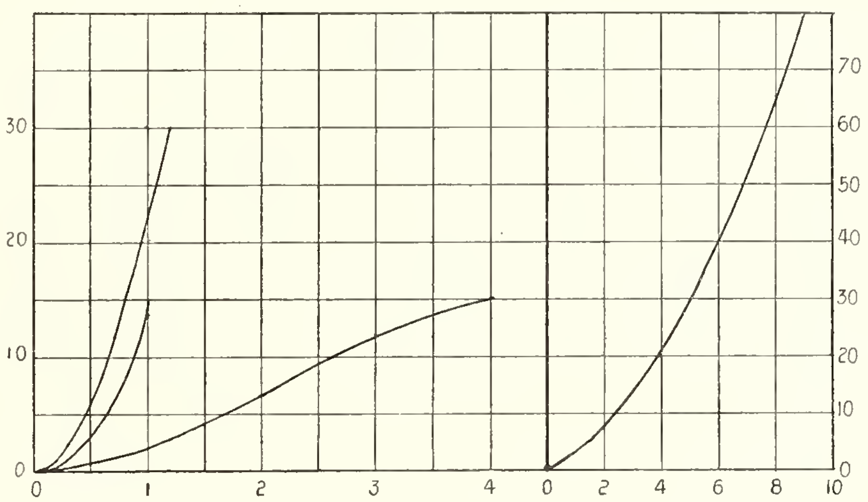

Fig. 5. Abscissæ, time in seconds. Ordinates, expansion.

Between each observation the bulb was left for a quarter of an hour in the dark, so that one experiment should not affect the next.

These curves show that we have an increasing rate of expansion with the increase of the time of illumination. The relation between the expansion and the time of illumination was also determined, in the course of one expansion, by marking the position of the index at intervals of one second after the beginning of illumination. With rapid motion of the index this method is difficult, but it has the advantage over the other method of following the whole course of the expansion in one experiment.

In the following table are given the results of experiments of this kind. The numbers in the last three columns represent the positions of the index at the time stated in the first column.

Time from beginning of insolation.	Expansion.		Experiment III.
	Experiment I.	Experiment II.	
1	3	3	5
2	18	26	22
3	34	51	41
4	47	73	59
5	60	90	79
6	73	106	91
7	84	119	105
8	92	128	115
9	99	131	123
10	104	132	130
11	107	—	132
12	108	—	—

These experiments also show that the rate of expansion increases with the time of illumination at first and then diminishes until the expansion is complete. After this, contraction at once sets in. Now it might be thought that this observed increase in the rate of expansion might simply be due to the inertia of the water index in the capillary tube—the viscosity of the water would tend to diminish the acceleration of the expansion. To perform a series of experiments that would eliminate this effect of inertia a series of illuminations, each lasting for one second, was made. Each illumination followed quickly on the preceding one, only sufficient time being allowed between the illuminations for the index to come nearly to rest. The actual interval between the observations below was from 10 to 15 seconds. In the following tables are given in the first column the numbers of the illumination of one second from the first, which was made with fresh gas that had always been in the dark. In the second column is the expansion observed for each illumination. The intensity of the light was different in the different experiments.

I.		II.	
Number of illumination.	Expansion.	Number of illumination.	Expansion.
1	3	1	7
2	4	2	11
3	6	3	14
4	6	4	22
5	6·5	5	20
6	8	6	23
7	7	7	33
8	12	8	30
9	11	9	25
10	11	10	33
11	12	11	30

III.		IV.	
Number of illumination.	Expansion.	Number of illumination.	Expansion.
1	10	1	28
2	12	2	39
3	14	3	37
4	20	4	44
5	26	5	46
6	29	6	51
7	35	7	60
8	33	8	73
9	35	—	—
10	45	—	—
11	39	—	—

After IV. the same gas was allowed to remain in the dark for three minutes, and was then again illuminated for one second. The expansion was 52. The mixture was again allowed to remain dark for six minutes, and the expansion for one second illumination was 29. Therefore in three minutes the gas has not attained its original condition. But six minutes is enough as far as the expansion is concerned to enable the gas to return to its initial state.

These experiments conclusively show that the expansion, for a definite quantity of light, depends not only on the amount of light, but also on the condition of the gases. In other words, *the expansion is dependent on the state of the induction.*

In every case in the above experiments some hydrochloric acid was formed, and the position of the index was such, therefore, that in each series of experiments a longer column of water had to be moved in each expansion than in those preceding it. The expansion, therefore, in any case is probably a little too small compared with the one preceding it. The effect of this is to make the acceleration of the expansion less than it should be. There remains no doubt that the acceleration exists. The reason that these experiments were made in such detail was that PRINGSHEIM* concluded that the amount of the expansion for a given quantity of light is independent of the state of the induction. It was partly on this conclusion that he based his theory that the first action of the light is to cause a dissociation of hydrogen and chlorine molecules into atoms.

§ 2. *The Relation to the Hydrochloric Acid Formed.*

The next point to be considered is the relation between the initial expansion and the hydrochloric acid formed. Experiments on this subject are considerably more difficult than experiments on the expansion alone. For the complete contraction, defining the amount of hydrochloric acid formed, takes a considerable time, and so very small and slow changes of temperature of the whole apparatus may cause relatively large errors. The expansion is complete in seconds, while the contraction requires minutes to come to an end. For this reason numbers expressing contraction are not very regular. It is also difficult to obtain a long series of comparable experiments, since small changes of the conditions of temperature and pressure alter the behaviour of the gas mixture by changing the relative proportions of hydrogen and chlorine in the mixture. In this way experiments from day to day may differ, even when the most careful precautions are taken for complete saturation of all the liquids involved.

The curves in fig. 6 represent the results of one experiment on the relation between the initial expansion and subsequent contraction representing the hydrochloric acid formed. In curve A the abscissæ represent the contraction (hydrochloric acid formed), the ordinates the initial expansion. In B are plotted the contraction and the ratio of initial expansion to the contraction. C is the early part of A enlarged.

The result obtained from such experiments is that the initial expansion is always followed by contraction, showing the formation of hydrochloric acid. The ratio of the expansion to the final contraction below the original volume increases as the final contraction diminishes. This is to be expected if the expansion be due to heat arising from combination, for the shorter the time of illumination the less heat can escape.

With the object of obtaining as short exposures as possible, the mixture was illuminated by the light from electric sparks. The sparks were obtained from an induction coil with several Leyden jars in circuit. No special care was taken to obtain sparks of constant length, the object being to see if, with instantaneous illumination, any hydrochloric acid at all was formed. The size of the spark could however be regulated so as to give expansions from 1 millim. of the capillary tube

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* 'Wied. Ann.,' 1887, vol. 32, p. 412.

upwards. Single sparks were obtained by working the contact breaker with the hand. The result obtained, from a large number of experiments, was that, however quickly illumination takes place, an expansion is always followed by a contraction,

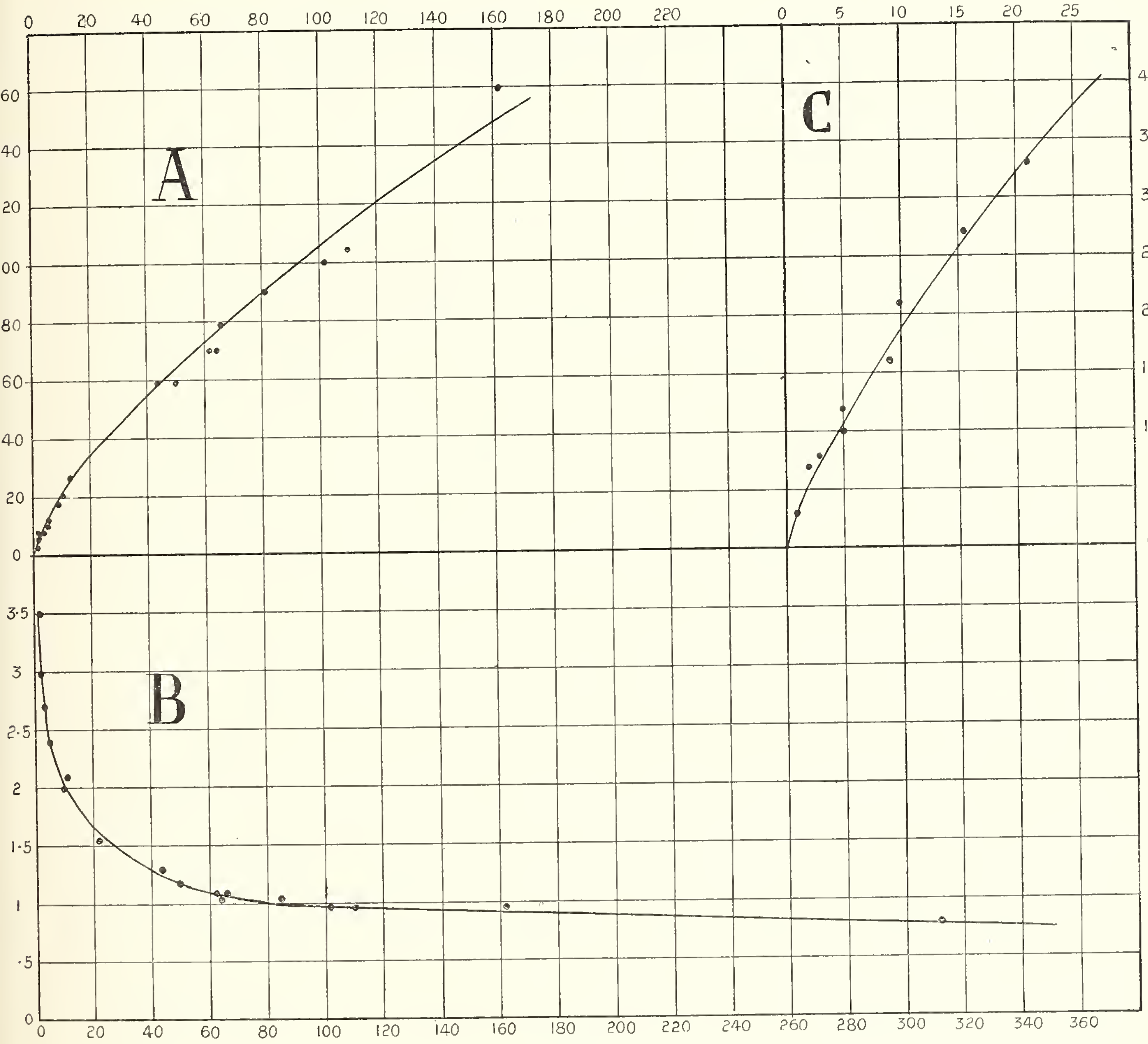

Fig. 6.

showing the formation of hydrochloric acid. For the smaller contractions noted the index was carefully watched with a lens to detect the small contraction.

The following table shows the results of some experiments, illumination being by a single spark :—

Expansion.	HCl formed.	Ratio.	Expansion.	HCl formed.	Ratio.
1	·2	5	3·5	1·7	2
1	·3	3	4	2	2
1·2	·2	6	4	1·5	2·6
1·3	·2	6·5	5	3	1·7
1·5	·3	5	5·2	1·6	3
1·5	·6	2·5	6·5	2	3·2
1·5	·2	7·5	8	3	2·7
1·5	·4	4	8	4	2
3·5	1	3·5	12	4	3

As the index even with an instantaneous illumination takes a finite time to move, all the heat liberated by the combination of the hydrogen and chlorine will not contribute to expanding the gas, but some will be dissipated in the walls of the insolation vessel and the water contained in it, so that the larger the amount of hydrochloric acid formed with instantaneous illuminations of different intensities, the smaller will be the ratio of expansion to contraction. This we find to be the case in the above experiments. The ratio tabulated diminishes as the contraction representing the hydrochloric acid formed increases. Thus, however small the initial expansion, we can conclude that there is always some hydrochloric acid formed. This conclusion was arrived at also by MELLOR (' Chemical Society's Transactions,' 1902).

§ 3. *The Temperature Change Associated with the Initial Expansion.*

The next series of experiments were made to determine directly the change of temperature in the mixture of gases, when light falls on it, during the period of expansion. The method employed was to find the change in the resistance of a platinum wire in the gas mixture during illumination. A large insolation bulb (about 8 centims. in diameter) was used for this purpose. A piece of platinum wire, ·001 inch in diameter and about 9 centims. long, was welded at each end to a stout wire of the same metal, and these stout wires were sealed into the bulb at opposite sides, so that the fine wire hung loosely in the insolation bulb. The wire was then connected with a Post Office resistance box in the ordinary Wheatstone bridge arrangement. A differential galvanometer was used, which could be easily made as sensitive as was required. The temperature coefficient of the wire was found *in situ*, and agreed very nearly with that of another specimen of the same wire. The galvanometer was so adjusted that the change of resistance of the wire in the insolation bulb was determined by reading the displacement of the spot of light on the galvanometer scale. The resistance of the wire at 0° C. was 20·650 ohms, and a change of resistance of 1 ohm corresponded to a change of temperature of 23° C.

It was found that on illumination of the gas mixture the resistance of the wire increased, indicating a rise in temperature of the mixture.

The curve represented in fig. 7 has for abscissæ the final contraction, indicating the amount of hydrochloric acid formed, measured in millimetres of the capillary tube, and for ordinates the rise in temperature observed. The points all lie about a line which at first is straight; and the deviations from this line are not greater than are to be accounted for by the unavoidable errors of experiment.

In this experiment then, there is an observed rise of temperature which for the cases when the amount of hydrochloric acid formed is small is proportional to the amount of hydrochloric acid formed. The time of illumination for these experiments was very short for the observations represented by the straight part of the curve, the illumination only lasting for a fraction of a second. (The longest illumination was about 1·5 second.)

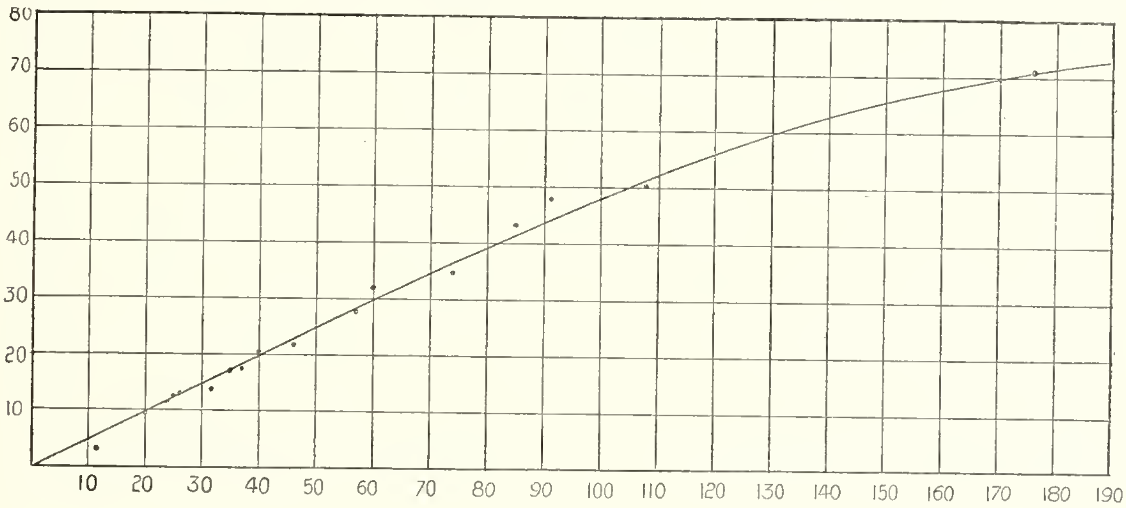

Fig. 7.

With the galvanometer made as sensitive as possible, a rise of temperature was always indicated with the shortest illuminations obtainable by means of an electric spark. Even when the illumination was adjusted so that the only observable effect on the index was an expansion of a small fraction of a millimetre, a rise of temperature could always be detected.

§ 4. *Conclusions.*

We conclude that under all conditions there is associated with the initial expansion a formation of hydrochloric acid and also a rise in temperature.

Taking Thomsen's value 22,000 cal. for the heat of formation of hydrochloric acid, the increase of volume of an equal mixture of hydrogen and chlorine, supposing all the heat expended in expanding the resulting hydrochloric acid, is such that the new volume equals 10·5 times the old volume. In the vessel used, in the experiments just detailed, a formation of hydrochloric acid, corresponding to a contraction of 1 millim. of the index, would cause a rise in temperature in the gas of very nearly ·01° C. In all cases the actual rise observed was less than this, so that the observed rise in temperature is fully accounted for by the heat of formation of the hydrochloric acid. We have already seen that the expansion is larger compared with the contraction, representing hydrochloric acid formed, the smaller the quantity of acid formed and the shorter the time of insolation; but the ratio of these two quantities always falls considerably below 10·5. For the bulb used, a rise of temperature of ·01° C. corresponds to an expansion of about 9 millims. of the scale, and in no case was the expansion observed as large as that value which would correspond to the observed rise in temperature. The reason that this value of the expansion is not observed is that the motion of the index is relatively slow, and the gas cools so quickly, with very short exposures, that the index cannot register the expansion corresponding to the total rise in temperature.

The conclusions then with regard to the initial expansion period are:—

(1) The expansion is due to rise in temperature of the gas mixture;

(2) This rise in temperature is caused by the heat liberated in the formation of hydrochloric acid.

The initial expansion period is therefore nothing more than a part of the period of induction as studied by BUNSEN and ROSCOE; and the condition necessary for the existence of the Draper effect is that the intensity of the light should be such that the combination can begin rapidly enough for the heat evolved to produce an observable effect.

§ 5. *The Expansion of Chlorine alone under the Influence of Light.*

In connection with this subject the results of experiments of BUDDE[*] and BAKER,[†] on the expansion produced in chlorine alone by the influence of light, are of interest. BUDDE found that under the influence of light damp chlorine expanded. In his first paper[‡] he states that the expansion cannot be due to a rise of temperature, but in a later series of experiments he found that a rise in temperature did occur, and although the rise in temperature did not agree with the expansion very well, he concluded that the expansion was a direct result of the heat resulting from the absorption of light. BAKER found that perfectly pure and dry chlorine did not change its volume when exposed to light.

PRINGSHEIM[§] showed that this expansion was very different from that in the Draper effect. With the most intense sparks procurable, there is no observable expansion in chlorine alone.

It seemed worth while, with the apparatus already described, to settle the question

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[*] BUDDE, 'Phil. Mag.,' 1871, vol. 42, p. 290.

[†] BAKER, 'Brit. Ass. Rep.,' 1894.

[‡] BUDDE, 'Pogg. Ann.,' vol. 6, 1873, p. 477.

[§] PRINGSHEIM, 'Wied. Ann.,' 1887, vol. 32, p. 413.

with regard to damp chlorine. The light from a Welsbach burner was allowed to fall on the bulb already described, and the rise in temperature and expansion were observed. The expansion was proportional to the rise in temperature as far as the accuracy of the method admits.

The following table gives the expansion, the rise in temperature, and the expansion for ·01° C. obtained in a series of experiments of this kind.

Expansion.	Rise in temperature.	Expansion for ·01° C.
	°C.	
48	·068	7·05
50	·053	9·4
50	·060	8·3
73	·092	7·9
85	·113	7·5

The mean of the numbers in the last column is 8·03. From the dimensions of the bulb and capillary tube a rise of temperature of ·01° C. should produce an expansion of 8·2 scale divisions. It thus appears that the expansion observed is accounted for by the rise in temperature of the gas. To test whether the slight warming of the apparatus affected the expansion, by liberating some of the chlorine dissolved in the water in the bulb, the rise in temperature of the chlorine was observed and the expansion due to the warming of the room during the course of the day. This expansion was very slow and was 9 scale divisions for a rise of temperature of ·01° C. The amount of chlorine, therefore, evolved is so small that it can be neglected.

2. *The Final Contraction.*

On cutting off the light after insolation has been proceeding, an increase in the rate of contraction is first observed. For example, the mixture of hydrogen and chlorine was exposed to light, and a continuous supply of fresh gas was kept running into the insolation bulb, to keep the index on the scale. After the maximum rate of action was reached—observed by stopping the supply of fresh gas for a short time—the light was cut off and the time of contraction through various lengths of the index scale noted. Fig. 8 represents the course of the contraction. The maximum action, when the light was on the mixture, was about 100 scale divisions in 4 seconds. It will be noticed that the initial rate of contraction, after the light was cut off, was about 100 scale divisions in 2 seconds. The behaviour on darkening before the maximum rate of action is reached is shown in the curves in fig. 9. In each case the phenomena are essentially similar to the case when the action, before light is cut off, has reached its maximum value. The rate of contraction is, on cutting off the light, greater at first than before the darkening, and gradually diminishes until the index comes to rest.

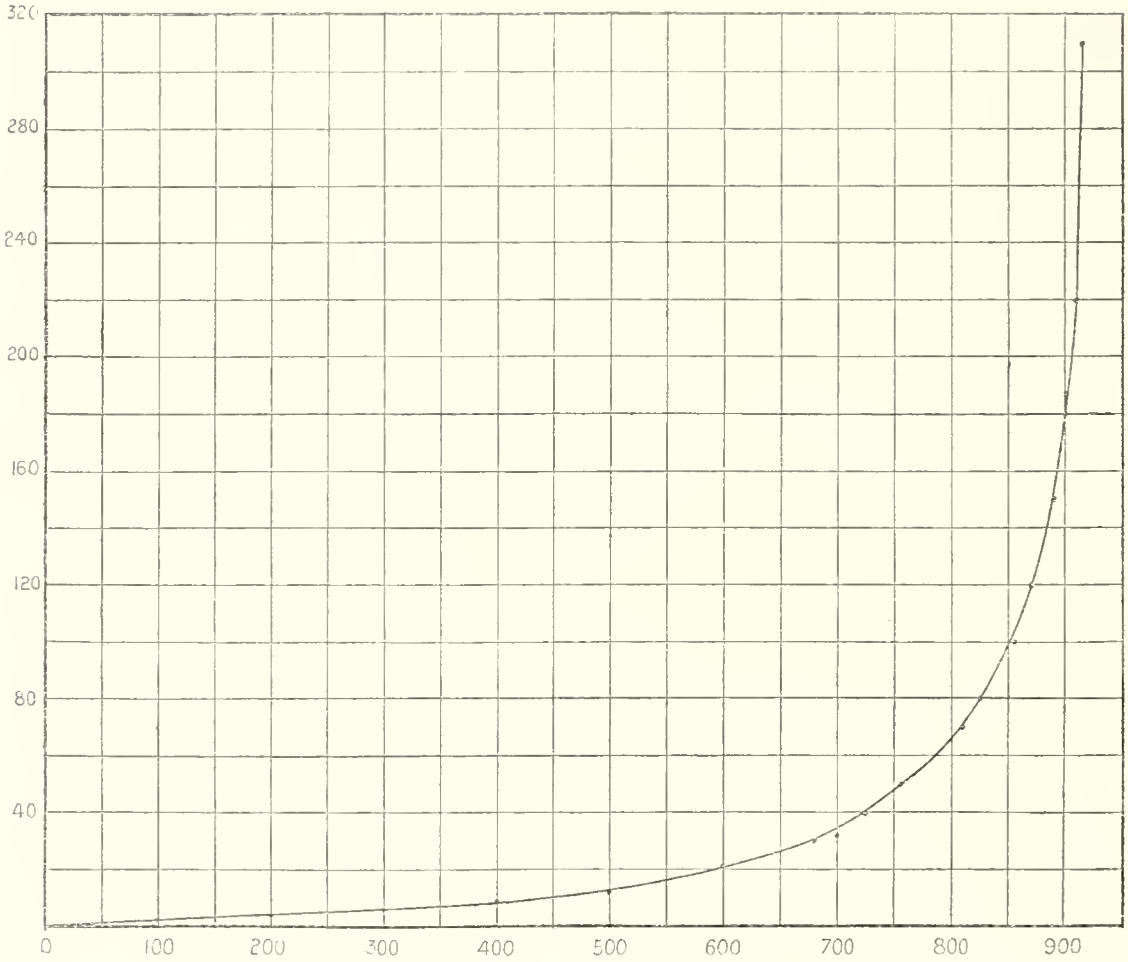

Fig. 8. Abscissæ, contraction from the time of cutting off light. Ordinates, time in seconds after cutting off light.

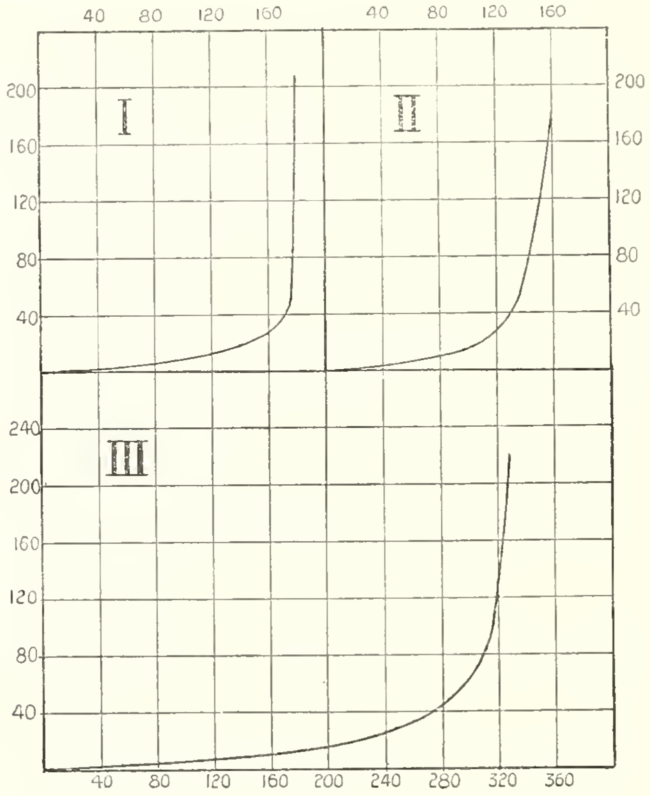

Fig. 9.

There are three causes to which this final contraction may be attributed :—(1) The cooling of the gas which has been heated by the combination ; (2) Continuation of the action, hydrochloric acid being formed for some time after darkening ; (3) Absorption of hydrochloric acid formed while the light was acting.

Bunsen and Roscoe concluded that the effect was due to the first cause, but the amount of contraction in their experiments was too small for much reliance to be placed in their result.

With the platinum thermometer used in earlier experiments it was easy to decide how much of the contraction was due to the first cause. The gas was illuminated ; on darkening, the temperature was found to fall as the contraction proceeded, and it was found that the contraction agreed, within the limits of accuracy of the experiment, with that corresponding to the fall in temperature.

The following two tables give the results for two series of experiments of this kind. In the first column is the observed fall in temperature, in the second the change of volume due to this fall, in the third the observed change of volume, and in the fourth the ratio of the numbers in the third and second columns.

Change in temperature in ° C.	Change of volume corresponding to change of temperature in first column.	Observed change of volume.	Ratio.
·28	230	240	1·04
·41	336	320	·95
·41	336	320	·95
·42	344	360	1·05
·42	344	395	1·15
·35	287	315	1·12
·43	353	353	1·00
·44	361	335	·93

The mean of the numbers in the last column is 1·024.

Change in temperature in ° C.	Change of volume corresponding to change of temperature in first column.	Observed change of volume.	Ratio.
·085	69	53	·77
·101	83	98	1·18
·146	120	150	1·25
·192	157	160	1·02
·283	232	232	1·00
·308	253	250	·99
·321	263	316	1·20
·341	280	280	1·00
·401	329	360	1·09
·401	329	340	1·03
·462	380	398	1·04
·481	394	400	1·01
·504	413	402	·97
·640	525	455	·87

The mean of the numbers in the last column is 1·030.

The contraction therefore, after the light is cut off, is nearly all due to cooling. If any hydrochloric acid is absorbed after darkening, it is very little, and we conclude that the formation of hydrochloric acid stops almost instantaneously when the light is cut off, and that the hydrochloric acid is absorbed almost as soon as it is formed.

3. *The Period of Induction.*

The problem is now simplified to a great extent. The Draper effect and the final contraction have been shown to be due to temperature effects, which complicate the initial and final phenomena. Fig. 4 represents the general course of the induction which takes place under all conditions of illumination. On illumination, hydrochloric acid is formed at first very slowly, the rate of formation increases, the acceleration of the rate of formation increases until a maximum acceleration is reached; then the acceleration decreases to zero, when the rate of action becomes constant, if the gases are present in the mixture in molecular proportions; if there be excess of one gas, the final rate gradually diminishes as the relative quantities of the two gases become more and more different.

We shall at present confine ourselves to the case when the gases are present in approximately molecular proportions, so that all through the experiments the amounts of uncombined gases are present in the same relative quantities.

§ 1. *Prolongation of the Period of Induction.*

In **Bunsen** and **Roscoe**'s experiment the period of inertness was never found to be more than 6 or 7 minutes. If, however, a much less intense light be used the induction period may be prolonged indefinitely, so that an interval of some hours may occur between the beginning of insolation and the formation of hydrochloric acid in large enough quantities to be observed.

In the following two experiments the time to the first visible contraction showing formation of hydrochloric acid was in the first 48 minutes, and in the second 178 minutes.

I.		II.	
Time from illumination in minutes.	HCl formed.	Time from illumination in minutes.	HCl formed.
48	0	177	0
50	5	178	1
51	10	180	3
53	24	184	9
55	39	188	17
60	86	190	23
70	214	194	41
—	—	201	81
—	—	205	104

The bulb used for these experiments was a large one, about 8 centims. in diameter, and the capillary tube was about 150 centims. long, so that the induction could be followed for a long time.

§ 2. *The Effect after Darkening.*

When feeble light is used for insolation the effect that remains after the light is cut off can be detected for a very considerable time. The effect is that after the gas has been illuminated and then darkened, on again illuminating the period of induction is shorter than in the first instance. That is, that all effect of the light does not cease when the light is removed. We have seen that the formation of hydrochloric acid stops almost immediately, but the gases are in a condition when they can combine more readily under the influence of fresh light. The gas is in a condition of insolation. In Bunsen and Roscoe's experiments this effect could not be detected after about 15 minutes in the dark, but it can be prolonged, and in one experiment was detected after the gas mixture had remained in the dark for over 22 hours. With more intense light the visible effect passes off in a very much shorter time, giving results agreeing with those of Bunsen and Roscoe. (For example, in the experiment on p. 85, the effect as far as it affected the initial expansion passed off in about 6 minutes.)

In figs. 10, 11, 12, 13 are represented experiments on this effect. The light

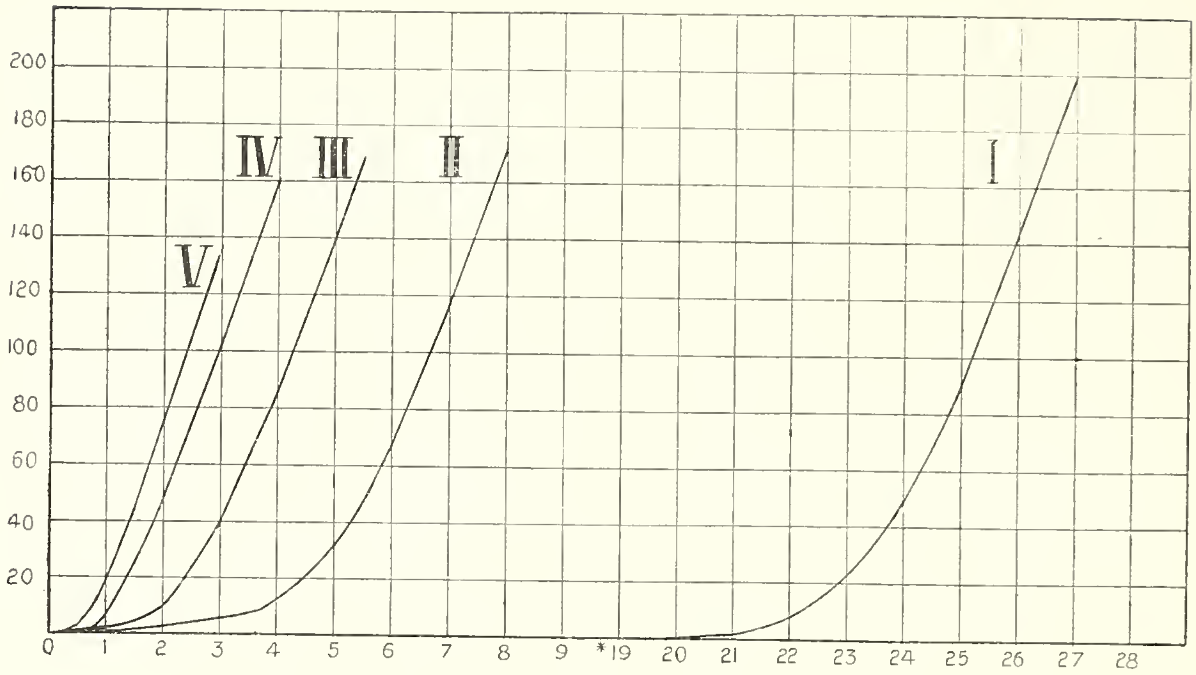

Fig. 10. Abscissæ, time after illumination in minutes.
Ordinates, HCl formed.

Curve I, induction in fresh gas.
,, II ,, ,, gas which had been darkened for 1 hour.
,, III ,, ,, ,, ,, ,, ,, 15 minutes.
,, IV ,, ,, ,, ,, ,, ,, 5 ,,
,, V ,, ,, ,, ,, ,, ,, 0·5 ,,

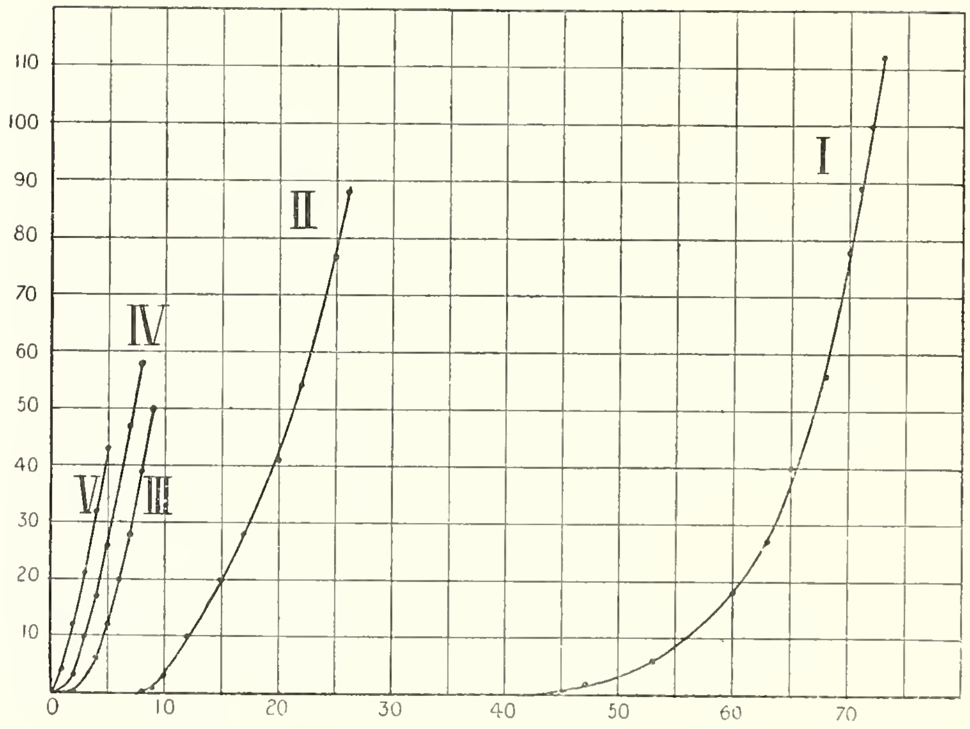

Fig. 11. Abscissæ, time after illumination in minutes.
Ordinates, HCl formed.
Curve I, fresh gas. Curve II, $4\frac{1}{2}$ hours dark. Curve III, 12 minutes dark.
Curve IV, 5 minutes dark. Curve V, 1 minute dark.

intensity was different for the four series of experiments, but the same through each series. The insolation vessels also were not all the same, so that the curves are not comparable except in each separate series. In fig. 12 the curve representing the experiment with fresh gas is not plotted, as the inert period in this case was about 90 minutes, and hence the curve could not be placed on the same diagram as the others of the same series without crowding unduly the other curves.

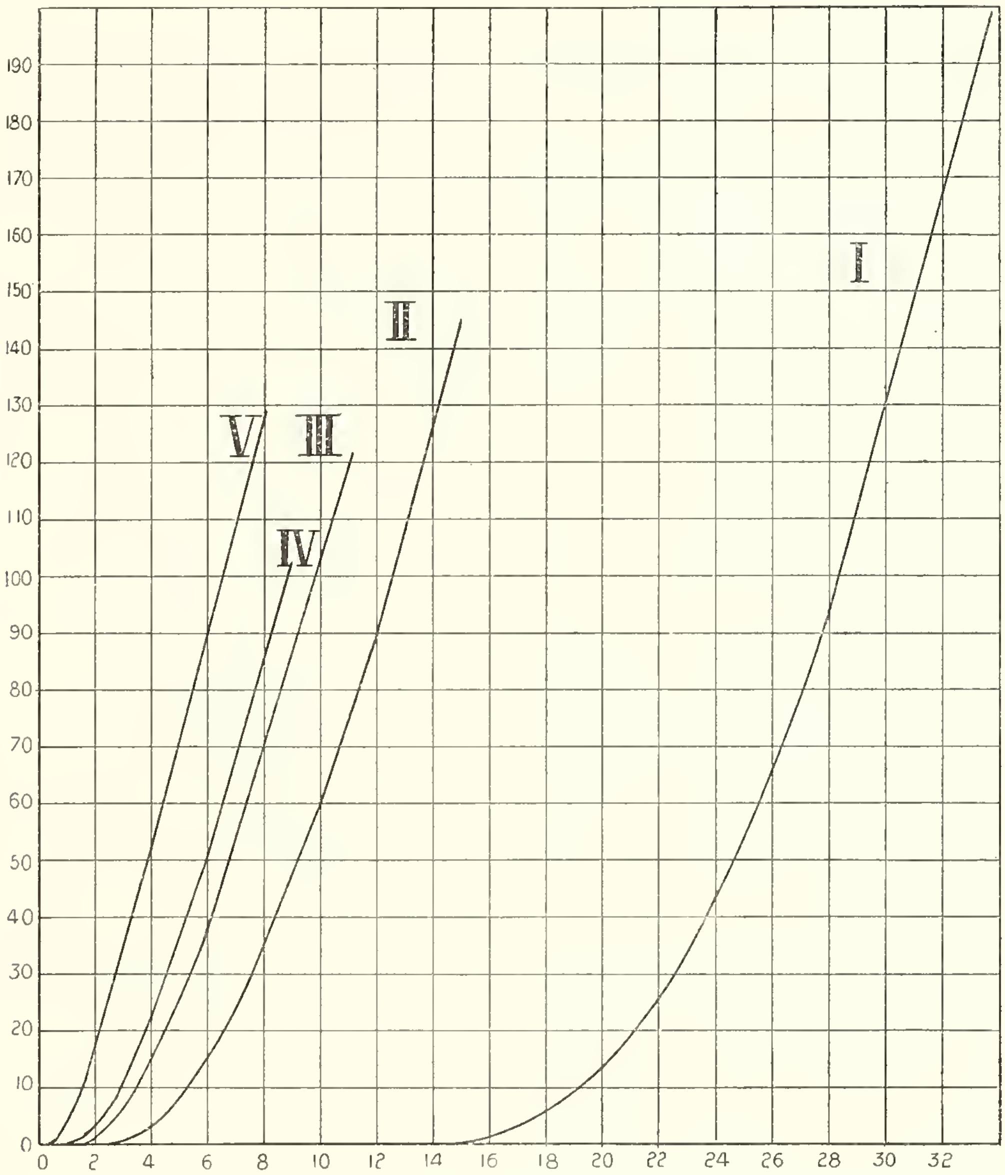

Fig. 12. Abscissæ, time in minutes from beginning of illumination.

Ordinates, HCl formed.

Curve I, 1 hour dark. Curve II, 15 minutes dark. Curve III, 10 minutes dark.

Curve IV, 5 minutes dark. Curve V, 1 minute dark.

With the same insolation vessel, and different intensities of light, the maximum action is proportional to the intensity of the light. (See Bunsen and Roscoe, 'Photochemical Researches,' Part II., p. 387.) Bunsen and Roscoe also showed that the time of exposure necessary to effect the first combination decreases with the increase of intensity of the light, and in a greater ratio than the increase of light, and that the time of exposure to reach the maximum action decreases with increase of light, but in a less ratio than the increase of the light. These conclusions were confirmed, but as they were so well established by BUNSEN and ROSCOE, there is no need to give the results of any of the experiments on these points.

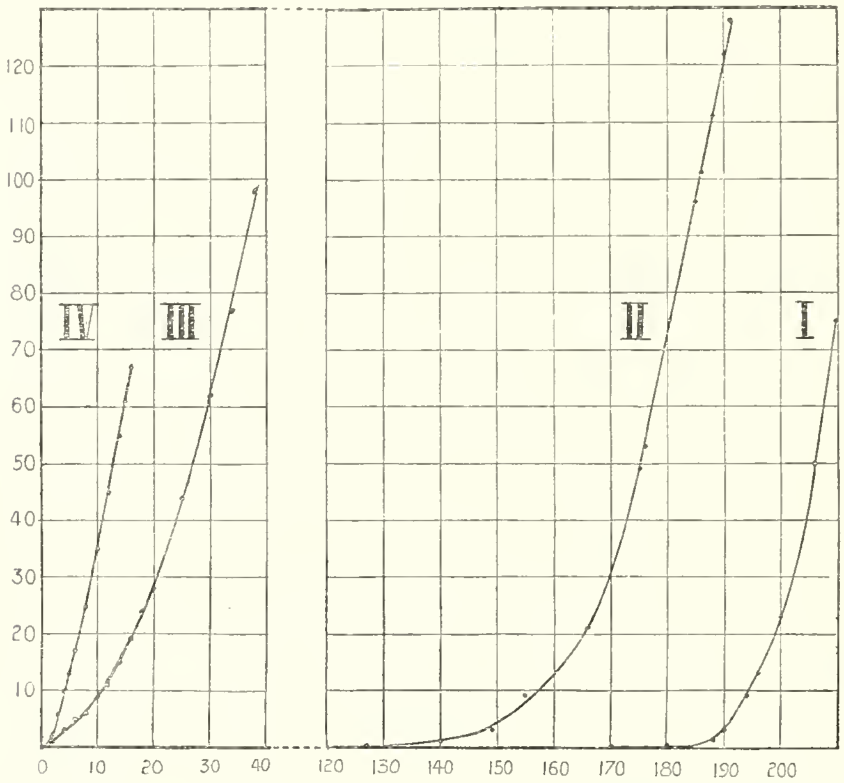

Fig. 13. Abscissæ, time in minutes from beginning of insolation.
Ordinates, HCl formed.
Curve I, fresh gas. Curve II, after 22 hours dark. Curve III, after $\frac{1}{2}$ hour dark.
Curve IV, after 5 minutes dark.

§ 3. *The Effect of Impurities.*

One of the most remarkable facts connected with the action under consideration is the large effect on the rate of combination produced by a small quantity of impurity. BUNSEN and ROSCOE showed that the addition of $\frac{5}{1000}$ parts of oxygen reduced the maximum action from 100 to 9·7. It is extremely difficult to prepare the gas mixture with a definite quantity of impurity in it, and as yet no experiments have been performed which are sufficiently comparable to determine the relation between the quantity of the impurity and the rate of the action. To quote the words of BUNSEN and ROSCOE: "It is perfectly useless to collect the electrolytic gas in a large vessel, then mix it with the impurity, and afterwards to allow the mixture to pass through the apparatus, for there is no possible means of collecting this pure mixture of hydrogen and chlorine in large masses, and again forcing it out in a given direction." In fact, any operation with the gas mixture is sufficient to alter its properties. The only method of procuring reliable results is to evolve the impurity required from a second electrolytic vessel and to pass it continuously through the apparatus together with the normal mixture for some days, using the same current for producing the hydrogen and chlorine and the impurity. However, even under these circumstances, the results obtained are not in any very close agreement. The only conclusion arrived at is that the effect of impurity is large at first, but the effect increases in a much less ratio than the amount of impurity.

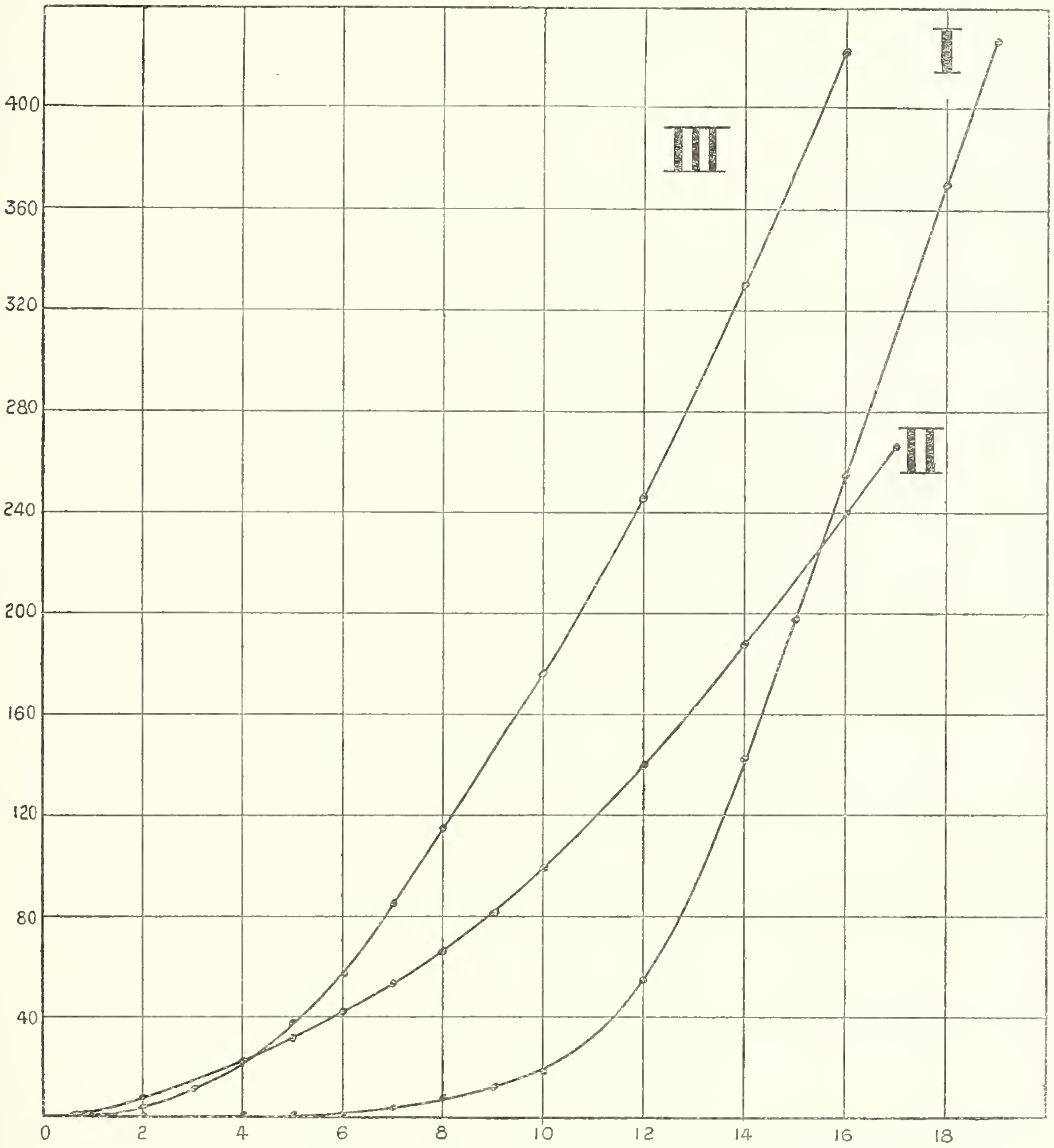

Fig. 14. Abscissæ, time from beginning of action in minutes.
Ordinates, HCl formed.

There is one form of impurity, however, which is not subject to such experimental difficulties as occur with others, and that is the uninsolated gas mixture itself. The uninsolated gas can easily be introduced into the insolation vessel while the action is progressing. If this be done, a large decrease in the rate of action is at once noticed, and the combination may cease altogether if sufficient quantity of gas be introduced. Then an induction period sets in as in the case of a fresh gas mixture. But the attainment of the original maximum is only performed gradually compared with the case of the fresh gases. This will be made clear by the experiments represented in fig. 14. At first the gas was illuminated and, after a period of inertness of about 20 minutes, the acceleration period represented in curve I, fig. 14, took place. After the maximum action had been reached, a quantity of uninsolated gas, occupying about 400 millims. of the index tube, was introduced while the light was still on the mixture. The index came to rest and an inert period of about 1 minute occurred. The acceleration period then set in, but was very much longer than in the case of the original gas; in fact, the rate of action was increasing slowly for as long as the index could be followed, and the maximum action was not attained. This is shown by the curve II, fig. 14, being very much flatter than curve I.

If the mixture be left in the dark for some time before illuminating, after fresh gas has been added, this retarding effect passes off to some extent, and the attainment of the maximum action is not so gradual. Curve III, fig. 14, represents the occurrences when the same gas as for curves II and I had again about 400 millims. of fresh uninsolated gas added, and was then darkened for 5 minutes. The action is seen to

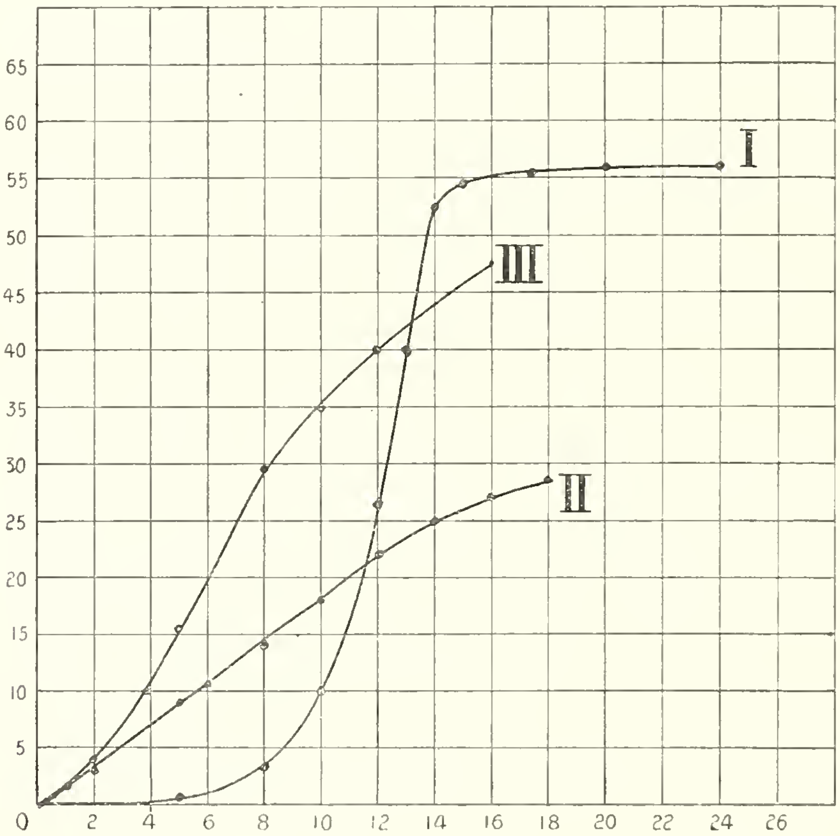

Fig. 15. Abscissæ, time in minutes from beginning of action. Ordinates, velocity of action.

be intermediate between that of the fresh gas and that when the light is kept on continuously while fresh gas is added.

The effect of the added uninsolated gas thus persists for some time and makes itself evident by the prolongation of the acceleration period. This is shown still more clearly on curves for the velocity of the action. In fig. 15 the curves I, II, III are the velocity curves corresponding to the curves in fig. 14. It is at once obvious from these curves that after the admission of uninsolated gas the attainment of the maximum action is slower than when action has begun after all the gas has been uniformly insolated. The fresh gas thus apparently exercises a retarding effect as long as it has not been brought to the condition of the rest of the gas. Mere contact with the insolated gas diminishes this retarding effect, since the maximum is reached sooner after the gases have stood for some time in the dark. This is shown by curve III in fig. 15 being intermediate in character between curves I and II.

The effect of admission of uninsolated gas increases with the quantity of fresh gas added. The velocity curves change from the type (1) to the type (2) as the quantity of fresh gas is increased.

§ 4. *The Effect of Previous Insolation of the Separate Gases.*

It has already been stated that DRAPER found that previous exposure of chlorine to light produced an increase in the rate of action, when the chlorine was mixed with hydrogen and exposed to light.

This conclusion was contradicted by BUNSEN and ROSCOE, but the explanation of this contradiction is that the chlorine in BUNSEN and ROSCOE's experiment was bubbled through water, after it had been illuminated, and this destroys the effect.

To investigate this effect two inverted burettes were placed side by side, the open ends dipped under water in a trough and the burettes were filled with water. Chlorine was slowly passed into the burettes, one of which was darkened by enclosing it in a metal tube. The tube had a slit through which the volume of the gas could be read. By passing the chlorine slowly into the tubes, the water in them becomes almost saturated, so that solution of chlorine in the water does not take place to any appreciable extent during an experiment. After the chlorine in the tube exposed to diffuse daylight had stood for two or three minutes, this tube was also darkened and approximately the same quantity of hydrogen was introduced into the two burettes, so that in each tube there was an approximately molecular mixture of the two gases. The tubes were then left for some time to give the gases opportunity for thoroughly mixing, and then the two tubes were simultaneously exposed to the light. Combination took place, the hydrochloric acid formed being absorbed by the water, which rose in the burettes, and thus afforded a means of measuring the velocity of the combination. In every case the tube which originally had been exposed to light with chlorine in it showed a greater velocity of action at the beginning. In some cases the originally darkened tube in a short time showed a more rapid action, but this occurred only after some time. In the following experiments the tubes were interchanged after each experiment—the one with darkened chlorine in one experiment being used for the illuminated chlorine in the next experiment, and *vice versâ.* The times of the observations were not recorded, but the water levels were read at the same instant, as all that was required was the relative rate of combination. The light used, being diffuse daylight on a bright day, caused fairly rapid combination, and the whole of an experiment occupied only from 30 seconds to 1 minute.

Experiment 1.

No. of reading	1	2	3	4	5	6	7	8
Contraction in tube containing hydrogen and illuminated chlorine	2	4	6	10	12	14	16	18
Contraction in tube containing hydrogen and non-illuminated chlorine	·5	2	5	12	15	18	20	22·5

Experiment 2.

No. of reading	1	2	3	4	5	6	7	8
Contraction in tube containing hydrogen and illuminated chlorine	3	6	10	13	15	16	18	20
Contraction in tube containing hydrogen and non-illuminated chlorine	0	1	3	6	10	13	17	19

Experiment 3.

No. of reading	1	2	3	4	5	6	7	8	9	10	11	12
Contraction in tube containing hydrogen and illuminated chlorine	2	5	11	13	14	15	16	17	18	19	20	25
Contraction in tube containing hydrogen and non-illuminated chlorine	0	1	5	7	8	10	12	13	14	14·5	15	18

Experiments were also made with the chlorine in both tubes treated similarly—both tubes darkened or illuminated before the admission of hydrogen. The contraction observed was similar in the two tubes, and so the initial increase in the case of the tube with insolated chlorine is due to the fact that the chlorine has been influenced by the light. These experiments were frequently repeated with different conditions of illumination, and in every case the phenomena were as in the experiments just tabulated.

No difference in the initial rate of combination could be detected if the hydrogen was first illuminated, and then mixed with chlorine in the dark, and the mixture exposed to light.

If the chlorine be exposed to light in a separate vessel, and then introduced into the burette through the water and mixed with hydrogen, the behaviour was as if it had not been exposed to light at all. The process of bubbling through the water thus washes out the substance in the chlorine which causes the difference between the insolated and non-insolated chlorine.

The anomalies observed in the final rates of formation of hydrochloric acid in these experiments are to be attributed to the differences in the mixtures in the two burettes. It is impossible to obtain with this method two exactly similar mixtures, and the effects of small changes in the composition of the mixture are large. If an excess of chlorine be present in the mixture, the results with different tubes are fairly comparable, much more consistent results being obtainable than with an excess of hydrogen. This fact agrees with BUNSEN and ROSCOE's result, that a small excess of hydrogen makes a very much greater difference in the rate of combination than that produced by the same excess of chlorine.

The effect of insolating the chlorine alone passes off if the chlorine and hydrogen mixture be left in the dark for some time. The behaviour is then similar to that of the ordinary insolated mixture.

There is, therefore, a change produced by the action of light on moist chlorine alone, which is apparent when the chlorine is caused to combine with hydrogen. DRAPER considered that an allotropic modification of chlorine was produced, which combined more readily with hydrogen than ordinary chlorine. It seems more probable that the effect is due to some action between the chlorine and the water vapour, which is always present in these experiments. For water vapour, if not absolutely necessary to the action, assists it very materially.

This view is also supported by the fact discovered by BAKER,* that perfectly pure and dry chlorine does not expand when exposed to light, while damp chlorine does so expand. We have already seen that the expansion of damp chlorine is attended by a development of heat. There is then, at any rate, some evidence that the first stage of the action to form hydrochloric acid is an action between chlorine alone and water vapour.

§ 5. *Expansion Experiments.*

To obtain further evidence of the existence of intermediate bodies in the initial stage of the action between hydrogen and chlorine, use was made of the expansion method of C. T. R. WILSON to discover if any cloud-forming nuclei were produced by the influence of light on the gas mixture. The apparatus was that described by

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* BAKER, 'Brit. Ass. Rep.,' 1894.

Wilson,* so that a sudden expansion of adjustable amount could be produced, as often as was desired, in the same sample of the gas mixture. Great difficulty was found to arise from the action of chlorine on the indiarubber stopper used for stopping the descent of the piston. Several artifices were tried to overcome this difficulty, which was never entirely removed. By covering the stopper with a thin coating of a mixture of solid paraffin and vaseline, if care was used in filling the bulb used, so that as little chlorine as possible should come in contact with the stopper, a single stopper could be made to hold a few days.

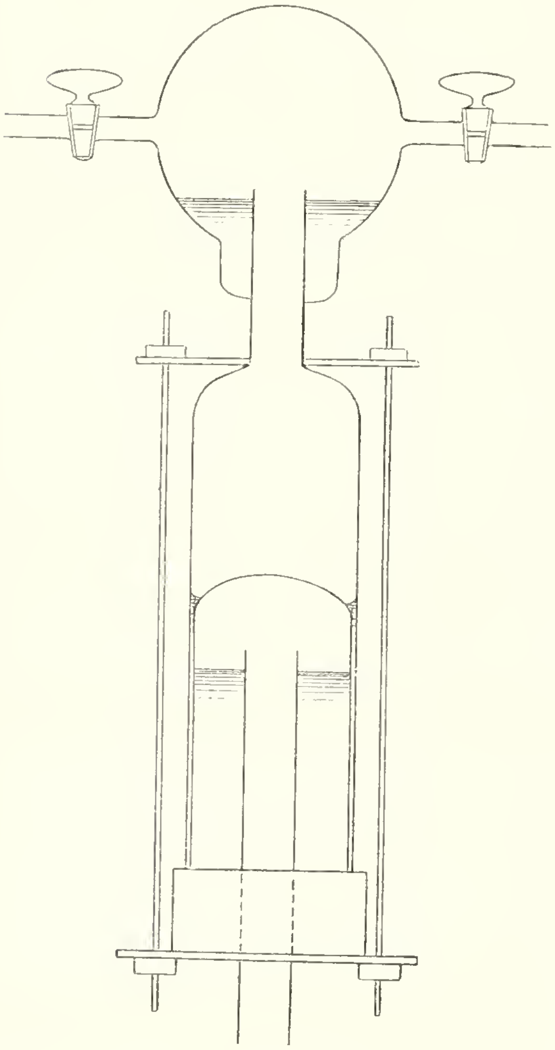

Fig. 16.

The expansion bulb, cylinder and piston, are represented in fig. 16. The rest of the apparatus was the same as in Wilson's experiments, and requires no further description. The method of reading the amount of the expansion was to measure the distance the piston descended in any experiment. After a series of experiments, the instrument was calibrated by attaching to one of the exits from the bulb a manometer, so that the distance travelled over by the piston could be expressed in terms of the change of pressure produced in the expansion bulb. The only part of the apparatus on which the chlorine could act was the stopper on which the piston falls; the taps to the exits were lubricated with water, and one tube leading into the bulb was sealed to the delivery tube of the generating and washing apparatus, which was the same as described on pp. 78 and 79.

The experiments with this apparatus showed that when light is allowed to fall on a mixture of hydrogen and chlorine, a nucleus-forming substance is produced, which causes condensation on a certain definite supersaturation. This condensation appears when an expansion is made greater than a certain definite quantity, and no condensation appears with the same expansion unless the gas has been illuminated. With chlorine alone the condensation appeared when the chlorine had been illuminated, and it was absent when the chlorine had not been illuminated. To observe the cloud or the absence of the cloud in non-illuminated gas, the image of a bat's-wing gas flame was formed in the bulb, the light previously having passed through yellow glass. The cloud produced in gas that had been illuminated was easily seen when illuminated by the bat's-wing flame, so that the difference between

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* 'Cambridge Phil. Soc. Proc.,' vol. 9, p. 333.

the "dark" and "light" expansions is not to be attributed merely to the difficulty of observing the cloud in the former.

(1.) *Experiments with Chlorine alone.*—C. T. R. Wilson showed that in dust-free chlorine a slight rain-like condensation took place, when an expansion, measured by P_1/P_2, greater than 1·30 and less than 1·45, was made. P_1 is the pressure before expansion, P_2 after expansion. With P_1/P_2 greater than 1·45, a cloud-like condensation occurs, increasing in thickness as the amount of expansion increases. In the present experiments the cloud-like condensation was observed to begin at $P_1/P_2 = 1·50$ approximately, and up to this value there were only a few scattered drops observed on expansion, when the chlorine was darkened. If, however, the chlorine be strongly illuminated, the phenomena are very different. The number of drops increases as the expansion increases from $P_1/P_2 = 1·27$ up to the value 1·46, when a thick fog is the result of the expansion. The following table represents the observations in a series of experiments of this kind:—

P_1/P_2.	Observation.
1·21	No drops seen.
1·24	" "
1·27	A few drops.
1·30	Fine rain.
1·33	" "
1·36	More rain with finer drops.
1·41	Thick rain.
1·43	Rain cloud.
1·46	Thick cloud.

If the chlorine be darkened, after a few expansions to precipitate nuclei left by the evaporation of the cloud, the behaviour is similar to that of the original chlorine; only a few drops are seen until the expansion reaches the limit $P_1/P_2 = 1·5$.

These experiments were repeated several times with light of varying intensity. The same result appeared always, so that it is clear that ordinary light (not ultra-violet light) produces in damp chlorine some substance which can act as nuclei for condensation.

(2.) *Experiments with the Mixture of Hydrogen and Chlorine.*—In the dark, expansions with P_1/P_2 less than 1·42, only a few drops were observed. With the expansion greater than this amount, the fog-like supersaturation cloud appeared.

With the mixture illuminated, the results were similar to those obtained with chlorine alone. The formation of drops began when the expansion was such that $P_1/P_2 = 1·22$, the number increasing with increasing expansion, until a thick cloud was produced with $P_1/P_2 = 1·36$. If the intensity of the light was altered, the cloud's thickness altered, but the same variation between the limits, 1·22, 1·36, occurred.

The next experiments made were to determine the effect of the time of illumination on the formation of nuclei. For this purpose an expansion corresponding to $P_1/P_2 = 1{\cdot}35$ (about) was used, as this expansion was well under the expansion required to produce condensation in the uninsolated gas. The following two tables give the results of two series of experiments, one with dim, the other with bright light :—

I. DIM Light. $P_1/P_2 = 1{\cdot}35$.

Time of insolation.	Observation.
1 second	Only one or two drops observed.
10 seconds	Several drops.
30 ,,	Fine rain.
40 ,,	,, ,,
60 ,,	Rain cloud.
4 minutes	Cloud indistinguishable from the last.
10 ,,	,, ,, ,,

II. BRIGHT Light. $P_1/P_2 = 1{\cdot}35$.

Time of insolation.	Observation.
1 second	Fine rain.
2 seconds	More rain.
3 ,,	Cloud.
5 ,,	Thick cloud.
10 ,,	Cloud indistinguishable from the last.
1 minute	Same cloud.

Experiments were next made on the gas after the illumination was cut off. The mixture was illuminated for some minutes before each expansion, and then the mixture was darkened and an expansion corresponding to $P_1/P_2 = 1{\cdot}36$ made after the time in the first column.

Time from darkening to expansion.	Observation.
10 seconds	Thick cloud.
1 minute	,, ,,
2 minutes	Cloud less than in last experiment.
5 ,,	Rain cloud.
10 ,,	Fine rain cloud.
1 hour	Fine rain.
2 hours	A few drops.

With chlorine alone similar results were obtained.

The fact that the cloud produced in the mixed gases is similar to that produced in chlorine alone suggests that in the mixed gases it is the chlorine alone that is efficient in producing the nuclei, and that the hydrogen is inactive. It might be expected that the cloud in the mixture might be formed on hydrochloric acid molecules produced after the illumination. But the cloud-forming nuclei appears before any hydrochloric acid is formed in measurable quantity, as the following experiments show. The expansion apparatus was joined to the ordinary insolation apparatus of fig. 2, and the two illuminated with the same light. The time to the first appearance of motion of the water index, indicating the absorption of hydrochloric acid, was noted. Expansions were also made and the character of the cloud after different times of illumination observed. In all cases the cloud produced on expansion had reached its densest appearance a considerable time before the hydrochloric acid began to be formed. The following numbers will show the kind of phenomena observed :—

Time to the first motion of water index of insolation apparatus . . . . 29 seconds.

Time of insolation before expansion in expansion vessel $P_1/P_2 = 1 \cdot 38$.	Observation.
1 second	Rain.
2 seconds	Rain cloud.
5 ,,	Thick cloud.

and no change in the character of the cloud appeared with longer exposures.

For more careful experiments of this kind a long capillary tube was sealed to the exit tube of the expansion bulb, in which a drop of water served as an index, so that the expansion bulb itself could be used as the insolation bulb (fig. 17). If the tap

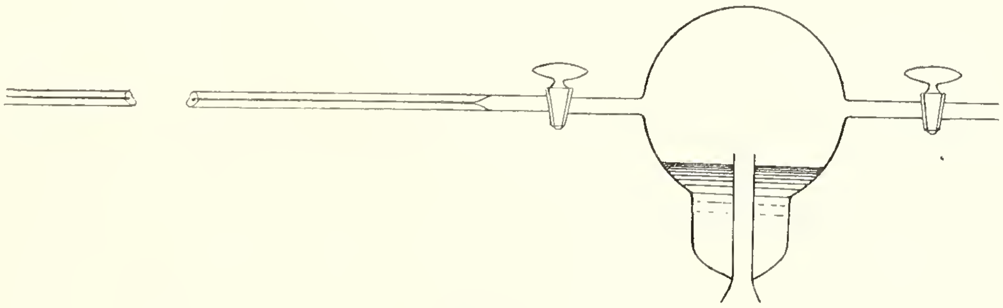

Fig. 17.

between the capillary tube and the expansion bulb was open, the drop of water in the index tube defined the volume of the gas in the expansion bulb; and the rate of formation of hydrochloric acid in the bulb could be followed by noting the motion of the index drop. With the same tap closed an expansion could be made of the same sample of gas. After the expansion had been made, the piston of the expansion apparatus could be allowed to return to its original position, and then, on opening the tap communicating with the capillary tube, the effect of the expansion on the rate of combination could be observed.

With this apparatus it was shown that the nuclei, on which condensation took place on expansion, appeared before any hydrochloric acid was produced. The effects were very much like those on p. 107. The hydrochloric acid is formed only after about five times the illumination required to produce the maximum cloud.

If after hydrochloric acid has begun to be formed an expansion is made, the formation of hydrochloric acid stops if the expansion is large enough to produce a cloud. If no cloud is formed, the expansion being less than corresponding to $P_1/P_2 = 1{\cdot}2$ about, then the hydrochloric acid formation is not affected. In an experiment of this kind, the inert period was found to be about 30 seconds. A cloud producing expansion was then made and, after allowing this cloud to settle, the piston was returned to its original position, and communication made with the capillary index tube; after the first motion of the index due to the adjustment of pressure between the capillary and the bulb the index remained at rest for 16 seconds, and after this began to show formation of hydrochloric acid again. The bulb was darkened for a short time after the expansion to allow the cloud to settle, but the effect of the darkening on the succeeding inert period was very small. An exactly similar experiment, excepting in the amount of the expansion, showed that when no cloud was formed there was no inert period in the second instance.

There is, therefore, some substance produced by the action of the light on the chlorine and water vapour which acts as condensation nuclei. The formation of this intermediate substance is necessary for the production of hydrochloric acid, and the removal of this substance by expansion and consequent precipitation stops the action when hydrochloric acid is being produced, and the induction period has to begin over again.

§ 6. *Experiments with Dried Gases, and other Experiments.*

(1.) *Experiments with Dried Gases.*—With dry gases the action is much less rapid than with damp gases. But the general phenomena of induction are the same when sufficiently intense light is used. There is a period of inertness and of acceleration. Absolutely dry gases have probably never been prepared, but the rate of combination diminishes as the gas mixture is made less moist. In a bulb with phosphorus pentoxide and the gas mixture combination is very slow even in direct sunlight.

(2.) *Effect of Röntgen Rays.*—Röntgen rays were found to have no effect on the combination. In the dark they produce no action; and no effect was found when the rays fell on the gas when combination was taking place under the influence of light.

(3.) *Radium Rays.*—The rays from a specimen of radium were found to produce no effect after two hours.

(4.) *Hydrogen Peroxide.*—Hydrogen peroxide was introduced into the insolation bulb, and the effect was, as in the case of other impurities, to diminish the rate of action.

III. Theory of the Action.

At present there is nothing that can be called a satisfactory theory of chemical action. In nearly all cases the process of an action is very much more complicated than is expressed by ordinary chemical equations. These represent only the initial and final stages which are observed. For example, in actions between electrolytes in solution the individuals taking part in the change are ions and not the salts themselves; and in gaseous systems there appears to be, in very many cases, the necessity for some catalyser to be present for any action to occur. The law of mass action has proved very fruitful as the foundation of chemical kinetics, but the most successful applications of this law have been in cases of actions between molecules in solution, and when gaseous actions have been used as subjects of investigation for the application of this law, the results have only in a few cases* been in agreement with what the law would lead us to expect. Even in these instances the initial stages of the actions have not been studied, so that the agreement with the expected results is only for the case when the action has progressed for some time. The hydrogen and chlorine action is the one to which most attention has been paid in the initial stages, and the initial phenomena do not at all agree with those to be expected from equations derived on the ordinary chemical kinetic theory.

The case of solutions is different from that of gases, as the action is between ions, and the mass law applies at once, for the final products result from direct combination of ions. In gaseous systems, however, we have at the beginning of the action stable gaseous molecules, and the production of the final compounds requires a decomposition, so that the atoms which originally were united become separated and attached to different atoms. An action of this kind therefore involves at least two steps—a decomposition and a composition. In most gaseous actions, in addition to the gases themselves necessary for the formation of the final products, some catalyser is also necessary for the action to proceed with a finite velocity.

The case of a gaseous action is thus still further complicated. In addition to the change from the one form of stable molecule to another, there is the part played by the catalyser to consider. Water vapour is the most commonly-occurring catalyser of this kind, and the natural assumption to explain its action is that intermediate compounds with the molecules of the re-acting gases are formed. We are thus led to

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* For example, "The Decomposition of AsH_3 and PH_3," Kooij, 'Zeit. Phys. Chemie,' vol. 12, p. 155; "The Formation of H_2S and H_2Se, and the Formation of HI," Bodenstein, 'Zeit. Phys. Chem.,' vol. 29.

consider the question of unsaturated and molecular compounds, and first of all, the doctrine of Valency. This doctrine, in spite of its very great use in the systematization of organic chemistry, has to some extent retarded progress by affording too rigid a view of chemical compounds. Until we possess a dynamical conception of a molecule, the theory of bonds can only be regarded as a method of expression of general facts, and not in the sense of giving a representation of actually existing links between atoms. Valency at present has no bearing on compounds which have been called molecular. But no line can be drawn between these compounds and definite atomic compounds. The fact of the existence of such controversies as that as to whether phosphorus penta-chloride was an atomic compound or a molecular compound of phosphorus trichloride and chlorine shows that there is really no difference in kind between these two classes of compounds. Compounds which are saturated under certain circumstances can under other circumstances combine with other systems, so that the difference between saturated and unsaturated compounds is merely one of degree. "Apparently the only saturated molecules known to us at present, molecules destitute of all power of exercising an external influence, are those of gases such as helium and argon."* There is therefore in all molecules, excepting those of the inert gases of the atmosphere, a tendency to form more complicated molecules, some residual affinity which is in many cases unaccounted for on the Valency theory. The difference then between molecular and atomic compounds is a difference of stability under certain conditions, and we must recognise that it is possible for additive compounds of all degrees of complexity to exist, provided that the conditions are suitable. In this connection, the views of NEF† with regard to certain organic substitutions are of importance, as suggesting an explanation of reactions which can be applied to gaseous systems with which we are specially dealing. NEF supposes that reactions take place by unsaturated molecules—compounds exhibiting double linking, or compounds with unsaturated atoms—forming additive compounds with other molecules; afterwards this additive compound breaks down into the final product of the action. For agreement with the Valency theory, NEF supposes that one of the compounds, at the moment of formation of the additive molecule, is dissociated. For example, consider the action of bromine on benzene. In this case, bromine is the unsaturated molecule

$$\mathrm{Br} \equiv \mathrm{Br}.$$

This combines with the benzene molecule, which undergoes a dissociation at the moment of combination, forming the molecule

$$\mathrm{C_6H_5 - Br = Br - H}.$$

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* ARMSTRONG, 'Encyc. Brit.,' Supplement, 1902, Art. "Chemistry."

† NEF, 'Liebig's Annalen,' 1897, vol. 202.

And finally this molecule breaks down into the more stable condition

$$C_6H_5 - Br \quad \text{and} \quad HBr.$$

There is no necessity for the action to be brought into formal agreement with the theory of Valency. We can think of the benzene molecule forming a molecular compound with the bromine molecule, in which system the individual atoms can exert forces on each other, so that an internal re-arrangement of atoms in the additive molecule can take place, resulting in an unstable molecule which breaks down into the final products. This conception gives us a reasonable picture of the process of substitution. We do not consider the atoms in a molecule as rigidly attached at certain definite positions with regard to the molecule, but whatever the forces between atoms may be, in the molecule all atoms can act on each other. Thus if a bromine molecule as a whole be brought into close enough proximity to the benzene molecule, then a bromine atom and a hydrogen atom form, at first as part of the molecule, a system without much effect external to itself and so without much connection with the molecule, in other words, the complex additive molecule is unstable and the HBr molecule splits off.

This view is in effect very much that of Kekulé* on double decomposition. If two bodies aa', bb' react, giving ab, $a'b'$, then at first there is a union and afterwards a decomposition. Kekulé represents the process thus :—

$$\begin{array}{c|c} a & b \\ a' & b' \end{array} \qquad\qquad \begin{array}{c} ab \\ a'b' \end{array} \qquad\qquad \frac{ab}{a'b'}$$

before action, during action, after action.

A somewhat similar view is that proposed by Armstrong, but here a group of three species, forming a voltaic circuit, is introduced, which seems unnecessary and gives really no simplification. Armstrong extends his view to include all actions. But actions which occur in solution are very much more simply explained, on the theory of electrolytic dissociation, as direct combinations. There are probably in gaseous systems cases of simple combination, though in the great majority of cases the action is more complex. An example of this simple combination in gaseous systems is probably to be found in the case of the action of chlorine on mercury. The action occurs when the substances are perfectly pure and dry (Shenstone), and there appears to be no reason to suppose that anything except direct combination takes place. But in very many gaseous actions the direct combination does not take place, at any rate with measurable velocity, and some catalyser is necessary. The experiments of Baker, Dixon and others on the behaviour of pure gases show that in most

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* Kekulé, 'Liebig's Annalen,' 1858.

cases the actions represented by the ordinary equations of chemistry do not occur. For example, the actions

$$2CO + O_2 = 2CO_2, \qquad P_4 + 5O_2 = 2P_2O_5,$$

$$S + O_2 = SO_2, \qquad CS_2 + 3O_2 = CO_2 + 2SO_2$$

do not take place, unless at a very high temperature. But, in the presence of water vapour, action goes on readily and the final products are the substances represented on the right-hand side of the above equations. Now these actions can all be explained on similar lines to those already put forward to explain the formation of the C_6H_5Br molecule. The distinctive character of the explanation is in the assumption that an additive complex molecule is formed at first before the final products are obtained. In most gaseous actions of this type water vapour is a necessary condition of the progress of the reaction. Now there is no molecule which shows a greater tendency to form additive compounds than water. This property is seen in the molecular species which contain water of crystallization. BRÜHL has investigated many other "unsaturated" properties of water and attributes them to the quadri-valency of oxygen, but for our purpose all we need to recognise is the fact that the water molecule tends to form molecular compounds. The part played by the water in a gaseous action we can suppose as follows: The gaseous substance which takes part in the action can unite with the water molecule directly forming a molecular compound. This new complex molecule can then exist for some time, during which its component atoms can re-arrange themselves, so that an internal settling down to equilibrium takes place. In this process a group of atoms may form a part of the whole molecule, which has little attraction for the rest of the molecule, so that it may split off and give rise to a molecule of the final product. We have in effect in this scheme an intermediate compound, but we recognise the possibility of this compound being not capable of isolation, and in many cases so unstable that its own existence may be practically for an infinitesimally short time.

Such a theory as the one now put forward requires direct evidence as to the existence of the compounds assumed, and, further, that it should lead to expressions for the velocity of the action consistent with the observed phenomena. We shall later on discuss the particular case of the hydrogen and chlorine combination; at present we shall examine some of the general results of the theory.

First of all, to define the kind of actions to which this theory can apply, we may divide chemical actions into four classes. We shall not consider actions which go on with a large change of energy, as under these circumstances the conditions of the action change altogether during the progress of the action, but for our purpose we shall suppose the action slow enough for the whole process to be practically isothermal. The first class is that in which the actions are simple combinations. For example, when an Ag ion combines with a Cl ion and forms an AgCl molecule. The second when the action is a simple decomposition, such as occurs when a complex sulphur molecule dissociates into simpler molecules. The third when a re-arrangement of atoms takes place in a molecule; and the fourth where the actions are complex and consist of firstly a combination and finally a breakdown of a complex molecule into simpler molecules. In this class it appears probable that all true substitutions and double decompositions should be placed.*

If we apply the Law of Mass Action to actions of the first three classes, we find in very many cases good agreement between the calculated and observed results for the velocity of the actions. But for the fourth class the case is different, as may be seen from an example.

Consider a double decomposition represented by

$$AB + CD = \{ABCD\} = AC + BD.$$

In the ordinary theory this is a bi-molecular reaction, and the equation for the rate of action is $dx/dt = kyz$, where x is the number per unit volume of molecules of AC or BD and y, z are the numbers per unit volume of molecules of AB and CD; we suppose that the action in the reverse way does not take place. For simplicity, let $y = z$ and $x = n - y$, so that AB and CD are originally present in the same concentration, n molecules per unit volume. Integrating the equation, we have

$$\frac{1}{y} - \frac{1}{n} = kt.$$

But if the intermediate compound ABCD exists, we must take into consideration another step in the action. Let w be the number of ABCD molecules present, then we should have

$$dw/dt = kyz - dx/dt \qquad \text{and} \qquad dx/dt = k'w,$$

with the condition that initially $w = 0$. At first, then, $dx/dt = 0$.

If k' is large compound with k, we should have after a certain time

$$dw/dt = 0 \qquad \text{and} \qquad dx/dt = kyz,$$

so that after a certain time the action would go on as a bi-molecular action. But up to this time the velocity of the action would increase from 0 to a maximum value. In other words, we should have a period of induction. The duration of this period of induction will evidently depend on the quantities k and k'. If k' were large

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* This view receives some support from the phenomena connected with the decomposition of organic compounds, alone, and in the presence of nitrogen, by means of the silent discharge. The compounds produced frequently contain more carbon atoms in the molecule than in the initial substances, and can be explained on the assumption of the breakdown of additive molecules. See BERTHELOT, 'Comptes Rendus,' 1898. The decomposition products of saturated hydrocarbons are also explainable in this way, *e.g.*, acetylene is produced on heating methane.

compared with k, the period of induction would be correspondingly short. In other words, the duration of the induction period will depend on the stability of the intermediate compound.

If, then, there is an intermediate compound formed, a period of induction is to be expected. This phenomenon is observed in many cases, and especially in those which require for their finite velocity the presence of a catalyser. For example, the hydrogen and chlorine action. The action of bromine on fatty acids.* The reduction of metallic oxides by hydrogen and carbon monoxide.† In these actions the evidence for the period of induction is complete, and it cannot be regarded as due to disturbances arising from secondary causes unconnected with the action. Secondary causes may produce acceleration or retardation of an action, but the period of induction proper must be regarded as a characteristic of the action itself. This is in opposition to the view of VAN 'T HOFF. He says: "An acceleration of this kind is incompatible with the principles laid down in this book" ('Studies in Chemical Dynamics'), and he goes on to examine certain actions, and concludes that the accelerations observed are to be explained by secondary reactions. The reactions, he considers, are the change of rhombic into monoclinic sulphur, the formation of water from hydrogen and oxygen, and the polymerization of cyanic acid. The first and third of these actions are probably simple combinations, so that no acceleration would be expected other than that due to the action of the monoclinic sulphur in the one case and the cyamelide in the other. In the case of the formation of water the experimental evidence is not sufficient to justify the conclusion that there is no period of induction, for this period may be short and its effect observable only in the very early stages of the action, which for this particular action have not been observed. The very definite and constant character of the induction period in the hydrogen and chlorine action, which is one of the few actions whose early stages can be observed accurately, is sufficient evidence of the essential character of this period, and we cannot agree with VAN 'T HOFF in his conclusion that the existence of the induction period is merely "an indication that some necessary precaution has been omitted."‡

We come now to consider in more detail the hydrogen and chlorine action. The rate of progress of this action depends largely on the presence of water vapour. The drier the gases are the slower the action is, so that when the gases are dried with great care they do not combine completely after three or four days' exposure to bright sunlight. It seems, therefore, reasonable to suppose that under ordinary conditions the water vapour plays an essential part in the combination, and that without any water vapour present the action would not take place with measurable velocity. The fact that illumination of the chlorine alone before mixing with

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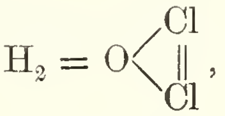
* URECH, 'Berichte,' vol. 13, p. 539, 1880.

† WRIGHT, LUFF and RENNIE, 'Journal of Chem. Soc.,' 1879, p. 495.

‡ 'Studies in Chemical Dynamics,' p. 98.

hydrogen makes the action take place more readily, leads us to conclude that the first stage of the action is the formation of an additive compound from the chlorine and water vapour. Chlorine does form a hydrate with water, and the departure of chlorine from HENRY'S law, and other anomalous behaviour in solution, shows that it does tend to form additive molecules with water. We have seen that there is direct evidence for the existence of some new substance when light is allowed to fall on damp chlorine, but as yet we cannot say what this compound actually is. It is possible that a compound analogous to hydrogen peroxide is formed by simple addition of one molecule of water to one of chlorine.

The constitution of this compound would be represented by the following formula,



$$H_2 = O\left\langle\begin{matrix} Cl \\ \| \\ Cl \end{matrix}\right. ,$$

adopting to some extent NEF'S view of the action of an halogen in forming an additive compound. Such a compound might exist, but it would probably be extremely unstable, and would, if left to itself, break down into water and chlorine again, or into the molecules HCl and HClO. The fact that damp chlorine, under the influence of light, does yield these two compounds, supports to some extent this view. However, in the absence of direct evidence for the constitution of this compound, we shall simply assume that an additive molecule $(H_2O)_{n_1}\,(Cl_2)_{n_2}$ is formed.

Illumination of the hydrogen alone, before mixing with chlorine, does not affect the rate of combination, so that there appears to be no direct additive compound of water and hydrogen formed. But on the present theory we suppose that the next stage in the action is the formation of a still more complex molecule, by the addition of one or more hydrogen molecules to the complex water-chlorine molecule. A molecule $(H_2O)_{n_1}\,(Cl_2)_{n_2}\,(H_2)_{n_3}$ is thus formed. In this molecule the hydrogen and chlorine atoms can come into action with each other. A pair, consisting of a hydrogen atom and a chlorine atom, may nearly saturate each other, and, thus forming a system with little effect on the whole molecule, may split off from the complex molecule as a molecule of hydrochloric acid. The hydrochloric acid then finally produced is the result of the breakdown of the complex hydrogen-water-chlorine molecule. The rate of formation of hydrochloric acid is proportional to the concentration of the complex molecules $(H_2O)_{n_1}\,(Cl_2)_{n_2}\,(H_2)_{n_3}$. The rate of formation of these is proportional to the concentration of the water-chlorine molecules and n_3th power of the concentration of the hydrogen molecules. And the rate of formation of the water-chlorine molecules is proportional to the n_1th power of the concentration of the water molecules, and the n_2th power of the concentration of the chlorine molecules.

As at present we do not know the composition of the intermediate compounds, we shall work out the case when the complex molecule is as simple as it can be, that is when $n_1 = n_2 = n_3 = 1$.

When the combination takes place in a vessel under constant pressure and where the hydrochloric acid is absorbed as soon as it is made, the concentration of the H_2O, H_2, and Cl_2 molecules can be considered to be constant, as the intermediate compounds are formed only in small quantities. If, however, as in GAUTIER and HÉLIER's experiments, the action takes place in a closed vessel, the active masses of the hydrogen and chlorine diminish, and this must be taken into consideration. We shall assume that the water-vapour has constant concentration throughout, as it is liberated in the final stage of the action.*

Taking this second case first, let ξ be the number of chlorine or hydrogen molecules per unit volume (supposing the gases present in equivalent proportions). Let x be the number of molecules of the formula $H_2O\ Cl_2$, y the number of molecules H_2O, Cl_2, H_2, and $2z$ the number of molecules of hydrochloric acid. Then, from the law of mass action for the formation of the HCl molecules,

$$dz/dt = c_1 y,$$

c_1 being a constant dependent on the stability of the H_2O, Cl_2, H_2 molecules;

$$dy/dt = c_2 x\xi - dz/dt,$$

for the rate of formation of the H_2O, Cl_2, H_2 molecules is proportional to the concentration of the H_2O, Cl_2 molecules and that of the H_2 molecules. And also for every two molecules of HCl formed, one molecule of H_2O, Cl_2, H_2 is lost (we assume that the number of H_2 molecules is not appreciably different from the number of Cl_2 molecules, *i.e.*, that x can be neglected when compared with ξ).

And finally we have in a similar manner

$$dx/dt = c_3\xi - c_2 x\xi.$$

And, since $2z$ is the number of HCl molecules formed, 2ξ the total number of H_2 and Cl_2 molecules, and there is no change in the total number of molecules (the number of intermediate molecules being negligible compared with those of hydrogen, chlorine, and hydrochloric acid),

$$\xi + z = \text{constant} = n.$$

For the case when the hydrochloric acid is absorbed as soon as it is produced, the concentration of the chlorine and hydrogen molecules remains constant and the equations are of the form,

$$\left.\begin{aligned} dz/dt &= c_1 y \\ dy/dt &= c_2 x - c_1 y \\ dx/dt &= c_3 - c_2 x \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (1),$$

---

* This assumption is perhaps not justifiable for some of GAUTIER and HÉLIER's experiments, as the gases were partially dried, and so there was only a small quantity of water-vapour present.

when the steady state is reached; dy/dt and dx/dt, both are zero, whence

$$dz/dt = c_3, \qquad \bar{x} = \frac{c_3}{c_2}, \qquad \bar{y} = \frac{c_3}{c_1},$$

where $\bar{x}$, $\bar{y}$ are the final values of x and y.

Integrating equations (1) we obtain

$$x = \frac{c_3}{c_2}(1 - e^{-c_2t}),$$

$$y = \frac{c_3}{c_1}\left(1 + \frac{c_2}{c_1 - c_2}e^{-c_1t}\right) - \frac{c_3}{c_1 - c_2}e^{-c_2t},$$

$$z = c_3t - \frac{c_3}{c_1 - c_2}\left\{\frac{c_1}{c_2}(1 - e^{-c_2t}) - \frac{c_2}{c_1}(1 - e^{-c_1t})\right\},$$

using the condition that x, y, and z are initially zero.

For the velocity of formation of the hydrochloric acid we have

$$\frac{dz}{dt} = c_3 - \frac{c_3}{c_1 - c_2}(c_1e^{-c_2t} - c_2e^{-c_1t}),$$

and for the acceleration

$$\frac{d^2z}{dt^2} = \frac{c_1c_2c_3}{c_1 - c_2}(e^{-c_2t} - e^{-c_1t}).$$

With regard to the constants c_1, c_2, c_3; c_3 is the final rate of formation of hydrochloric acid, and this was found to be proportional to the intensity of the light by BUNSEN and ROSCOE. c_3 is also a measure of the rate of formation of the chlorine-water additive molecules, and, as we have seen in the description of the cloud experiments on p. 106, the more intense the light the more rapid is the formation of the cloud producing nuclei. For the other two constants we have seen that the water-chlorine molecules are produced some time before any hydrochloric acid is formed, so that the last two stages of the action do not take place so rapidly that the first intermediate compound has a very short existence. Both c_1 and c_2 are, therefore, not very large. Further, BUNSEN and ROSCOE showed that there was a definite absorption of light associated with the combination—more than was absorbed by an equal quantity of damp chlorine. One, therefore, or both of the constants c_1, c_2 depends on the light intensity. This also appears from the fact that the effect of insolation persists for some time after the mixture is darkened. If c_1 and c_2 were both independent of the intensity of the light, we should expect that in a short time the H_2O, Cl_2 molecules would all be used up, and that the gas would very soon return to its normal condition. But the effect of previous insolation can persist for several hours. This is explained if we suppose that the H_2O, Cl_2 molecules are able to exist for some time, and are not liable to rapid spontaneous decomposition into the original molecules H_2O and Cl_2, or into new molecules HCl and HClO. That this complex molecule is to some extent stable appears both from the expansion experiments in damp chlorine, and from the fact that pre-insolation of damp chlorine alone makes the subsequent combination with hydrogen more rapid (p. 101), for in these last experiments the chlorine was darkened while hydrogen was admitted, and this operation lasted sometimes for several minutes. Owing, however, to the difficulty of obtaining comparable results with these experiments, all that can be said is that the H_2O, Cl_2 molecules can exist at any rate for several minutes. The constants c_1, c_2 cannot at present be more accurately defined, but we may suppose them both to depend on the intensity of the light.

The value for dz/dt,

$$c_3 - \frac{c_3}{c_1 - c_2}(c_1 e^{-c_2 t} - c_2 e^{-c_1 t}),$$

represents the general features of the acceleration period. Originally dz/dt is zero, and also d^2z/dt^2 and higher coefficients. d^2z/dt^2 is always positive, and increases to a maximum at a time given by

$$\frac{e^{c_1 t}}{c_1} = \frac{e^{c_2 t}}{c_2}.$$

After this time d^2z/dt^2 decreases until dz/dt is constant.

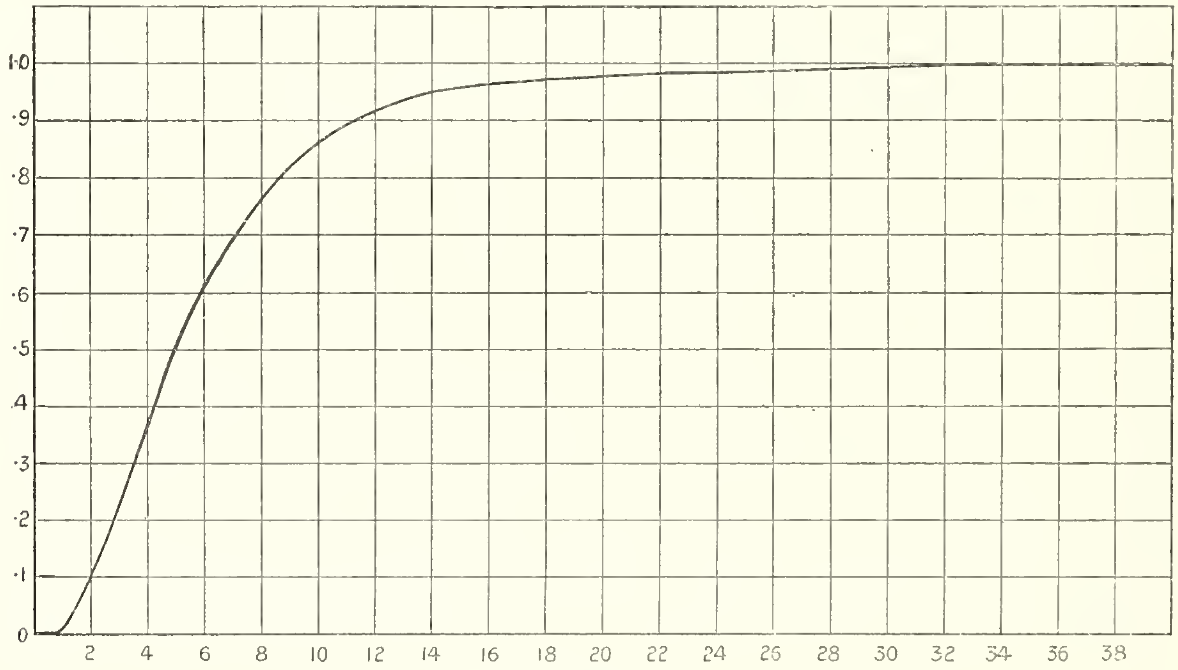


Fig. 18.

In fig. 18 the curve representing $1 - e^{-c_2 t} - \frac{c_2}{c_1}(1 - e^{-c_1 t})$ is plotted for the value $c_2/c_1 = \cdot 9$. This expression is proportional to dz/dt, and so the curve in the figure should represent the velocity curve of the reaction. The essential features are the same, we have a period of inertness, a period of acceleration, and, finally, the constant value for the velocity, as we have in the experimental curves.

The main features of the induction period are therefore given by the formula we have obtained. If we make the more general assumption with regard to the intermediate compounds, we should considerably complicate the results, but it is easy to see that the inert period and acceleration period would be represented; but as at present we do not know what these compounds are, it is not worth while working out any more detailed results. We can at present only regard the expressions found above as giving the qualitative nature of the reaction, for we have omitted various possibilities of which account must be taken for a more exact theory. For example, we have neglected to take account of spontaneous decomposition of the intermediate products. We know that the water-chlorine molecule decomposes or is absorbed by the solution. We should have, therefore, in the equation for the rate of formation of this body another term, say Cx, so that the equation would become

$$dx/dt = c_3 - (c_2 + \mathrm{C})\, x,$$

where C is a constant, independent of the light intensity.

If then the light intensity be very small, c_3 would be small compared with C, and so x will increase exceedingly slowly, so that the apparently inert period may be prolonged to a very large extent. In any case, more terms in the equations of this type indicate prolongation of the period of induction, and especially the early part of this period.

With regard to the action of impurities, we can explain the phenomena if we assume that an action can take place between the impurity and the intermediate compounds. In this way a relatively small quantity of impurity would produce a large effect on the final rate of action, since the quantity of the intermediate products is always small.

If now we again consider the equations on p. 116 for the action when the hydrochloric acid is not absorbed, we notice that after the induction period is over, the action settles down to that represented approximately by the monomolecular equation

$$dz/dt = c_3 \xi.$$

But here again the effect of spontaneous decomposition will be to change the character of the action. Assuming as before that the chlorine-water molecule spontaneously decomposes, we have, after the period of induction for the rate of formation of hydrochloric acid,

$$\frac{dz}{dt} = \frac{c_2 c_3 \xi^2}{c_1 (\mathrm{C} + c_2 \xi)}.$$

If C be large compared with $c_2\xi$, then the action is approximately bi-molecular.

These considerations show that for such an action as we are considering, we cannot assume that the normal course is of the ordinary mono-, bi-, or polymolecular type. By varying the conditions of the action, the relative values of the constants are changed, and the result may not agree with any of those deduced from the simple types of equation.

The hypothesis of the existence of intermediate compounds, formed with the water-vapour present in the gas mixture, leads us to equations which represent the phenomena observed, at any rate qualitatively. The catalytic action of the water-vapour in this case is due to its taking an essential part in the process of combination. The action is therefore on this theory more than a mere quickening of the action which would go on slowly without the catalyser. It is possible that the action takes place very slowly in dry gases, but it seems probable that, if so, it occurs in a different way, as for example, by the direct combination of dissociated atoms. The function of the water-vapour we have assumed to be to form a centre about which the hydrogen and chlorine molecules can assemble, so that the atoms come into each other's spheres of action and can re-arrange themselves, giving rise to a system of greater stability. This process we have supposed to take place by the formation of molecular compounds, and we have seen that a great many of the facts are explained on this hypothesis. We can regard this catalytic action as not essentially different from the catalytic action of such substances as platinum black. In these cases the gases in the action, helped by such a catalyser, probably form condensed layers on the catalyser, and thus the actual molecules of the combining gases are brought into very intimate contact, and re-arrangement of the atoms may take place.

In the particular case of the hydrogen and chlorine action, we have evidence of an unstable water-chlorine molecule, or, at any rate, aggregate, formed at the expense of the energy of the light, and it seems probable that in the case of other actions conditioned by the presence of water-vapour, the action proceeds by the aid of similar intermediate compounds. If this be so, we have seen how the action may not proceed in the way indicated by the ordinary theory, and so we have an explanation of the many anomalous results obtained in experiments on the rate of combination in gaseous systems.

SUMMARY.

I. *Experimental.*

(1.) The initial expansion is the result of heat developed in the combination of hydrogen and chlorine.

(2.) The initial expansion is an effect different from that observed when chlorine alone is acted on by light. This last effect is due to a rise in temperature, the energy for which is supplied by the light.

(3.) The action ceases almost instantaneously when the light is cut off.

(4.) The combination is made very much more rapid by the presence of water-vapour.

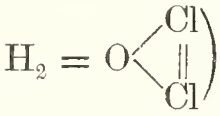
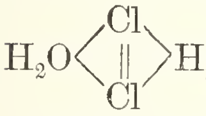
(5.) Small quantities of impurities produce a great decrease in the rate of action.

(6.) The induction period may be prolonged indefinitely, but its general character remains the same.

(7.) Previous illumination of chlorine, before mixing with hydrogen, makes the action, when light falls on the mixture, faster to begin with—shortens the induction period. This property of insolated chlorine is lost if the chlorine be bubbled through water. Previous illumination of the hydrogen is without effect.

(8.) Before any hydrochloric acid is formed, some intermediate body is produced which can act as nucleus, on which a cloud can form on a certain expansion.

II. *Theoretical.*

(1.) The induction period is an essential part of the action, and occurs owing to the formation of intermediate compounds from water-vapour and the two gases. The nature of these compounds is not discovered; but it seems probable that, first, an additive compound of chlorine and water is formed (perhaps  $H_2 = O\left\langle\begin{matrix} Cl \\ \| \\ Cl \end{matrix}\right.$), then a hydrogen molecule becomes attached to this, forming the compound  $H_2O\left\langle\begin{matrix} Cl \\ \| \\ Cl \end{matrix}\right\rangle H_2$, and finally this complex body breaks down into H_2O and $2HCl$.

(2.) This view of the process of the combination explains the phenomena of the period of induction and the effect of pre-insolation of the chlorine, and makes it possible to understand the great effect of impurities.

(3.) This view of the action of water molecules, in forming additive compounds, can be extended to all those actions where water-vapour, as a catalyser, seems to be necessary for the progress of the action with finite velocity.

(4.) In the case of actions in gaseous systems, conditioned by the presence of a catalyser, a period of induction must be expected to occur, and the application of the law of mass action to such cases must be made with reference to the intermediate compounds formed. There is, therefore, no reason to expect that agreement will be found between the theory of mass action as applied to the end product equation and the actual experimental results.

In conclusion, I wish to express my thanks to Professor J. J. Thomson for having suggested this investigation, and for his advice during the course of the experiments, which were performed at the Cavendish Laboratory.

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[PLATE 12.]

METEOROLOGICAL OBSERVATIONS OBTAINED BY THE USE OF KITES OFF THE WEST COAST OF SCOTLAND, 1902

BY

W. N. SHAW, Sc.D., F.R.S.,

AND

W. H. DINES, B.A.

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III. *Meteorological Observations obtained by the Use of Kites off the West Coast of Scotland*, 1902.

By W. N. Shaw, *Sc.D.*, *F.R.S.*, *and* W. H. Dines, *B.A.*

Received April 28,—Read May 14, 1903.

[Plate 12.]

The investigation, of which the results are given in the following pages, was undertaken by a Committee of the Royal Meteorological Society appointed in the spring of 1901, with the co-operation of a Committee appointed by the British Association at Glasgow. Towards the cost of the experiments £75 was contributed by the Government Grant Committee of the Royal Society, £75 by the British Association, and £25 anonymously by a Fellow of the Royal Meteorological Society. The remainder of the cost, amounting to £106, was defrayed by that Society.

The Meteorological Council lent the instruments required for a base station at Crinan, and defrayed the cost of maintaining the station. The Council have afforded further assistance to the investigation by undertaking the tabulation of the curves and the preparation of the necessary diagrams. This work has been carried out in the Observatory branch of the Meteorological Office.

The experimental arrangements were designed and carried out by Mr. Dines, with the assistance of his two sons.

For many years past observations on the temperature and humidity of the upper air lying over the United States and the Continent of Europe have been obtained by means of kites, but although this method of investigation was originally started by Dr. Watson, of Glasgow, in 1749, Mr. Archibald seems to have been the only person to make much use of kites for meteorological purposes in England. It was felt by many interested in meteorology that, as the British Isles lie close to the usual track of the cyclonic disturbances which reach Europe from the Atlantic, information as to the conditions prevailing in the upper air over their surface, and more particularly over their Western Coasts, is of especial importance.

In the spring of 1901 a Committee was appointed by the Royal Meteorological Society to consider what could be done, and in the same year, at their Glasgow meeting, the British Association appointed a Committee to co-operate in the matter. These Committees, working together, decided to obtain the necessary apparatus, and to make observations during the three summer months of 1902 at some convenient place on the West Coast of Scotland. It was decided that, if possible, a steam vessel should be employed, since this would enable observations to be made in comparatively calm weather when otherwise no ascent could be made.

Locality of Observations.

The observations were made partly from a small island in Crinan Bay, Argyllshire, but chiefly from the deck of a steam tug in the Sounds of Jura and Scarba, or on the open sea lying to the South of Mull. The position is indicated by circles with Crinan Harbour as centre, drawn in the charts included in fig. 5, p. 135. Could anyone have ascended with the kites, he would on every occasion have had a clear view, apart from mist or clouds, of the Atlantic Ocean lying to the westward, and since the winds, with a few exceptions, were from some westerly point, the results obtained may be taken as approximating to the conditions prevailing over the open sea.

Apparatus and Methods.

Details of the apparatus used and the methods employed for raising the kites are published in the 'Quarterly Journal of the Royal Meteorological Society,' vol. 29, p. 65, 1903. It will be sufficient to state here that flying a single kite from a small steam tug is a very simple and easy process under all ordinary conditions of weather. With a vessel steaming 12 knots, a kite, with recording instruments attached, could be sent up at any time that the wind did not exceed force 8 on the Beaufort scale. The tug used at Crinan could not steam more than 7 knots, and a kite could not be started unless there were sufficient wind to make a ripple on the surface of the water. Unfortunately the summer of 1902 was not a favourable one for kite work in that particular locality, as there were a large number of very calm days. On these days, with the assistance of the tug, there was always a chance of raising a kite to at least 1000 feet, but it was not always possible to get sufficient lifting power to raise the instruments. On the other hand, there were a few days on which the wind equalled or exceeded force 7, a moderate gale; on these days a kite could be, and in fact was, sent up, but as the Committee were unable, for want of funds, to provide a spare set of recording instruments, it did not seem advisable to risk the loss of the single set by sending them up in very strong winds.

Between June 19 and August 26, 71 ascents were made with an average height of 4200 feet (1280 metres). In 40 of these, with an average height of 5900 feet (1798 metres), records from self-recording instruments were obtained. Those on July 4 and 7 were from land, the others from the tug. The great advantage of a steam vessel for this purpose is shown by the fact that whereas during the three weeks when ascents were made from the land, it was only found possible to get a kite up on ten occasions and the instruments on two occasions, during the seven weeks when the tug was used 61 ascents were obtained; a height of at least 1350 feet was reached on every day on which it was available, and the instruments were raised 38 times. A far greater average height would have been obtained had there been a spare set of recording instruments; as there was only one set, and as the risk of losing the instruments is greatly increased by using additional kites, not more than two kites were used for any ascent until the last week.

The average angular elevation given by the kites with a short length of line was 62° 30′. The greatest heights attained were 5500 feet (1676 metres) with one kite, 9200 feet (2804 metres) with two, 12,400 feet (3790 metres) with three, and about 15,000 feet (4500 metres) with four. In the last case the instruments were lost through the breaking away of the top kite on August 26, and the precise elevation is unknown.

Recording Instruments.

The recording instruments were of the well-known form made by Messrs. RICHARD FRÈRES, of Paris, in which a single drum is used for three pens, recording in aniline ink, on ruled paper, the height in metres, the temperature in degrees centigrade, and the humidity in percentages of saturation. As regards the sensitiveness of graduation of the instruments, it may be remarked that the rulings on the sheet were such that a sufficiently fine trace would give a reading of the height to 10 metres, of temperature, with somewhat less certainty, to ·1 °C., and of humidity, with still less certainty, to ·1 per cent.

No special calibration of the instruments was made. Temperature comparisons with ordinary thermometers were made from time to time at ordinary temperatures, and for the range of observation, which was not large, the differences were found to be within the probable errors of reading and exposure. The temperatures are accordingly taken from the curves without correction. No claim is made to any high degree of accuracy in the measurement, but differences of temperature are probably recorded with sufficient accuracy for this stage of the inquiry.

In view of the uncertainties attaching to the estimation of heights by an aneroid barometer, independent measures of the height of the kites were made for the purpose of correcting the instrumental readings. With a kite ascent from land, this is not very easy, since a kite is seldom stationary, and it is difficult to identify the time on the chart exactly with the time of an observation. It is different when using a vessel, for by altering the speed or direction of the vessel, the angular elevation of the kite can, as a rule, be varied at pleasure within wide limits, and by this means a decided crest or hollow, that is easily identified on the trace, is obtained. The angular elevation corresponding to the top of the crest or the bottom of the hollow is observed by a sextant, and this, together with the known length of wire out and a small correction for sag,* gives the height with fair accuracy.

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* 'Monograph on the Mechanics and Equilibrium of Kites,' by C. F. MARVIN, U.S. Weather Bureau, Washington, 1897, p. 69.

The heights, as read on the trace, corresponded with the computed heights within about 5 per cent. until July 23, when the instrument fell into the sea. Upon its recovery it continued to give satisfactory curves, but direct observations of height showed that the scale-value had become altered, and from that date a correction of 15 per cent. was applied to the readings of height on account of the change of scale-value, the percentage being determined from observations of height in the manner described. With these corrections the determination of heights reached an accuracy of about 5 per cent.

The estimate of the humidity depends on the extension or contraction of a bundle of hairs. Very accurate results are certainly not obtainable in this way when the hygrometer is used over the sea, and it is doubtful whether they are in any case. In rough weather the spray flew over the tug, the hairs were at times wetted with salt water; then also during rain, and when the kite was in a cloud, they were actually covered with drops of water. The charts frequently show the condition of over-saturation, and all that could be done was to set the pen frequently by the screw provided for the purpose, so that in saturated air it should indicate a humidity of 100.

In spite of these disadvantages, the hygrometer retained its sensitiveness during the ascents, but it was felt that no great degree of accuracy could be attributed to the readings, and on that account, in dealing with the results, only four stages of humidity have been used, viz. :—Very dry (V.D.), under 60 per cent.; dry (D.), from 60 per cent. to 80 per cent.; moist (M.), from 80 per cent. to 95 per cent.; and saturated (S.), above 95 per cent.

Another question that requires consideration is the relation between the temperature and humidity of the instrument and the temperature and humidity of the air which surrounds it. The current of air which supports the kite, whether due to wind or the motion of the vessel carrying the apparatus, must in any case be considerable, and under ordinary conditions the whole instrument may be supposed to take up rapidly the temperature of the air current within narrow limits of accuracy, but in the moist atmosphere which is generally to be found not far from the surface of the coasts of the British Isles a special difficulty arises. The temperature of the air, and, in consequence, that of the instrument, decreases as greater heights are reached, and increases during the descent. In descending, the instrument is therefore exposed to successive layers of air warmer than itself, at the same time the humidity not infrequently increases during the descent, and some condensation of water from the moist air may result if the change of height is rapid. Such condensation would be slight, and perhaps with sufficiently slow descent its effect might be neglected. In the actual experiments a good deal of water was certainly found occasionally in the wire during the winding in. Sometimes a constant drip took place from a piece of cotton waste placed on the wire to prevent the water reaching the reel of wire. This was attributed to drops of water collected by the wire from clouds and not to condensation. Water would be collected in a similar manner by the exposed parts of the instrument, including the hairs of the hygrometer, but the thermometer was protected from rain and, to a certain extent, from drifting particles of water by its case. If the thermometer became wet, it would for a time give a wet bulb instead of a dry bulb temperature; but, under the conditions of deposition of the moisture, the difference would not be large. It would, in effect, show the temperature in descent less than that in ascent. The readings obtained do not give any clear indication of any such effect.

A further uncertainty as to temperature readings arises from the variation in actual temperature of the atmosphere from point to point in the same horizontal layer. The primary object of the temperature observations may be said to be the determination of the vertical distribution of temperature; but an inquiry of not less interest, though of greater difficulty, would be the examination of the details of horizontal distribution of temperature. Two striking instances of horizontal variation of temperature may be mentioned. First, the temperature recorded on Ben Nevis is generally several degrees below that at the same level over the sea at Crinan, 60 miles away, and, secondly, the cloud level indicated by the disappearance of the kite was always much higher than the cloud layer on the hills of the near land, sometimes, as on July 16, by as much as a thousand metres. This matter will be referred to later on. But besides these instances, it may be mentioned that a characteristic type of weather in the neighbourhood was indicated by detached cumulus clouds forming first over the land, but sometimes drifting over the sea. These well-marked detached cumulus clouds were a very common feature, and they certainly indicate a want of horizontal uniformity of condition as regards moisture, probably as regards temperature also. Probably contiguous portions of a horizontal layer are moving, one upward and the other downward, with considerable difference of temperature. The descending column may perhaps be traced in the ruffling of the surface, which is characteristic of "catspaw" weather. On several occasions, notably on August 8 and August 20, convection currents, which would correspond with this state of the atmosphere, produced a noticeable effect on the kites, the angles of which varied from time to time in a very irregular manner. The apparatus employed is not sufficiently refined for the records to identify these differences without very special observations; they have accordingly been disregarded in the discussion of the observations.

Tabulation of the Traces.

The meteorograph was raised 40 times between July 4 and August 25; single ascents were obtained on 23 days, two ascents were made on eight days, on one of which, July 26, a third ascent was made. The clock stopped at the commencement of the ascent on August 21 and before the conclusion of the ascent on August 18. In the other ascents more or less satisfactory records of temperature were obtained, less satisfactory records of humidity.

The traces recorded on the drum give the variations of height, temperature, and humidity with time. As a specimen, a reproduction of the original trace is given for August 11 (fig. 1).

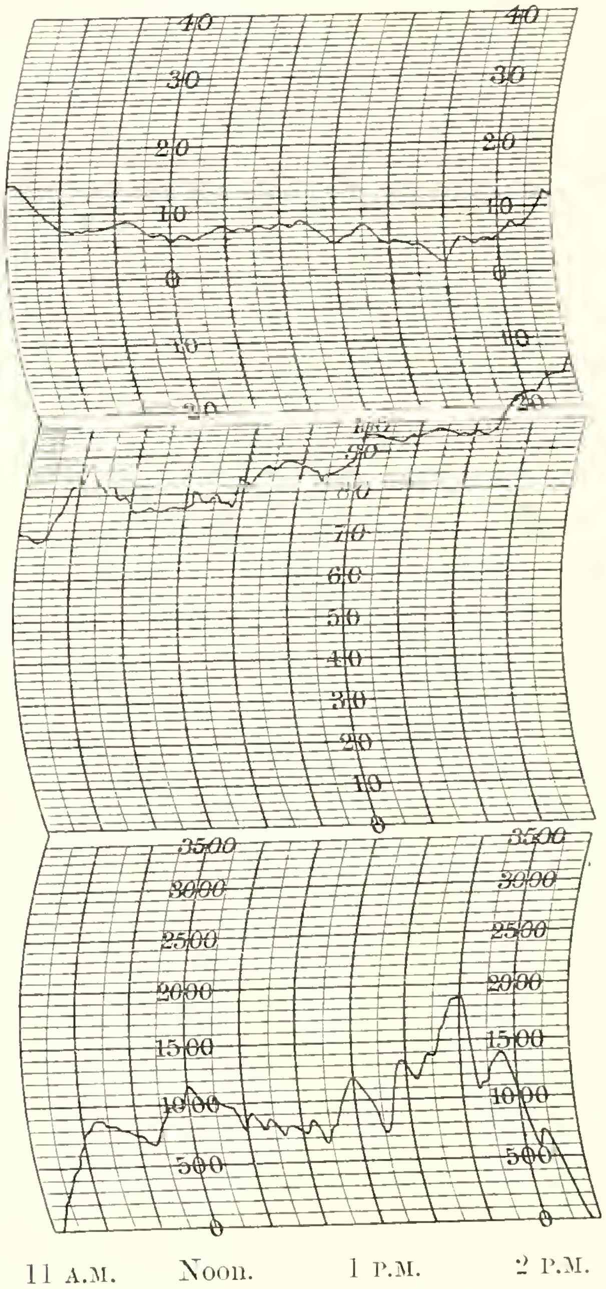


Fig. 1. Facsimile of records of the ascent of August 11.

Notes of the ascent. August 11. Scarba Sound and sea south of Mull.

11.3 A.M., 250 feet of wire out, 60° angle of kite wire, 30 lbs. pull, wind W.N.W.
11.27 ,, 6000 ,, ,, best angle 37°, 20 ,, ,, N.W.
11.40 ,, Second kite.
12.1 P.M., 11,450 feet of wire out, 23° 55′ angle of kite wire, 40 lbs. pull.
Third kite.
1.20 ,, 18,000 feet of wire out. First kite in clouds; commenced winding in; got 2000 feet extra height by winding in.
2.15 ,, All in.

First kite generally below and to right of second, ditto second with regard to third. Wind above N.W. and evidently light. Shower in W. at 2 P.M.

To ascertain the variations of temperature and humidity with height, it is necessary to obtain simultaneous readings of all three elements from the curves. This presents some little difficulty. The time scale of the paper is 2 centims. for 50 minutes, or a millimetre for $2\frac{1}{2}$ minutes. Simultaneous readings could be easily obtained if the pens were always so adjusted that the lengths of the levers for the several records were always equal, but the displacement of a pen by half a millimetre implies a difference of more than a minute in time, and the winding in was occasionally sufficiently rapid to give a variation of height of upwards of 100 metres per minute (see fig. 1). From an examination of the curves it appeared that the setting of the temperature pen as compared with the height pen might show a time difference of from a minute fast on the one side to six minutes slow on the other. During the ascents, if the wind is strong, the levers are subject to considerable mechanical vibration, and the setting of the pen, which is simply slid on to the lever and held by small clips, is not sufficiently secure. In any future ascents it will be desirable to pay special attention to this part of the apparatus, with a view to securing really synchronous readings without difficulty. In the present discussion an error of 50 metres of height must be regarded as not improbable, on account of the uncertainty of the correspondence of the time scales.

One might expect to obtain a series of truly synchronous readings from the curves as they stand by taking readings at salient points, such as are given by projections from the height curve with corresponding projections on the temperature or humidity curve. Such a series of salient points is very conspicuous in the curves for August 11 (fig. 1), but to proceed in this way first assumes that the instruments register the maxima or minima of the separate elements simultaneously, though such an assumption is not necessarily justified, and, secondly, it prevents the use of a continuous curve to smooth the effects of isolated peculiarities which may arise from the peculiar circumstances of the moment, or even from the instruments themselves.

The process adopted with the traces under discussion was to tabulate each curve according to its own time scale for each two minutes of time, and subsequently to determine by a careful examination of the original traces the proper equation of time between them.

Curves of variation of temperature and height were plotted for each ascent. The curve thus obtained for the ascent of August 11 (represented in fig. 1) is given in fig. 2, p. 130. The adjustment of the time scales was subjected to careful scrutiny, and to obtain a final curve of variation of temperature with height the observations were re-plotted, after the scrutiny, and a mean curve taken between the curves of ascent and descent; with a little practice it is easy to recognise in the plotted curves the eccentricities due to want of synchronism, and in the correspondence finally adopted the observations are synchronous within a minute. The smoothed curve probably gives the relation between temperature and height well within that limit. More accurate equivalence of the scales could be obtained by closer tabulation as

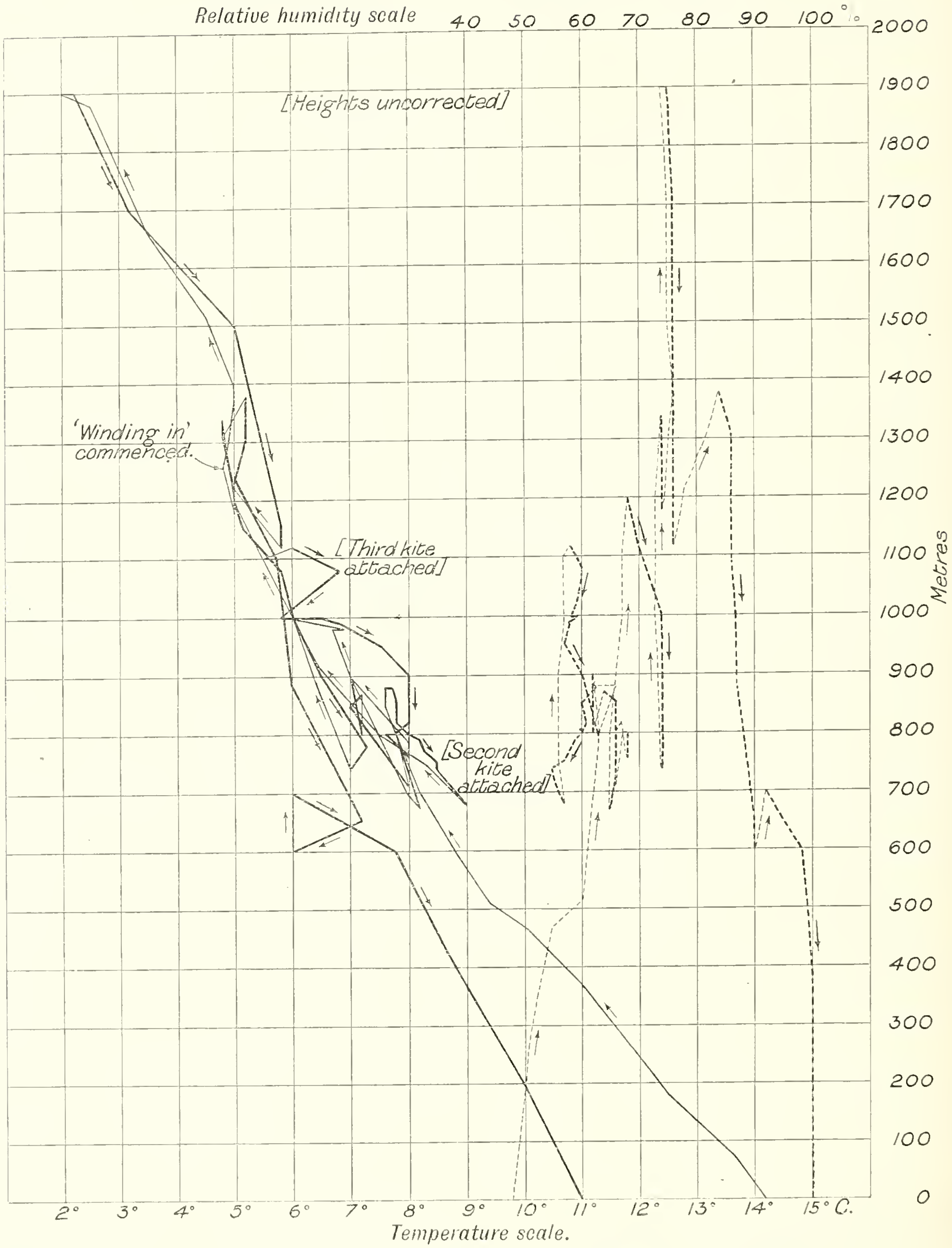


Fig. 2. Temperature and humidity gradients on August 11. Obtained from the tabulation of the curves of fig. 1.

Full lines show the relation between temperature and height.
Dotted ,, ,, ,, humidity and height.
Arrows show whether the kite was rising or sinking.

regards time, but such a proceeding would entail an amount of labour quite out of proportion to the increased accuracy, having regard to the character of the traces obtained. It has been already mentioned that the mechanical vibration of the levers was considerable in high winds, and this gave rise to a thickening of the lines of the traces, sometimes to almost undecipherable smudges. The stability of the aneroid lever is considerably greater than that of the others, so that the height trace is generally sharp and distinct, while the others are relatively blurred, so much so in some cases that the reading cannot be relied upon to within a division of the paper scale or a degree of temperature. The difficulty that may arise from this cause is illustrated by the record for August 23, the highest obtained, which is reproduced in fig. 3.

As a degree of temperature C. could in no case correspond to less than a hundred metres of height, the system of tabulation and adjustment of time scales may be regarded as sufficiently accurate in comparison with the other uncertainties of the experiments. But the method of recording is a matter which requires very careful attention with a view to increased accuracy. The results as they are here presented must be regarded as giving the general relation between height and temperature; any local variations, due to differences in parts of the same horizontal layer at short intervals, have been smoothed out by the process of reduction. Such variations form a separate subject of study, which requires apparatus specially adapted for this purpose.

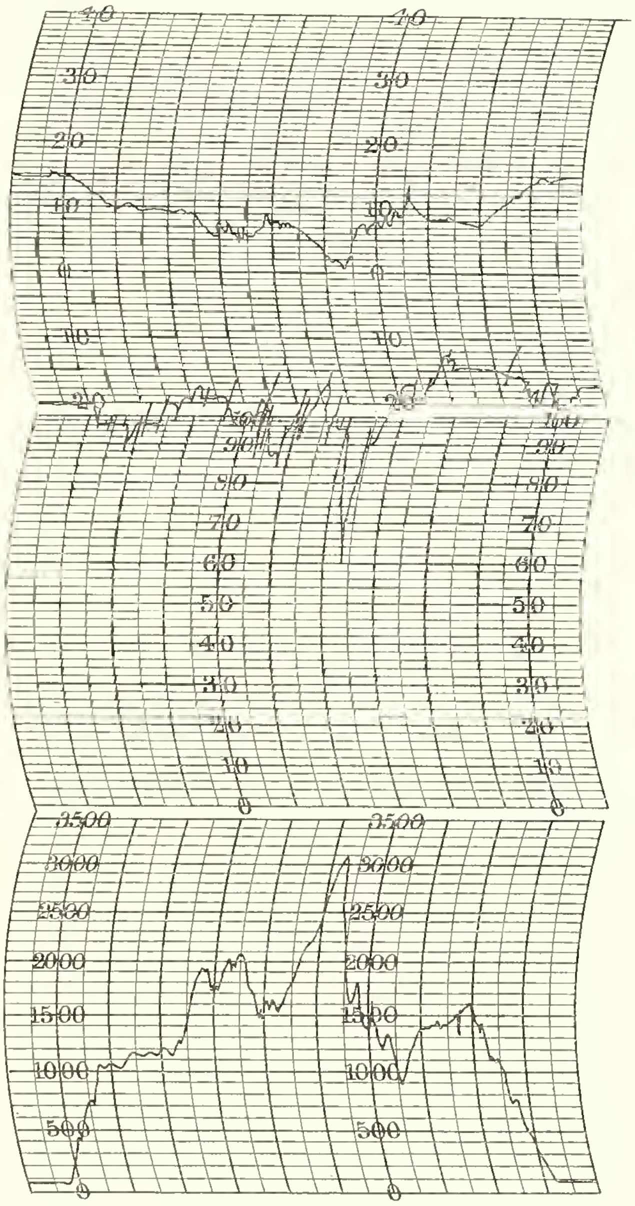


Fig. 3. Facsimile of record of August 23.

It has been pointed out already that the humidity traces are subject to special disadvantages, so that as a rule only rough approximation can be regarded as secured. On two occasions, however, very interesting traces were obtained, namely, on July 31 and August 12, when the air became dry at some distance above the surface (see diagram, fig. 4). July 7 also gave an interesting record of humidity (see Plate 12). In a number of cases the humidity trace was either lost or undecipherable, owing to the relative instability of the pen lever.

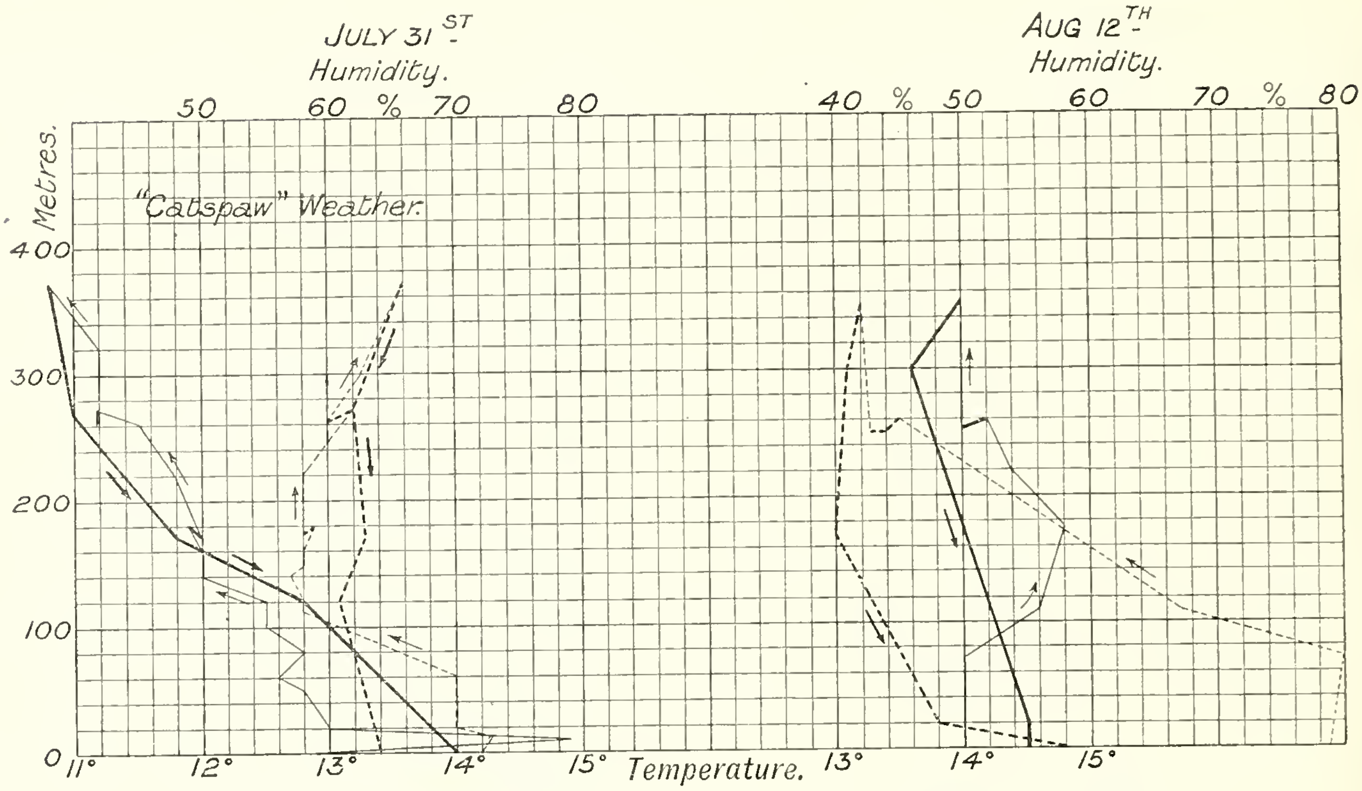


Fig. 4. Exceptional variations of temperature and humidity with height.

Full lines represent the relation between temperature and height.
Dotted ,, ,, ,, humidity and height.
Arrows indicate whether the kite was rising or sinking.

NOTE.—No importance is attached to the large variations of temperature at the commencement of the ascent of July 31, which may have been due to accidental causes.

Results of the Observations.

The final results obtained for temperature are plotted on a diagram (Plate 12), and where ascents were obtained on consecutive days the heights of corresponding temperatures are joined by full lines. As a guide to the eye, dotted lines have been added to connect lines of corresponding temperature. The state of the air as regards humidity at the different levels is represented by the letters V.D., D., M., and S. respectively with the meanings already given. When the letters have not been inserted, the humidity trace has failed.

During the course of the ascents notes were made of the disappearance of the kite in clouds and of its reappearance. From these observations the heights of the cloud layers were determined. The position of the first visible cloud layer thus indicated is shown on the diagram, and varies between 450 metres on July 8 and 2000 metres August 25 ; two cloud layers were identified in this way on August 1.

The determination of the heights of clouds by this method is not altogether free from uncertainty when detached clouds are drifting across the sky. The kite may become invisible, although it is not itself in cloud, because a cloud drifts under it.

The distinction between the two cases is not so easily drawn in practice as might be supposed.

The direction of the wind was observed at the surface, and is represented by arrows at the base of the diagram. The direction of the wind in the upper air was estimated by the direction of the kite wire, and is indicated by arrows at the top of the isotherms for the different days. In making the estimate the motion of the vessel was allowed for, but the estimates do not claim minute accuracy. On every occasion on which a difference of direction is shown in the upper current the wind had veered aloft.

The weather on the days of the ascents is indicated by letters of the Beaufort scale at the foot of the diagram.

Temperature Gradients.

From the diagram a table (Table A) of results for temperature variation with height for each 500 metres on each day of ascent has been compiled. In each case the figures represent the *fall* of temperature for the range of height specified. The differences of temperature are given to the nearest half degree only. Some of the numbers for the last step of height have been obtained by extrapolation for a short distance of height when the diagram did not actually reach the upper limit. Such numbers are enclosed in square brackets.

For the purpose of a comparison, which will be referred to later on, the differences of temperature between the sea level at or near Crinan and the top of Ben Nevis have been added.

In order to complete the comparison of the variations of temperature gradients with the meteorological conditions at the time of observation, reference may be made to the barometric curves for Fort William and Ben Nevis, which are plotted above the diagram from the hourly observations forwarded to the Meteorological Office, and to the charts of the paths of depressions in the monthly summaries of the "Weekly Weather Report" for July and August. The latter are reproduced in fig. 5. The position of the sea area at which the series of observations were made is indicated by a small circle on the maps. As a matter of fact, the barometric variations were comparatively inconspicuous during the period of observations, and the weather presented a succession of nearly calm days of a somewhat uninteresting character.

Barometric observations were also made at Crinan, and they have been utilised in the comparison, but the variations follow so closely the variations at Fort William for which a continuous curve is available that it has not been thought necessary to represent the Crinan observations on the diagram.

The conditions under which the kite ascents were made during the period of the experiments tended to confine the higher ascents to days upon which the weather has a particular feature, namely, a moderately strong wind in the upper strata.

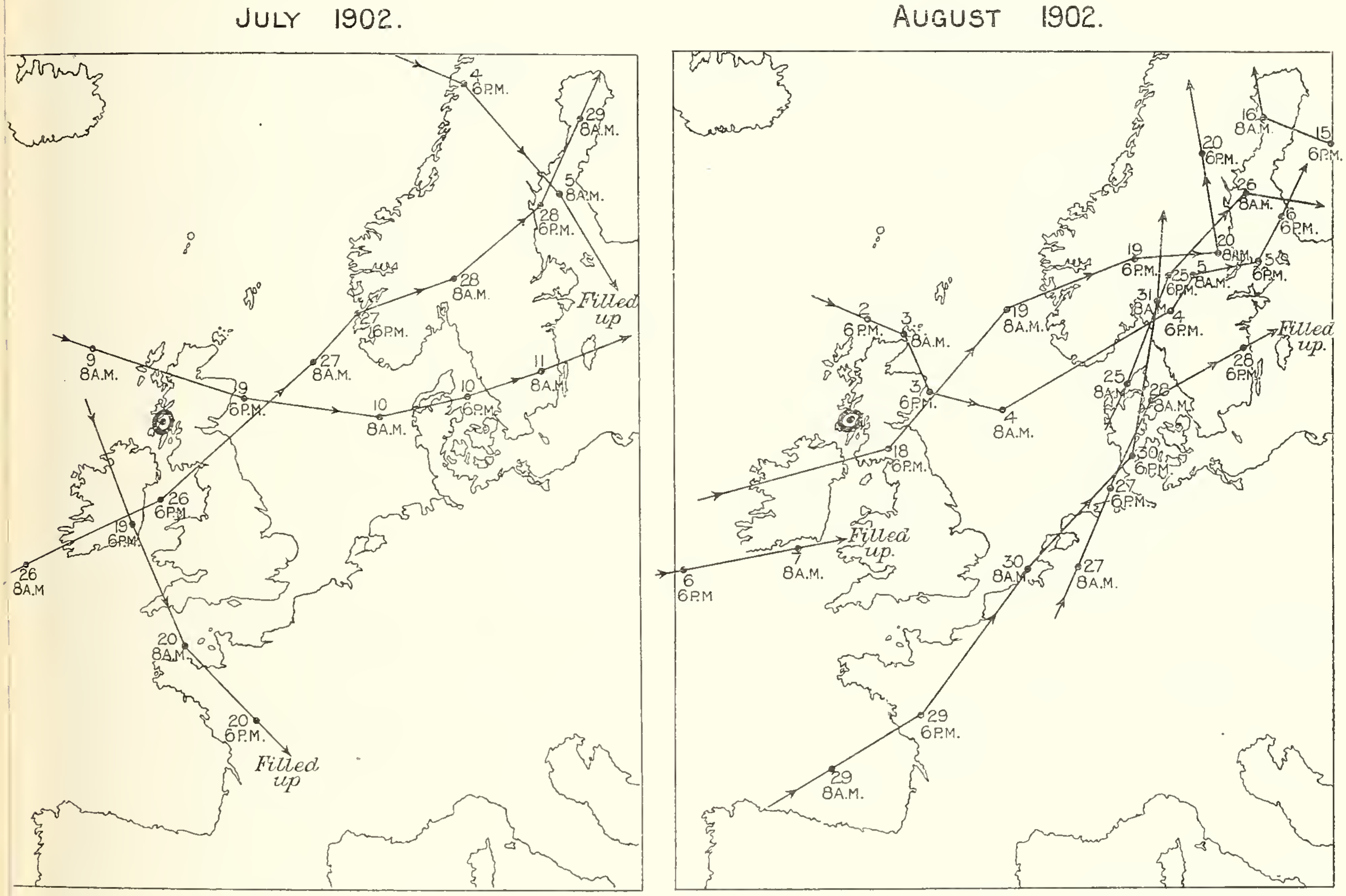
TABLE A.—Diminution of Temperature for each 500 Metres of Height in Degrees Centigrade.

July.	4.	7.	8.	9.	11.	12.	15.	16.	17.	18.	21.	23.	24.	26.	28.	29.	30.	31.	Average.
metres																			
0–500	2	4	2	2·5 3	?	?	4 3	2	2·5 3·5	3·5	4 2·5	3	4	2·5 2	2·5	3·5 3	3	3	3·0
500–1000	—	1	—	3	—	—	3 2·5	2·5	3 3	3·5	2	—	3	4 2·5	3	3 3	2·5	—	2·8
1000–1500	—	0	—	2	—	—	3	1·5	—	[3]	—	—	[3]	2	—	2	3	—	2·2
1500–2000	—	—	—	—	—	—	[2]	—	—	—	—	—	—	—	—	—	2	—	2·0
2000–2500	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2	—	2·0
Temperature at sea surface above that at Ben Nevis (1342 metres)	—	5	6	6 8	—	—	9·5 9	7·5	9	11	—	—	—	—	—	—	11	—	8·2

August.	1.	2.	6.	8.	9.	11.	12.	19.	20.	22.	23.	25.							Average.
metres																			
0–500	3	3 2	3	3	3	4	1	3	2	2·5	1·5	3	—	—	—	—	—	—	2·6
500–1000	4	2 3	3	3	3	2·5	—	3	2·5	—	2·5	2·5	—	—	—	—	—	—	2·8
1000–1500	3	2 [2]	—	2·5	2·5	2	—	—	2	—	2	3	—	—	—	—	—	—	2·3
1500–2000	[2]	2	—	2	2	2	—	—	2	—	2·5	4	—	—	—	—	—	—	2·1
2000–2500	—	[2]	—	—	—	—	—	—	2	—	2		—	—	—	—	—	—	2·0
2500–3000	—	—	—	—	—	—	—	—	2	—	2	—	—	—	—	—	—	—	2·0
3000–3500	—	—	—	—	—	—	—	—	2	—	1·5	—	—	—	—	—	—	—	1·7
Temperature at sea surface above that at Ben Nevis (1342 metres)	12	9 9	—	11	10·5	12·5	—	—	9	9	9	13	—	—	—	—	—	—	10·5

When the winds became very strong, for the reasons already given, only one kite was used and the height was limited in consequence, and if the winds were only light a great length of wire could not be supported.

The Fort William barometer curve shows that the pressure was as low as 29·5 inches on three occasions only during the two months, and exceeded 30 inches on eight occasions. There were five well-marked minima, viz., on July 9–10, July 26–27, August 2, August 18, with a secondary minimum on the 20th, and August 22–24; otherwise the variations were inconspicuous.


JULY 1902.

AUGUST 1902.

Fig. 5. Movements of depressions.

Turning now to the table of temperature gradients, it will be seen that in July the average fall of temperature for the first 500 metres, computed from 22 ascents, is 3°; for 500–1000 metres (16 ascents) 2°·8; for 1000–1500 metres (9 ascents) 2°·2; 1500–2000 metres (2 ascents) 2°·0; and for 2000–2500 metres from a single ascent 2°·0. In August the corresponding figures are 2°·6 (13 ascents), 2°·8 (11 ascents), 2°·3 (9 ascents), 2°·1 (7 ascents), 2°·0 (3 ascents). In that month also higher stages were reached, 2500–3000 metres on two occasions, with a fall of temperature of 2°·0, and 3000–3500 metres on the same two occasions with a fall of 1°·7. There is considerable irregularity in the gradients for the first 500 metres. These irregularities may, perhaps, be accounted for partly by uncertainties attaching to the temperatures at the start and finish of the ascent when the instruments have to be handled by the observer. The range of gradient was between 4° C. and 1° C. for the 500 metres. The first case of gradient 4° (*i.e.*, ·8° for 100 metres) is on July 6, when an anti-cyclone was beginning to give way to an approaching depression, and the gradient, although very high near the surface, disappeared altogether at 1000 metres, where an inversion of gradient was disclosed with very dry atmosphere above a layer of clouds. Another occasion of similarly steep gradient under very similar barometric circumstances was on 24th July, but there was apparently no inversion of gradient. The depression in this case passed to the south of Crinan (see fig. 5) and gave north-easterly winds, while on the 9th it passed to the northward and gave westerly winds. The other occasion on which a steep gradient was observed in the lowest region presented no specific characteristics; it may, however, be noticed that the temperature gradient up to 500 metres may be a good deal affected by the land in the neighbourhood which here and there reaches a height of some 1500 feet.

The very slight gradient of 1° C. for 500 metres on August 12 was connected with an inversion of temperature gradient not far from the surface.

For the step between 500 and 1000 metres the fall of temperature reached 4° C. on two occasions, July 26 and August 1. Both occasions corresponded with the initial stages of advancing depressions. The former passed south of Crinan, the latter north. It seems that a general characteristic of the passage of a depression is that the isothermal lines on the diagram open out and a steep gradient becomes transformed into a slight one. As examples of this may be cited the transition between the 7th July and 9th July, which is better represented in the diagram than in the table; between morning and afternoon of the 26th; between the 1st August and the 2nd; between the 19th August and 20th, and between the 22nd and 23rd.

Taking such corresponding heights for these dates as are available, there is an average diminution of gradient of as much as 50 per cent., and the indication would seem to be that the columns of air in depressions are columns of relatively warm air. There are not enough observations at sufficient heights to confirm this suggestion. It is noticeable that in the depression the gradient does not reach that of the adiabatic gradient of saturated air in the higher regions. It will be noticed, on reference to the maps, that in every case the centres of the depressions were at some distance from the place of observation; they passed it on all sides.

In both months the temperature gradient fell off in the higher regions, and amounted to 2° for the steps of 500 metres beyond 1500 metres.

Comparison with Previous Results.

In order to compare the general results obtained from the experiments with more or less corresponding results obtained elsewhere, the following table has been compiled from data quoted in HANN'S 'Meteorologie,' and the references in the first column are to the pages of that work.*

TABLE B.—Table of Average Temperature Gradients, in Degrees Centigrade, for 100 Mètres, for Vertical Columns of Different Heights.

Height of column in metres	500.	1000.	1500.	2000.	2500.	3000.	3500.	4000.
Berlin balloon ascents (p. 157)	—	·50	—	·50	—	·51	—	·52
Kite ascents, U.S. Weather Bureau (p. 124)	1·10	·80	·71	·68	—	—	—	—
Average gradient for mountains (p. 128)	·56° C. per 100 metres approximately equal to 1° F. for 300 feet of height.							
Average gradient for Ben Nevis – Fort William, July and August (p. 131) .	—	—	[1340] metre. ·70	—	—	—	—	—
Adiabatic gradient for saturated air (p. 756). Initial temperature, 12° C.	·52	·54	—	·53	—	·62	—	·70
Average results for Crinan experiments, July and August, 1902	·56	·56	·52	·50	·48	·46	·43	—

The average results of the Crinan experiments, for the whole series of ascents, are given in the last line of the table. Up to 2000 metres they agree closely with the adiabatic gradient in saturated air for the initial temperature of 12° C., exceeding that gradient somewhat for the lower strata, for which the results agree with the average temperature gradient of ·56° C. for 100 metres (or 1° F. for 300 feet), which is derived from observations at high level stations, and which is in general use in this

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* The results of the Crinan experiments must be regarded as being more or less preliminary, and in the present paper we have thought it desirable to deal only with the general features of the results.

country for the reduction of average temperatures at a network of stations to a common level. They are much below the results of the kite ascents at 17 stations in the United States, obtained by the Weather Bureau, but they agree very closely with the results of the Berlin balloon ascents. With regard to these last, however, a higher figure should be taken for the lowest stage of 500 metres for day ascents in the summer.

All these differences may probably be satisfactorily accounted for by the circumstances of the Crinan ascents, which were over the sea on the edge of the Atlantic, where the daily range of temperature is almost negligible. At greater heights the Crinan results are substantially lower than the Berlin results and the adiabatic gradient, but the number of high ascents is very small, and, as already stated, they refer to a particular type of summer weather which is probably different from those of the balloon ascents.

The average gradient for Ben Nevis—Fort William for the corresponding months, ·70°, is considerably higher than the Crinan gradient for the same height. The actual differences between the temperature at the sea level at Crinan and the top of Ben Nevis, on the days when the Ben Nevis temperature was reached by the kites, as shown in Table A, vary between 13° on August 25 and 5° on July 7, the average being 9·3°. The height in the free atmosphere, at which the Ben Nevis temperatures were reached by the instrument, is shown by the cross marks on the Diagram (Plate 12).

The differences of temperature between the summit of Ben Nevis and the free air at the same level over the sea near Crinan, as determined by the kite experiments, are shown in the following table (Table C). The same table gives also the wind direction and force, and the wet and dry bulb readings for the mountain and for Fort William.

TABLE C.

Date.	Fort William.		Ben Nevis.					Temperature differences.
	Dry bulb.	Wet bulb.	Dry bulb.	Wet bulb.	Wind.		Weather.	Ben Nevis − Free air at same height.
					Direction.	Force.		
	° C.	° C.	° C.	° C.				° C.
July 7, 12.25 P.M.	14·7	12·7	4·4	4·4	Var.	0–1	d.m.	−3·3
,, 9, 12.5 ,,	12·9	12·6	6·1	6·1	W.	0–1	d.m.	−1·6
,, 15, 11.30 A.M.	13·7	13·1	5·7	5·7	W.	1–2	m.	−0·3
,, 15, 5.40 P.M.	15·8	12·8	4·3	4·3	W.	1–2	m.	−1·8
,, 16, 12.10 ,,	13·2	12·4	4·8	4·8	S.W.	2	r.m.	−1·8
,, 18, 12.10 ,,	13·2	10·0	1·7	1·7	N.	0–1	f.	−2·7
,, 24, 6.0 ,,	12·9	8.3	−0·7	−0·9	N. & W.	0–1	f.	−1·7
,, 26, 10.45 A.M.	10·2	9·4	3·1	3·1	E.	2–6	r.m.	−1·4
,, 26, 8.5 P.M.	10·6	9·2	2·0	2·0	N., N.E.	1–3	m.	−4·7
,, 28, 7.0 ,,	11·9	11·0	3·1	3·1	S.S.W.	0–2	r.m.	−1·9
,, 29, 12.30 ,,	13·1	10·6	1·8	1·8	Var.	0–2	m.	−2·0
,, 29, 7.40 ,,	12·1	8·9	0·6	0·6	Var.	2–3	m.	−2·8
,, 30, 11.10 A.M.	12·7	9·0	1·0	1·0	Var.	0–1	r.s.m.	−2·2
Aug. 1, 7.0 P.M.	11·1	10·5	2·3	2·3	S.	1–3	r.m.	−1·6
,, 2, 12.10 ,,	12·4	12·1	3·9	3·9	S.W. & S.	1–2	d.m.	−1·1
,, 2, 5.0 ,,	13·3	12·7	3·5	3·5	N.W. & W.	1	r.m.	−2·0
,, 6, 1.40 ,,	15·7	10·9	1·9	1·9	E.S.E.	3	m.	−5·3
,, 8, 5.10 ,,	13·9	10·2	2·4	2·2	N.E.	1–2	f.	−2·8
,, 9, 5.0 ,,	13·3	11·2	3·1	3·1	N., Var.	1	r.m.	−1·9
,, 11, 12.5 ,,	11·9	10·1	1·5	1·5	N.N.E.	1	r.s.m.	−3·4
,, 11, 2.0 ,,	12·8	10·2	1·3	1·3	Calm	0	r.m.	−3·6
,, 12, 10.30 A.M.	13·0	9·9	4·4	2·9	N.	2	f. to N. & E.	−0·7
,, 19, 3.30 P.M.	15·0	11·2	2·4	2·2	Var.	0–1	f.	−2·8
,, 20, 11.0 A.M.	13·5	11·5	2·8	2·8	Var.	0	r.m.	−3·3
,, 20, 1.0 P.M.	12·3	10·5	2·3	2·3	E.	1	m.	−3·8
,, 23, 11.40 A.M.	14·4	13·8	5·6	5·6	S.W.	0–2	m.	−3·3
,, 23, 1.30 P.M.	14·8	14·0	5·7	5·7	W. & S.W.	1–2	m.	−3·1
,, 25, 3·40 ,,	16·5	13·1	3·4	3·4	N. & N.N.W.	1–2	f.	−5·5
							Mean . .	−2·6 °C.

Although it could hardly have been expected that actual agreement would have been found, the differences are striking, and it is desirable to consider whether it is possible to suggest a reasonable explanation without attributing them to instrumental errors. As the ascents were in the daytime, any effect of the daily range of temperature on the mountain would probably give a result in the opposite direction.

The following considerations would tend to account for such a gradient:—With westerly winds the actual air particles that pass through the thermometer screen on the mountain are probably those which a short time previously have been close to the sea surface, for the stream lines must more or less follow the form of the bounding surface. The temperature on the mountain is therefore not likely to differ much from the temperature at the surface of the sea diminished by the adiabatic decrease due to the altitude; or to put it in another way, the potential temperatures on the mountain and at the sea surface are not likely to be very different. At the place where the kites were flown, the stream lines, apart from convection currents, are probably horizontal, since the disturbance produced by the mountains cannot extend very far to windward. The temperature gradient has been shown to be generally less than the adiabatic gradient in undisturbed air. In any fluid that expands with heat the potentially coldest layers will be at the bottom. The opposite condition can only be transient, otherwise it would involve the continuance of a state of unstable equilibrium. Admitting therefore that these two suppositions are correct, namely, that the temperature gradient over the Atlantic is generally less than the adiabatic one, and that the air rises from the sea level up the slopes of the mountain and in its ascent follows the adiabatic law of cooling, the temperature on the mountain must be less than that in the free air over the sea at the same level.

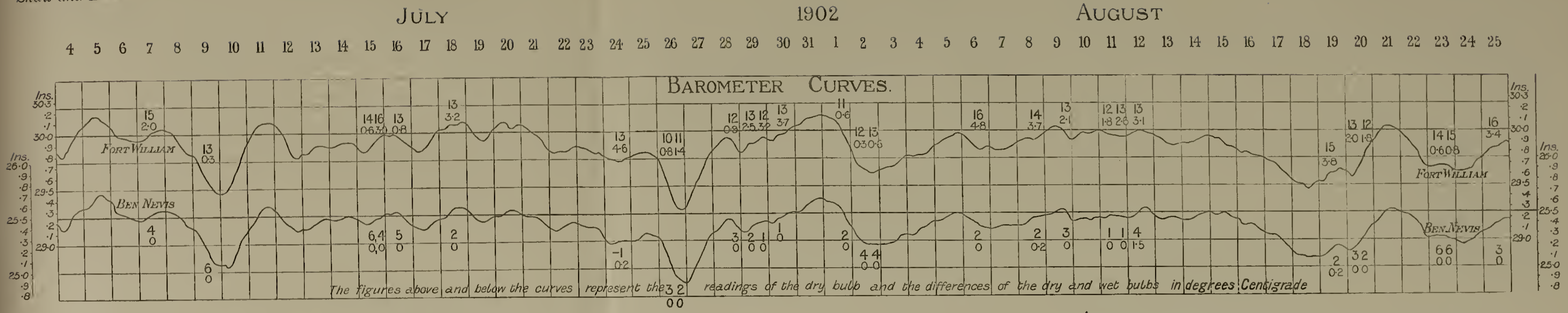
The adiabatic fall of temperature for the height of Ben Nevis would be 13°·5 C. for dry air, and 7° for saturated air, with an initial temperature of 12° C. The observed differences between the temperatures of the Ben and at sea level near Crinan are between these limits, except on July 7. The peculiar conditions of the atmosphere on that occasion are well illustrated by the diagram, Plate 12. The differences may therefore be accounted for by circumstances which tend to produce an adiabatic gradient in the air, as it is found near the sea level. For example, on the 25th August, the day of the greatest difference, the wind was due west, and though the weather was showery, the cloud level is set at 2000 metres over the sea, and the surface temperature, 16° C., is the highest recorded during the experiments. The mass of the mountain itself, therefore, was probably relatively cold, and the drift of surface air over the land might give a temperature difference even exceeding that of the adiabatic gradient for dry air, but the difference of 11° on July 18, when there was a northerly wind, *i.e.*, blowing from the mountains towards Crinan, with cloud over the sea at 750 metres, cannot be explained in a similar way. No other single suggestion is more fortunate. But the fact that the Ben Nevis—Fort William average gradient in July and August, though it agrees with the kite gradient of the United States Weather Bureau, exceeds the Berlin balloon gradient and the average mountain gradient, points to an explanation depending on some differences of effect of a high level station in that position as compared with a layer of free air at the same height.

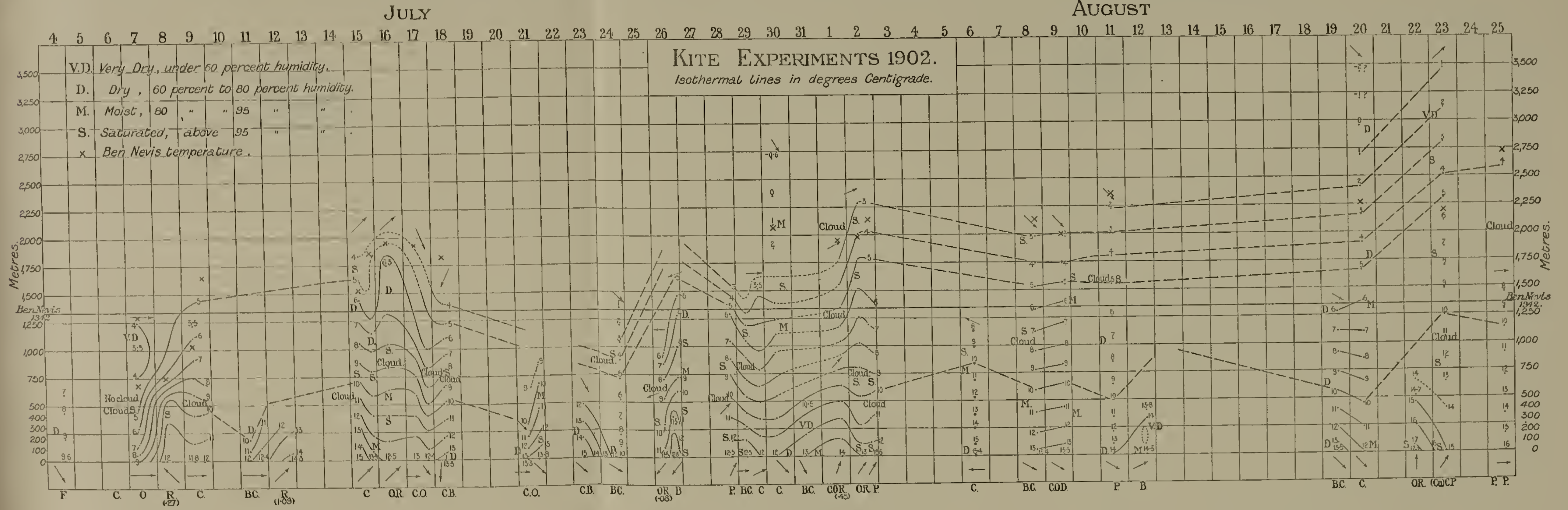
It will be noticed, on comparing the readings of temperature at Fort William (Table C) with the initial temperature of the kite ascents (Plate 12), that there is no corresponding difference between the sea-level temperatures at the two positions.

There is another fact which supports the idea that the Ben Nevis temperatures are below those of the free air at the same altitude. The level at which the kites entered the clouds was invariably higher than the level at which the clouds lay upon the mountains. The Paps of Jura, some 2500 feet (760 metres) high, were often covered with clouds at times when the kites did not reach the cloud level under 4000 feet (1220 metres), and the same rule held for lower altitudes. If, then, the lower cloud surface over a limited district be considered as approximately coinciding with an isothermal surface, and this does not seem improbable, it follows that mountain temperatures are lower than those of the free air; at least this was the case at Crinan last summer, for the clouds were undoubtedly lower when in contact with the mountains than they were when formed over the surface of the neighbouring sea.

Thus the existence of such cloud layers on the mountain slopes at a level considerably lower than the clouds over the adjacent sea may be taken as an indication of the effect suggested, although it must be allowed that it might also be attributed to evaporation from the lower mountain surface.

Further and more minute investigation alone can really decide what the explanation of the difference is.


JULY
1902
AUGUST
4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
BAROMETER CURVES.
Ins.
FORT WILLIAM
BEN NEVIS
The figures above and below the curves represent the readings of the dry bulb and the differences of the dry and wet bulbs in degrees Centigrade


JULY
AUGUST
4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
KITE EXPERIMENTS 1902.
Isothermal lines in degrees Centigrade.
V.D. Very Dry, under 60 percent humidity.
D. Dry, 60 percent to 80 percent humidity.
M. Moist, 80 " " 95 " "
S. Saturated, above 95 " "
× Ben Nevis temperature.
Metres.
Ben Nevis 1342.
Cloud
No cloud
F.
C.
O.
R.
B.C.
C.O.
C.B.
O.R.
P.
C.O.D.
B.

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THE ELASMOMETER, A NEW INTERFERENTIAL FORM OF ELASTICITY APPARATUS

BY

A. E. H. TUTTON, D.Sc., F.R.S.

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Measuring Microscope—Method of Reading to a Thousandth of a Millimetre by a single Screw without Backlash.
Tutton, A. E. H. Phil. Trans., A, vol. 202, 1903, pp. 143–163.

IV. *The Elasmometer, a New Interferential Form of Elasticity Apparatus.*

By A. E. H. TUTTON, *D.Sc., F.R.S.*

Received May 12,—Read May 14, 1903.

BEING desirous of extending the investigation of the physical characters of the crystals of isomorphous salts to the subject of their elasticity, the question arose as to the best form of apparatus to employ for the determination of the coefficient of elasticity. The most accurate form hitherto devised is that of KOCH ('Ann. der Phys.,' N.F. 1878, vol. 5, p. 251, and 1883, vol. 18, p. 325). It was subsequently employed in the researches of BECKENKAMPF ('Zeitschr. für Kryst.,' 1885, vol. 10, p. 41, and 1887, vol. 12, p. 419), of VATER ('Zeitschr. für Kryst.,' 1886, vol. 11, p. 549), and of NIEDMANN ('Zeitschr. für Kryst.,' 1888, vol. 13, p. 362). The amount of flexure of a thin plate of the crystal was determined by the interference method, sodium light being employed. The plate was laid on the edges of two sloping blocks, and a bending weight applied above its centre, through a point at the end of a hook or a stirrupped knife-edge. The lower surface of the plate, and the upper surface of a totally-reflecting prism supported very closely beneath it, with only a thin film of air intervening, were the two surfaces the light reflected from which was caused to interfere and to produce bands.

A complicated and somewhat cumbersome arrangement for suspending the weight from the hook or stirrup, through a hole in the table on which the instrument was supported, and of regulating and graduating the application of the weight, formed an essential part of the apparatus.

The great convenience and high accuracy of the optical part of the interference dilatometer, which the author has previously described ('Phil. Trans.,' A, 1898, vol. 191, p. 313), suggested the advantage of utilising it as interferometer for the measurement of the amount of flexure of the plate, and many other possible improvements on the apparatus of KOCH also suggested themselves. Eventually the instrument now described was devised. It is applicable to solid substances in general, whether transparent or opaque, and whether polishable or not. It has been constructed by Messrs. TROUGHTON and SIMMS, the makers of the dilatometer.

A general view of the whole apparatus, including the interferometer, is given in fig. 1, as it appears during the progress of an actual determination. The elasticity apparatus is shown in fig. 2, with the three principal parts well detached in order to reveal them clearly.

The Interferometer.

The observing telescope, with its auto-collimator and attached hydrogen Geissler tube, shown in fig. 1 standing on the adjustable pedestal in the foreground, is precisely as described in the dilatometer memoir (*loc. cit.*, p. 324).

The similar pedestal in the background carries the train of two reflecting prisms; these are arranged to direct the particular rays to be employed, those corresponding to the red C-hydrogen line, down the vertically suspended tube, of which the greater portion is of Berlin porcelain, on to the interference apparatus. With the exception of the counterpoise on the backward prolongation of the arm from which the tube is suspended, which experience since the publication of the dilatometer memoir has shown to be a valuable addition, this portion of the apparatus is also exactly as described in that memoir (p. 321) as far as the lower end of the porcelain tube and its short gun-metal continuation.

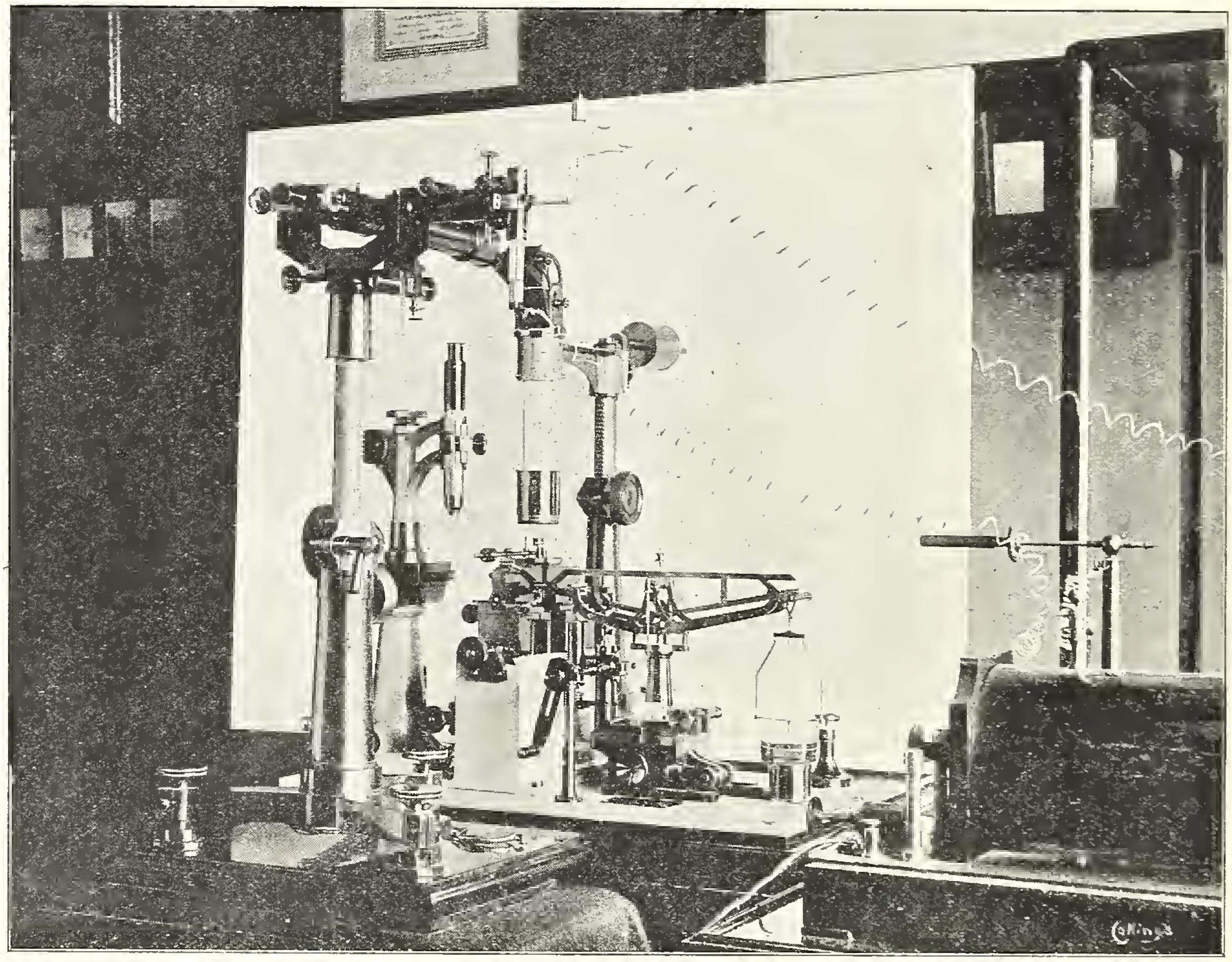

Fig. 1.

From the end of the latter the interference chamber of the dilatometer has been removed. The interference tripod is carried by the new apparatus itself, immediately below the end of the vertical tube. As the removed interference chamber carried at its upper end a thick glass disc, which, being equally slightly wedge-shaped (35 minutes) and arranged in the inverse way, corrected for the slight dispersion of the large glass disc of the interference apparatus, a milled cap is provided to contain this correcting disc. The new cap screws on to the lower extremity of the suspended tube; it has the same adequate clear aperture as the removed interference chamber, and is similarly provided with two raised points in its rabbett to tilt the disc to the minute extent required to throw its reflections out of the way of the interfering rays from the interference apparatus.

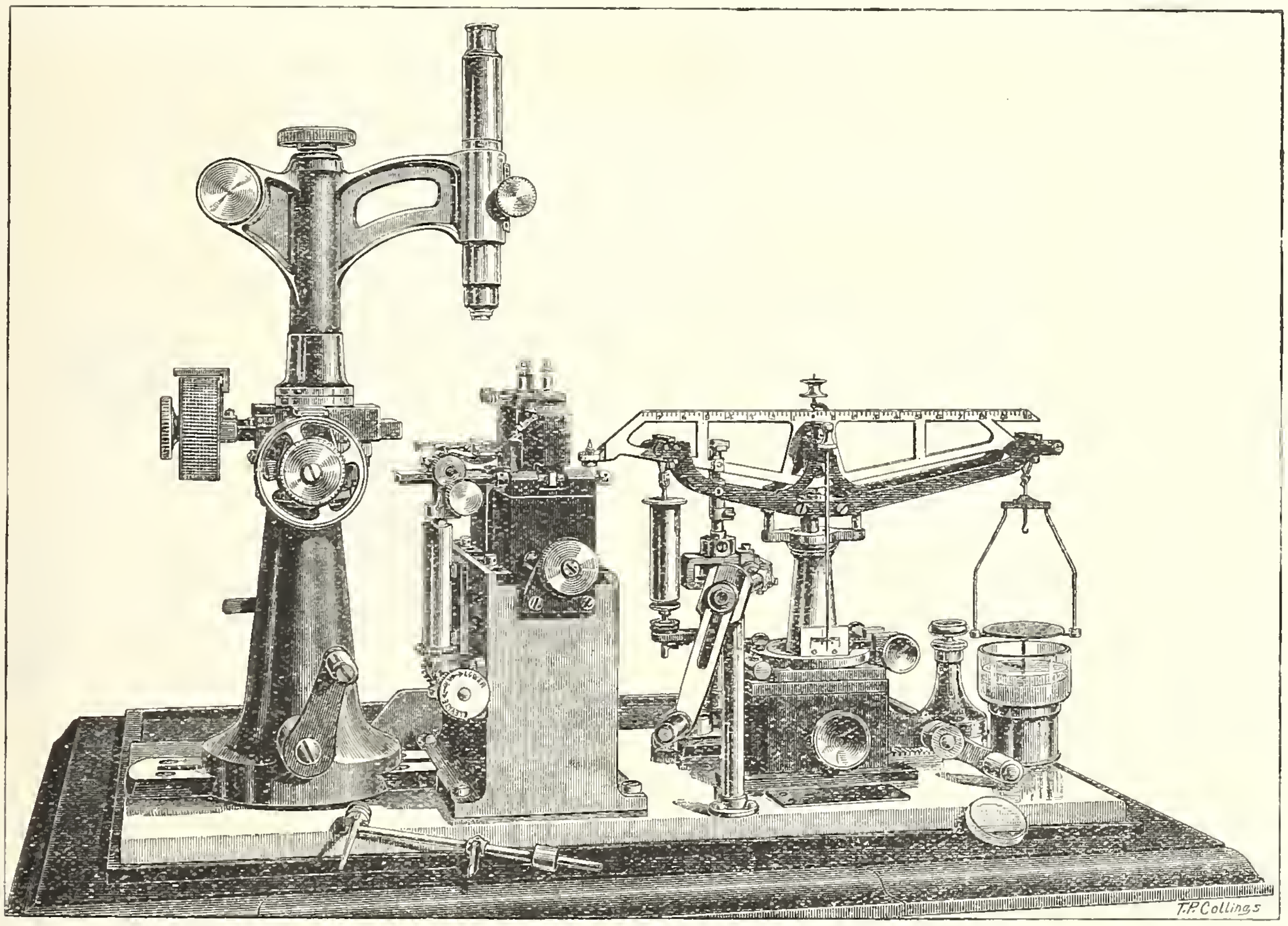

Fig. 2.

The Elasticity Apparatus.

The new apparatus consists of three distinct portions: (1) the apparatus which carries (*a*) the knife-edges, against which the plate of the substance under investigation is to be bent, (*b*) the transmitter of its bending movement, (*c*) the interference tripod, and (*d*) a pair of mechanical "fingers" for adjusting the plate; (2) a delicate balance, through a point at one end of the beam of which the bending weight is applied, and a device for controlling its application; (3) a measuring microscope, reading in two rectangular directions to a thousandth of a millimetre.

The whole of these parts, together with the pedestal of the suspended optical tube of the interferometer, are mounted on a rigid enamelled iron slab, rectangular in its front portion, the front edge being 71 centims. long and the sides 37·5 centims. The slab is continued backwards in the form of a broad arm for a further 22 centims., somewhat to the left of the centre, for the support of the back foot of the pedestal.

The iron base is in turn mounted on a rectangular mahogany base, on the plinth of which fits a glass case with strong mahogany framework, to cover the whole apparatus when not in use. One end of the case is removable, and the latter can then be readily drawn off, the bottom of the frame being covered with cloth to facilitate the sliding.

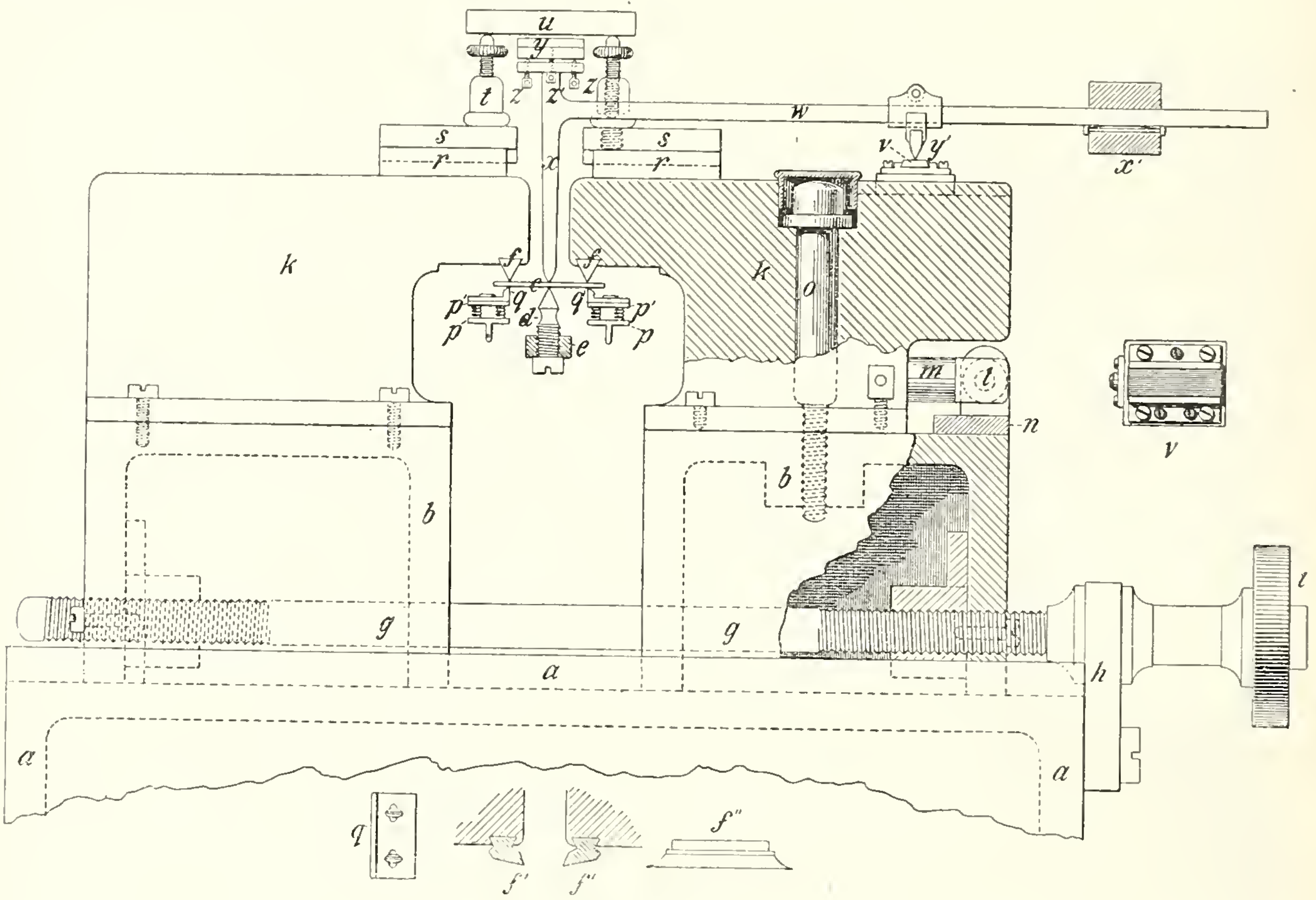

Fig. 3.

The telescope of the interferometer is mounted on a mahogany base 44 centims. by 38 centims., of the same thickness as the main base, to which it is attachable by three pegs fitting in holes in the front edge of the plinth, the outer moulding of which is here detachable to admit it. The smaller base is then continuous with the main base, and brings the telescope up quite close to the top prism of the refracting train, about 5 centims. being the best distance for clear focussing of the silvered reference ring carried at the centre of the large glass disc of the interference apparatus.

The Blocks and Knife-Edges for supporting the Plate.

Somewhat to the left and front of the centre of the iron basal slab an enamelled iron block is fixed (*a* in the accompanying vertical section, fig. 3), with one end facing front and the long edges parallel to the sides of the slab; it is 17 centims. high, 25 centims. long, and 9·5 centims. wide, except at the base, where it is broadened to 14 centims., in order to furnish a flange on each side, through which it is screwed down to the slab. This block carries above it, and sliding in a dove-tailed bed, two gun-metal blocks *bb*, intended to support the plate of the substance under investigation, *c*. The latter is not laid upon the edges of the blocks, as in KOCH's apparatus, but is pressed upwards from below, by a point *d* carried at the end of the balance beam *e*, against two platinum-iridium knife-edges *ff*, arranged edge downwards in the roof of recesses in the blocks.

The amount of movement of the centre of the plate, induced by the bending weight, is observed from above instead of from below, which latter is the method employed by KOCH. The optical arrangements of the author's interferometer are consequently directly applicable, and the totally-reflecting prism carried by the Koch apparatus in the space between the blocks under the plate is eliminated. The plate is brought up to the knife-edges, and also prevented from falling out of position, when the upward pressure of the bending weight is removed, by a delicately adjustable pair of spring supports *pp'q*, which gently press the plate up against the knife-edges without bending it.

The two sliding blocks *bb* are 8 centims. long by 6·2 centims. broad and high, and each is widened at the base into a dove-tail to fit the corresponding guides of the bed. For the purpose of ensuring adequately tight sliding, the left guide is furnished in each case by a stout bevelled rod of gun-metal, let in between an upright flange of the steel block and the dove-tail of the sliding block. Each is fixed by two screws to the steel block, just sufficiently tightly to permit of steady travelling; a third screw, with capstan head and lever handle, is placed mid-way between them, and acts both as an adjusting screw wherewith to modify the tightness of the sliding, and as a clamping screw to fix the blocks in any desired position. The motion of the two blocks is arranged to be equal and opposite on each side of the centre, by means of a long shaft *g* passing through both, having a left-handed screw cut in its hinder portion and a right-handed one in the portion near the front, where it is rotatable in a stout bearing *h* fixed to the end of the iron block. It terminates in a large milled head *i*, rotation of which, in the direction of the hands of a watch, causes the blocks to recede from each other, while rotation in the opposite direction brings them nearer together.

The upper parts *kk* of the blocks which carry the platinum-iridium knife-edges *ff* are separate castings fixed on the top of these sliding parts, and are 5·7 centims. high and 2·1 centims. wide, except at the base, where they are widened to 4·4 centims., to permit of screwing down to the sliding blocks. This is done rigidly by four screws in the case of the hinder block; when they are screwed home the platinum-iridium knife-edge is truly parallel to the basal slab. In the case of the front block, means of adjustment for both azimuth and altitude are provided, to enable the platinum-iridium knife-edge which this block carries to be set absolutely parallel to that carried by the hinder block. The azimuth adjustment is effected about a pivot *o* by two tangent screws *l*, directed horizontally towards each other and against a projection *m*, which they thus press between them, carried in a recess by the upper part of the block ; they work in a bearing-piece *n* fixed above the front end of the lower part. The adjustment for altitude is effected by means of three capstan screws, screwing through the basal flanges of the upper block, but not into the lower block, one on the right and two on the left side. After adjustment by these three screws and the two azimuth screws, the upper part of the block can be rigidly fixed to the lower part by means of a strong screw *o* (also acting as pivot) passing as a smooth shaft right through the upper part and screwing into the lower part; its square head is deeply countersunk in a well in the top of the upper block, of adequate size to admit the end of a T-shaped capstan key, wherewith the screw is manipulated. The well is covered with a cap, consisting of a short tube fitting the well and furnished with a flat top, after removal of the key.

The two upper parts of the blocks are 10 centims. long at the top, and they overhang the lower parts at the inner ends by about a couple of centimetres. At 2 centims. below the top at the inner end in each case a recess is commenced, which proceeds horizontally for 2·5 centims., then downwards vertically for about 3 centims., and finally curves outwards again as a basal flange of 0·8 centim., corresponding to the side flanges. It is within the commodious space formed by these two recesses that the balance beam *e* with its pressure point *d* can be introduced, as also the apparatus *pp'q* for supporting and adjusting the plate *c* of the substance under investigation.

The platinum-iridium knife-edges *ff* are fitted in small dove-tail grooves in the under sides of the overhanging parts, as close to the ends as is compatible with rigidity. The platinum-iridium fittings are drawn out to a fine point at each end, the actual knife-edge being the truly straight line joining the two points. The latter project for 6 millims. on each side of the blocks, so that they are visible in the reading microscope when it is arranged over them. Each is labelled with an engraved letter, which is visible in the field of the measuring microscope simultaneously with the point. The left point of the back wedge is marked A and the right one B ; the left point of the front wedge carries the letter C and the right point is engraved with D. The lengths of the edges AB and CD have been made equal, and the azimuth adjustment enables AC and BD to be adjusted equal. Two alternative pairs of platinum-iridium wedges are provided. Those shown in position in fig. 3 are of isosceles triangular section, as offering the greatest rigidity of the knife-edge. They are preferable whenever the substance under investigation is of considerable hardness, and good-sized plates of it can be obtained. The alternative pair are shaped as shown at the foot of the main drawing ; *f'f'* represents a section through them, and *f''* an elevation of one of them parallel to the edge and as seen from the other. The angle of the wedge is about the same as that of the first pair, but is turned inwards, so as to bring the two sides nearly horizontal and vertical, with the apex (representing the knife-edge) the lowest point and also that nearest to the corresponding section of the fellow wedge. There are three advantages offered by this form, namely, the knife-edge is less likely to cut into a relatively soft substance, a smaller plate of the latter can be employed, and the whole of each edge can be seen in the reading microscope.

The Interference Tripod.

At the top of each block, at the inner overhanging end, a guiding bed *r* is fixed for a sliding table *s* slightly over 3 centims. square, but with the inner corners cut off, so as not to impede the view through the microscope of the platinum-iridium points. The slider on the back block carries, near the middle of its inner edge, a single vertical screw *t* of hard white metal and very fine thread, and furnished with a milled head a few millimetres below its rounded summit, by means of which it can be raised or lowered in the brass columnar nut fixed to the slider. The slider on the front block carries two such screws, arranged also close to the inner edge and with their axes 2 centims. apart. These three screws form a tripod for the support of the colourless glass disc *u*, 4 centims. in diameter, whose lower surface, which has a minute silvered ring at its centre, is to assist in reflecting the interfering light. This disc is shown in the foreground in fig. 2, to the right, leaning against the edge of the iron base. The two sliders can be fixed in the positions found most convenient for supporting the disc, by means of two horizontal clamping screws at their left sides.

The Transmitter.

The front block also carries on the top of its front end a sliding agate table *v*, for the support of the agate wedge of the transmitter. The bevelled agate plate is capable of being accurately levelled by being fitted into a dove-tailed gun-metal setting, which is attached to the sliding table by three levelling and four fixing screws; the guides are grooves cut out of each side of the block, for a length parallel to the top edges of 4 centims. The slider can be fixed in the desired position by means of an oblique clamping screw carried on the left side.

The transmitter consists of a T-piece arranged on its side. It is shown in the foreground, to the left, in fig. 2, resting on the base. Its horizontal stem *w* is a rigid gun-metal rod of circular section and 17 centims. long, which joins perpendicularly the shorter upright cross-piece *x*, 6·2 centims. in length, at a point nearer to the upper than to the lower end. The latter terminates in a platinum-iridium point, intended to rest upon the centre of the plate *c* under investigation, while an agate wedge carried near its middle by the horizontal stem rests on the agate table. At the upper end the vertical rod carries a cylindrical head-piece, 1·5 centim. in diameter and 1 centim. deep, which is made up of three discs, the middle one being slightly thicker than the outer ones, and the parallel surfaces of which are approximately horizontal. The uppermost disc *y* is of black glass; its upper surface furnishes the second of the interfering reflections, and has been ground and polished an optically true plane. The particular disc employed was chosen as the best of six which had been prepared with the greatest possible care, the test being the production of rectilinear and regular interference bands when used, as in the determinations, in co-operation with the silver-ring surface of the large colourless glass disc. The selected disc is cemented by its ground under surface to the somewhat thicker disc of brass. The third metallic disc is rigidly screwed at its centre on to the end of the vertical rod, and upon it the thicker brass disc with its attached glass one is mounted in a manner which permits of adjustment, by means of four capstan-headed screws arranged at equidistant intervals from each other near the circumference. Two *zz* are situated along the diameter parallel to the horizontal stem of the rocker, and are adjusting screws, screwing only through the third fixed disc and merely pressing upwards against the middle disc; the other pair *z'*, along the diameter at right angles, are fixing screws, and pass loosely through the bottom disc, but screw into the middle one. The black-glass surface can thus be adjusted by the screws *zz* about that diameter as axis which is perpendicular to the plane of the T-piece. Fine adjustment about the diameter parallel to the stem is afforded by the two fixing screws *z'*, and is roughly provided for in the mode of attachment of the agate wedge *y'*. This latter tapers to a knife-edge 2·1 centims. long, from which the greater portion of the actual edge about the centre has been hollowed away, leaving only the two end parts with which to rest on the agate plate *v*. The wedge is mounted in a metallic holder carrying above its centre a split collar, through which the horizontal stem of the T-piece readily slides; a tightening capstan screw, passing through flanges standing up from the split edges, enables it to immovably grip the stem when the agate wedge has been adjusted to its proper position.

Between the agate wedge and the free end of the stem a short cylindrical counterpoise *x'* is arranged, which is adjustable to the required position for nicely balancing the weight on the other side of the wedge. The stem slides somewhat tightly through the counterpoise on account of a bent spring let into a groove cut along its bore, which serves also the purpose of automatically fixing the counterpoise on the stem after adjustment.

When in position, it will be obvious that the transmitter rests in stable equilibrium, in accordance with three-point contact, with the point of its vertical rod on the centre of the plate under investigation and the two end-points of the agate wedge on the agate plane. The position of the latter can be regulated along its guiding bed so as to suit the particular separation of the blocks, as determined by the size of plate available, so that the wedge shall lie symmetrically along its middle line. The counterpoise can be adjusted so as to regulate the weight with which the platinum-iridium point presses on the plate of the substance down to zero, which, however, it is advisable to stop just short of. The stem lies approximately horizontal and passes with ample room between the two screws of the interference tripod carried by the slider on the front block. The vertical rod passes readily between the two inner overhanging ends of the upper block, and the black-glass surface at its head is at a convenient height about level with the tops of the interference tripod screws when the latter are screwed fairly deeply into their columnar nuts. The black-glass surface can be adjusted absolutely horizontal by the means which have been indicated, and with the aid of a miniature spirit level provided; it is then immediately capable of receiving the rays of light directed down the vertical tube of the optical apparatus, and of reflecting them back again along the same path. The tripod screws can then be adjusted to support the colourless glass disc, so that its lower surface is separated from the black glass by the necessary thickness of air-film to allow for the further approach, without touching, of the black to the colourless glass, which accompanies the bending of the plate. The further fine adjustment required for the production of suitable interference bands, and the measurement of their position with respect to the reference centre of the silver ring, are carried out precisely as described in the dilatometer memoir (p. 339).

Mechanical "Fingers" for Adjusting the Plate.

These are carried by a fitting to the left side of the steel block. The immediate supports of the plate are two gun-metal knife-edges carried on a pair of miniature spring-tables, provided with adjustments for height, mutual separation, and for movement in an out of the recess between the blocks. The fitting consists of a thick plate screwed to the iron block, carrying as part of the same casting a thick-walled cylinder. Within this slides a shaft, on the lower part of which a screw thread is cut, and which is made capable of vertical motion only by the usual slot-and-pin device. The upward or downward motion is effected by rotation of a horizontal bevel wheel, situated near the base of the cylinder and provided within with a screw thread gearing with that of the shaft, so that it acts as a driving nut. This gears with a smaller vertical one mounted at the end of a long axle terminating within easy reach of the observer in a milled head. This axle is supported in two bearings, about which it is flanged, one forming part of the main casting of the fitting and the other being fixed to the iron block near the front end.

The vertical shaft carries a stout head-piece, which terminates above in a grooved bed, for the sliding horizontal in-and-out motion parallel to the front edge of the basal slab; the slider carries a rack beneath, gearing with a strong pinion carried in a hollow of the head-piece and manipulated by a milled head at the front end of a somewhat long axle. The slider in turn carries another horizontal grooved bed at right angles to the first. There are two sliders on this bed, each carrying one of the little supporting tables for the plate under investigation. They are arranged to move equally from or to the centre by means of a right and left-handed screw, carried in the bed and capable of rotation only, and gearing with corresponding nuts fastened beneath the sliders in a way which permits of some adjustment of the centre. The screw terminates in front in a milled head, just above that which effects the in-and-out motion. Each slider carries, flush with and in the middle of its inner edge, a little firmly screwed plate, from which springs a light arm pointing towards the recess between the blocks and suitably curved, carrying a little tabular termination, 2 centims. by 1 centim. (*p* in fig. 3). Above this is a second similar table, p', the pair being separated by four little spiral springs arranged at the corners, each fixed at its ends to both plates.

Manipulation of the top milled head thus adjusts the two tabular supports as regards their distance apart; the lower one enables the observer to move them into the hollow between the blocks until they come right under the platinum-iridium knife-edges, and out again; and the milled head down below, and in a vertical line with the front edge of the basal slab, enables them to be raised or lowered at will, in order to press the plate of the substance which they support up against the knife-edges, or to remove it from that position.

The two little tables $p'p'$, which may be considered as mechanical finger tips, are all that is necessary for the temporary support of the plate during the preliminary adjustments. But a slight addition is made to each of them to enable them, if desired, to be retenable during the whole determination. The addition consists of a similar table of gun-metal *q*, carrying a raised knife-edge along the inner side. It is fitted on the permanent table p' in a readily detachable manner, by means of a couple of flat oval-headed screws carried by the table p' near its ends, well out of the way of the plate, corresponding with two similarly shaped holes in *q*; the two fittings are rigidly attached together when the screws are rotated 90°. The knife-edge side is arranged along the inner side of the table, so that for any given separation of the two knife-edges there is the maximum amount of clear space between the two "finger tips" for the pressure-point end of the balance beam to operate in.

The "finger tips" are to be so adjusted that the gun-metal knife-edges lie precisely under the platinum-iridium edges, and they are then to be raised until the plate laid on the gun-metal edges is gently pressed up into full contact with the platinum-iridium edges. As the gun-metal edges are exactly under the others, no bending of the plate is possible.

If the method of carrying out the determination of the bending of the plate from the initial position of true planeness is adopted, and the gun-metal knife-edges are consequently retained in action, they should only be allowed to exert the minimum pressure. This is easily found, for the instant it begins to be further reduced sudden total derangement of the interference bands occurs. A careful partial turn of the milled head in the reverse direction will then usually suffice to bring the bands again into their former adjusted position, corresponding with the attainment of just full contact of the plate with the platinum-iridium knife-edges.

For the more convenient setting of the long edges of the plate perpendicular to the platinum-iridium knife-edges, a pair of horizontal milled-headed adjusting screws are added to the "fingers," one to each; they are mounted parallel to each other at the level of the plate in small uprights from the sliders, which curve inwards towards the top in order to bring the screws adequately nearer to each other than the knife-edges to enable them to clear the latter. To allow for varying compression of the springs, and consequent variable level of the plate, the screw-ends are expanded into little discs perpendicular to the length of the screws.

The Balance.

A specially constructed form of long-beam balance is employed, designed for maximum strength of beam and to take loads up to 500 grammes. The balance part proper was made by Mr. Oertling to the author's design, and Messrs. Troughton and Simms subsequently mounted it on a movable base and fitted it with the control apparatus. Its general appearance will be gathered from figs. 1 and 2. It is arranged on the right-hand part of the basal slab.

The beam is 35·5 centims. long, has a horizontal top bar graduated as usual for a rider, and is rendered very rigid by four transverse struts. This length of beam was just adequate to admit of the insertion, on the left side, of the control apparatus and a counterpoise for the weight of the pan on the right side.

The central agate fulcrum plane is 3·2 centims. long, and the knife-edge resting upon it, rigidly carried by the beam and about which the latter swings, is 4 centims. long and cut out of a single block; the swinging is consequently exceptionally steady. The central supporting pillar of the balance is shorter than usual, but adequately long for accuracy of the pointer's readings on the ivory scale of the usual kind.

The arrangements at the right-hand side of the column are of the type usually provided by Mr. Oertling in his most accurate form of long-beam balance for a load of 500 grammes. The thick wire suspending arrangement of the pan is shorter, however, corresponding to the shortened column, and by means of the small hook at its summit the pan is hung from a large inverted stirrup, whose upper horizontal bar is provided with an agate plate by which it rests on the adjustable agate knife-edge of the beam; it is maintained in the proper central position thereon by two small cones carried by the supporting frame, fitting in corresponding conical countersinkings under the bar, until the balance is released from support. This latter is achieved in the usual manner by rotation of a large milled head at the foot of the balance, which pulls down the inner shaft of the column and brings down with it the beam-supporting frame which it carries above; three very rigid guides are provided, one on each side and a larger one behind, which also carries the agate fulcrum plate, to maintain the motion of the frame steady and certain.

The arrangements at the left-hand side of the column are different. The free end of the right half of the horizontal bar of the beam, overhanging the pan-support, has no counterpart on the left half, the beam passing down immediately into the steeply inclined end bar, by which it joins the lower bar. The end is carried out beyond the junction to the same length as on the right side, but the tabular expansion, 18 millims. wide, carrying the agate wedge, in which it terminates on that side, is curtailed in width to 8·2 millims. on the left side. This enables it to be readily inserted not only between the blocks which carry the platinum-iridium wedges, but also between the little spring tables supporting the plate under investigation. At precisely the same distance, on this left side, from the fulcrum knife-edge, as is the pan-supporting knife-edge on the right, an upright agate point, the "pressure-point," is erected. It is mounted at the end of a short screw, passing through the beam-end from underneath, which serves the purpose of enabling it to be adjusted so that its point lies precisely in the same straight line with the agate fulcrum and the pan-supporting knife-edge.

To compensate for the pan and its fittings on the right side of the balance, there is provided on the left, at 5·8 centims. from the pressure-point, a tabular expansion carrying an adjustable agate wedge, over which is suspended a stirrup with agate plate, similar to those on the right; a hollow cylinder is suspended from the stirrup by a short rod terminating in a hook, within which a load can be carried of the extent necessary for perfect compensation. The supporting frame is correspondingly modified on the left, being much shorter and curving upwards so as to support the top bar of the stirrup by a pair of inverted cones as on the right side. A transverse strengthening bar forms the extreme right end of the frame, and a similar bar is inserted on the left side, just before the frame begins to curve upwards. The load within the cylinder is a block of lead, made slightly heavier than required, and subsequently pared until its weight has become exactly such as to bring the total weight on the left side of the balance equal to that on the right. The beam carries above its centre the usual adjustable gravity bob and vane, so that the last trace of adjustment can be effected by the latter.

The balance is mounted on a rectangular gun-metal box which carries the raising and lowering gear of the supporting frame within it, the milled head for working which emerges in front. The box is arranged to be capable of 5 centims. of motion parallel to the front edge of the basal slab, so that the pressure-point end of the beam may be advanced into or withdrawn from the recess between the blocks. This is achieved by providing the front and back bottom edges of the box with dove-tail flanges, which slide in corresponding guides screwed to the basal slab. The back guide has a clamping slip inserted between it and the flange, which can be driven rigidly against the latter by a strong inclined thumbscrew when it is desired to fix the balance base after adjustment. The motion is effected by means of a strong central rack screwed to the basal slab, and an equally strong pinion borne in bracket bearings projecting from the right side of the box and rotated by means of a winch handle.

The balance is also provided with a fine azimuth adjustment to enable the pressure-point to be placed precisely in the vertical plane half-way between the platinum-iridium knife-edges. This, with the rack adjustment, enables the point to be adjusted with great exactitude under the centre of that portion of the plate of the substance investigated which lies between the knife-edges. The azimuth movement is effected by mounting the central column on a circular dove-tailed base, which rotates in an outer circular guiding bed correspondingly bevelled but not quite so thick, and screwed down to a square basal plinth sufficiently tightly to prevent play; a thumbscrew passing through this outer ring, above which it is flanged, into the square plinth enables the inner rotating base and the column which it carries to be rigidly clamped down to the plinth after the adjustment has been completed. The inner rotating disc carries above it on the right a stout plate, from which projects an arm, the end of which lies between a milled-headed screw and spring piston mounted in uprights from the square plinth. Rotation of the milled head one way or the other thus brings about the desired rotation of the column and all that it carries. A pair of spirit levels are carried along the left and back edges of the plinth.

The height of the balance has been carefully arranged, so that when at rest in its supporting frame the pressure-point is at a level about a millimetre lower than the plane of the platinum-iridium knife-edges. Hence, when a plate is in position under the latter, and the pressure-point is brought under its centre, there is a space of at least one or two-tenths of a millimetre left between the point and the under surface of the plate, supposing the latter about the usual thickness of something under a millimetre. Hence the supporting frame can be left in operation up to the last moment, and when the beam is eventually released it remains practically horizontal during the bending of the plate.

There is one occasion, however, when the beam should be lowered by about a centimetre, namely, when a test is being made for any movement of the knife-edges under the blocks with respect to the interference tripod screws on the top of the blocks. In the form of apparatus now described this movement is practically *nil*, but it is well to have a means of confirming the fact by a direct determination. In Koch's apparatus it amounts to as much as the equivalent to two interference bands, as the second reflecting surface is not supported by the blocks, but independently. For this purpose instead of a plate a block of glass, 1 centim. thick, has been provided, which may be assumed to be unbendable, and any movement of the interference bands on allowing the weight to act as usual must be due to movement of the parts of the blocks, from knife-edges to tops of screws.

In order to provide for this determination the square plinth is separated from the rectangular basal box by a similar square plate of brass 1 centim. thick, and the fixing screws are long enough to pass through both plates into the box top. When the determination in question is to be made, this insertion plate is removed, and the square plinth fixed directly to the box. The beam will then be at the right height for the experiment.

A support for the pan is provided to prevent it swinging and to remove strain from the beam when not in use. It consists of a short, hollow cylindrical column, with heavy solid base covered underneath with cloth, carrying at its summit a rotatable but vertically immovable nut with milled flange; gearing within is a screw carrying at its head a table of ebonite, hollowed to the shape of the under part of the pan. When the accessory is placed under the pan, the table can be raised to support the latter by rotation of the milled nut.

A removable support is likewise provided for the counterpoise on the left, in the shape of a little table of the diameter of the cylinder, which can be raised to support the latter by means of a similar milled nut carried, however, at the end of a horizontal arm whose other end is a doubly split, and therefore detachable, collar gripping round the column of the control apparatus described in the next section.

The determination of the position of the interference bands at the conclusion of an observation, when the control is removed and the full weight on the pan is operating in bending the plate, is considerably disturbed by flickering of the bands, unless absolute quietude is obtained and absence of all vibration. The difficulty can, however, be entirely overcome by fixing a horizontal disc below the pan and immersing it in oil. A disc of aluminium is provided, of the same diameter as the pan, to which it can be rigidly fixed by means of a stout aluminium rod, 3·5 centims. long; one end of the rod is screwed firmly into the centre of the disc, washers above and below aiding the rigidity, and the other end screws into a little boss fixed permanently underneath the bar on which the pan is mounted. It is thus readily detachable if not required. The disc, when in use, is immersed in oil, cedar oil being found admirable for the purpose, contained in a glass dish with perfectly parallel sides and of a slightly larger diameter than the disc, which, of course, must not touch the glass. The resistance which the oil offers to the vertical motion of the disc effectually steadies the bands, so that the final position can be measured with the utmost accuracy.

Cedar oil possesses the two advantages of not solidifying, and of being so slightly viscous as scarcely to impair at all the sensibility of the balance.

The amount of vertical motion of the beam ends and the pan is so slight, not amounting to a millimetre from first to last if the supporting frame is kept in action up to the moment of beginning the bending, that the amount of the rod which is wetted by the oil is practically constant. It is therefore found sufficient to add to the counterpoise on the left side a weight, previously determined with the greatest care, and made in the form of a platinised disc, which precisely balances the aluminium fitting as immersed in oil. It is laid on the top of the cylindrical compensator, and has a radial notch to enable it to fit round the suspending rod. Any slight remaining inequality of the weights on the two sides of the balance is not more than can be corrected by slight movement of the adjustment vane carried above the centre of the beam

The Control Apparatus.

About the middle of the lower bar of the beam on the left side a little saddle is fitted, on the top of which is fixed a platinum-iridium cone, the "control-point," similar to the agate "pressure-point." Control of the movement of this point, and therefore of the whole beam with its pressure-point, is afforded by a horizontal agate plate, mounted above the control-point in a fitting capable of extremely fine vertical movement. This fitting is a rectangular double bracket, which envelopes the saddle on three sides, above, behind, and below, the vertical back limb being long enough to leave about 4 millims. space for the bar of the beam to swing in. The agate plate is fitted underneath the top limb. The bracket is carried as part of the same casting at the head of a vertical hollow cylinder of gun-metal 2·8 centims. long, fitted at its lower end with a steel split-collar furnished with a tightening screw, which enables it to be fixed at a convenient height to a vertical shaft, on the upper end of which it slides as far as the bore permits, rotation being prevented by groove and pin. Below the part down which the cylinder can slide the shaft thickens to 1·2 centims., and the whole of the lower portion slides tightly in a gun-metal column 2·8 centims. diameter and 12 centims. long, which is mounted below on a stout bracket fixed to the left side of the rectangular basal box on which the balance is mounted. An exceedingly fine screw thread, whose pitch is one-fourth of a millimetre, has been cut with the greatest possible accuracy on a part of the shaft within the column; rotation of the shaft is prevented by groove and pin, but it can be propelled upwards or downwards by a rotatable but vertically immovable nut, furnished with a correspondingly fine thread within and worm-wheel teeth without. The column is broken to admit the nut at a point 2·2 centims. from the top, and rigidity of the two parts is secured, as well as a suitable support for the bearing of a driving endless screw, by means of a hollow rectangular box-piece, open in front and behind, cast with the two parts of the column. The diameter of the nut is somewhat greater than that of the column, and the peripheral oblique teeth are 72 in number; one revolution of the endless screw rotates it to the extent of one tooth. This corresponds to the vertical movement of the shaft through 0·0035 millim. The bearings of the endless screw are attached to the box by an enveloping double claw, cast as one piece; the front bearing at the crossing is a horizontal cylinder from which the screw shaft emerges. The end of the latter is notched diametrically, to admit of the attachment of either a simple milled head 3·2 centims. diameter, whose short cylindrical stem bears inside its bore a transverse bar fitting the notch, or of a Hooke's-joint arrangement, which brings the manipulating head nearer to the observer without interfering with the movement of the whole balance, and also enables a more delicate mode of rotation than a simple milled head to be employed. It consists of a short tube with similar inner cross-bar, carried at one end of an equally short but thick rod whose other end bears one semicircular fork of the Hooke's-joint; the other fork forms one end of a gun-metal shaft 9 centims. long. The two semicircular forks are rotatable about a pair of rectangular axes, passing through a brass sphere which each fork half encircles. The shaft is loosely supported near its front end in a stout ring carried at the head of a strong gun-metal tubular column, fixed near the front edge of the basal slab. The ring has a short stem rotatable in the bore of the column, but made incapable of vertical motion by groove and pins. The front end of the shaft is notched to gear with the same milled head that fits the head of the endless screw itself. The length of shaft is adequate to permit of the full extent of racking of the balance in or out of the recess between the blocks, so that whatever the position of the balance the control apparatus is equally available.

During an actual determination, after the final adjustment of the pressure-point to the centre of the plate, experience shows that it is of some advantage to the attainment of absolute steadiness in the motion of the bands to substitute for the Hooke's jointed shaft a simple rigid shaft which is also provided; it is fitted with a tightening collar at the end of the barred bore, where it grips the endless screw head, to prevent the slightest chance of slipping. Being twice as long as the jointed shaft, its front end is nearer to the observer, and is supported in a special bearing fixed on the small mahogany base near the telescope pedestal.

In order to render the control still more delicate, so that the bands shall march past the cross-wires with great deliberation, rendering their counting a very easy matter, the milled head can be replaced by a handle at the end of a long radial lever. To the end of a short thick tube, provided with inner cross-bar to fit the shaft notch and also a tightening collar to firmly grip the shaft, a strong plate is fixed, out of the front of which a sliding bed is cut for the lever to slide in; by means of a longitudinal groove in the latter and a clamping screw, the lever can be fixed to the plate in any position, and thus the radius of the circle described by the ebonite handle can be modified as desired. When the lever is at its full length the radius is 10 centims., and the circumference of the circle 63 centims. As one complete rotation corresponds to a rise or depression of the control screw, and therefore of the control point on the beam, of 0·0035 millim., one-tenth of this, namely 0·00035 millim., corresponds to a movement of the handle of 6·3 centims. The pressure-point, however, moves through twice the distance that the control-point traverses, so that a movement of 0·00035 millim. on the part of the pressure-point corresponds to a movement of about 3 centims. on the part of the handle manipulated by the observer. This, however, is a very large amount of movement, of which a tenth part is still a very appreciable quantity.

It so happens that the half-wave-length of the red C-hydrogen light which the author usually employs is 0·00033 millim. As a change in the thickness of the air-film equal to half a wave-length corresponds to the interval between the passage of two consecutive interference bands past the reference spot, it will be clear that the handle has to be turned through a distance of 3 centims. for each transit of a whole band, and therefore that the transit can be controlled with a high degree of delicacy.

In actual practice the control screw is found to work even more admirably than the author anticipated. The bands pass with the utmost steadiness, and their counting is extremely easy.

The Measuring Microscope.

The measuring microscope is mounted, on the left-hand part of the basal slab, on a stout column of circular section, tapering to the summit and expanding at the base to a flange of 14 centims. diameter. The under side of the base is cut with a bevelled groove, by which the column slides over a correspondingly dove-tailed guiding bed of iron, 22·5 centims. long. A strong rack is longitudinally sunk in the bed, and gears with a pinion borne within the lower part of the column, which has here a projection coming out to the flange in front to afford a rigid axle-bearing and permit of the attachment of a winch handle. One half-turn of this handle causes the column to travel rapidly over the rack from left to right or *vice versâ*, so as to bring the microscope over the blocks or remove it out of the way. It can be rigidly fixed in any position on its path by a very strong vertical binding screw, furnished at its head with a lever handle, and screwing through the basal flange, at the back of the column; the screw shaft terminates below in a conical head, which lies within a corresponding conical hole in a bevelled clamping slip inserted against the back guide. Rotation of the handle for half a revolution draws up the cone sufficiently to press the clamping slip tightly against the guiding bed, and so binds the column to the basal slab.

The column is 22·5 centims. high, and carries on its expanded tabular top the two rectangular measuring movements. The guiding bed of the lower one, which is that at right angles to the front edge of the basal slab, and all that it carries is rotatable for about 20° in the horizontal plane about the axis of the column, and capable of a considerable amount of fine adjustment and of eventual rigid fixation at any azimuth within those limits, by means of two opposite capstan-screws directed, through the sides of a rectangular hollow bracket projecting from the back of a collar round the tabular top, against a stud projecting into the hollow from below the guiding bed. This enables the upper right-and-left measuring movement to be set exactly parallel to the fixed platinum-iridium knife-edge AB carried by the hinder block. The thick slider, 8·5 centims. square, which moves over the lower guiding bed carries the guiding bed of this second movement, fixed exactly at 90° to the lower one. The similar slider which moves over this bed carries a vertical column 20 centims. high, from an arm of which the microscope is vertically suspended. The column consists of a fixed conical core and a rotatable outer part, so that the microscope can be swung readily out of the way of the interferometer. The outer rotatable part of the column can be fixed in any position about the core, by means of a washer, with hole to fit a squared part of the core, which projects above the rotatable column, followed by a large milled-headed clamping nut which screws on a thread with which the core terminates.

The column has two curved arms cast with it, on opposite sides of the axis; one bears the microscope and the other a compact counterpoise for the latter. The microscope arm is a double one and the parts are of T-shaped section to give rigidity; it terminates in a vertical hollow cylinder in which the microscope is capable of vertical motion by means of the usual rack and pinion. The magnification provided is about 15 diameters. The eye-piece is carried in an inner sliding tube which affords an adjustment for the focussing of the rectangular spider-lines; the outer tube in which it slides screws into the carrier for the latter, which in turn slides tightly in the main optical tube, and is provided with a flange by means of which the azimuth of the spider-lines may be adjusted.

The rectangular measuring movements have been constructed in a manner which ensures both rigidity of their parts and complete absence of backlash in the working of the screws. The total thickness of the two sliders and their beds amounts to 6 centims. Provision for regulating the fit of the sliders about the beds is made in each case by making one of the guides of the slider take the form of a thick bevelled rod inserted between the correspondingly bevelled side of the bed and an outer flange of the slider provided to contain it, and slightly larger than the gap between them, instead of cutting the bevel out of the slider itself on this side, as is done on the other side. The pressure of the bevelled rod against the bed is determined by two fixing screws and a regulating capstan screw between them. The two capstan screws can also be used to fix the movements in any desired position.

The measuring screws, which lie longitudinally along the centre of the beds and are mounted in closely fitting and very rigid bearings, have been cut with the utmost attainable accuracy. They have a pitch of 1 millim. A finer screw than this was undesirable, in view of the distances to be measured. The length of traverse provided in the case of each screw is about 33 millims., just enough to enable the two end-points of either knife-edge to be brought into the centre of the field of view of the microscope.

In order that there should be no backlash between them and the nuts attached to the sliders which they drive, a special device has been adopted. It consists in making each of the nuts in two parts, which are forced continuously apart by a strong spring. The double nut is cylindrical in shape, with a broad stud projecting above by which it is fixed to the slider. The cylinder has an internal bore of about twice the diameter of the screw, extending from one end along three parts of its length; the remaining quarter forms one part of the nut, being bored and tapped with a screw thread corresponding to that of the screw. The other part of the nut slides like a bored and tapped stopper into the open end of the cylinder, and, being of the same length as the part which is solid with the cylinder, fills up the outer third of the large bore. The outer end of the stopper-nut has two steadying pins projecting radially at the opposite ends of the same diameter, which fit in notches cut to receive them in the cylinder end, so that rotation of the stopper-nut about the cylinder and the nut which is solid with it is prevented. The middle widely bored part of the cylinder accommodates the spiral spring. In fitting the arrangement, the loose or stopper-nut is pressed into its place and compresses the spring; the screw is then inserted. This immediately secures the two sections together, and on removing the finger-pressure the spring exerts its force and pushes the loose nut away as far as any trace of backlash in the fitting of screw and nuts permits. In all positions of the compound nut along the screw, the latter is thus gripped between the two sections of the nut, and all possibility of backlash between the screw and the slider carried above and fixed to the cylinder is eliminated.

The guiding bed of the front-and-back movement carries on the left side a silver scale graduated in millimetres, and that of the right-and-left movement carries a similar one along its front edge. Each slider carries a little silver plate on which the indicating mark is engraved, and which is arranged to slide closely against and partially over the graduations on the scale. The microscope is made to read accurately to a thousandth of a millimetre in each of the two rectangular directions, by a method which entirely avoids the use of an additional micrometer screw. The screw shaft in each case carries, between the bearing from which it emerges and the milled head by which it is rotated, a drum 8 centims. in diameter, fitted with an outer tyre of silver 2·8 centims. broad. This silver cylinder is engraved with eleven equidistant circles parallel to each other and to the cylinder ends, the two outside ones being only a millimetre distant from the latter. The nine inner circles thus divide the cylindrical surface up into ten circular strips 2·5 millims. broad. The two outside circles have each been divided into 100 equal parts 2·5 millims. long, and every alternate division of that edge-circle nearest the bearing has been engraved with its number. The division of these edge-circles has been done so that a line drawn parallel to the shaft axis from any division on one of them would meet the other at a division. A hundred parallel lines have then been drawn obliquely across the cylinder from each division of the numbered circle to the preceding division on the other edge-circle, thus covering the cylindrical surface with 1000 parallelograms. The space between any two divisions of the numbered circle is in this way sub-divided into ten parts by the intersections of the oblique line with the ten other circles, and an indicator in the form of a straight line parallel to the axis of the cylinder, suspended close above the latter, enables the observer to read off directly at which circle the intersection corresponding to the position of the microscope occurs. This indicating straight line is engraved on a glass plate and coloured red to distinguish it from the lines on the cylinder. The glass plate is fixed in a rectangular frame supported horizontally just over the surface of the cylinder, by a bracket standing up from the end of the guiding bed. The red line has numbers from 1 to 10 also engraved against it and coloured red, exactly over the several circles in turn which follow the numbered circle next the bearing. It will be obvious that the position of the microscope at any time, along either of the two rectangular directions, is afforded by taking the reading of the last whole millimetre from the scale on the guiding bed, and then adding the reading for the fraction of a millimetre obtained from the drum; the first two places of decimals are given directly by the numbered circle next the bearing, and the third place is immediately indicated by the red number above the circle whose intersection with the oblique line falls exactly under the red indicating line. In practice this mode of determining the thousandth of a millimetre proves the easiest the author has yet worked with. The fact that a single screw is alone concerned, and one which is absolutely freed from backlash by the double-nut device, renders the method highly accurate.

The microscope is required for the measurement of the free length of the plate of the substance under investigation, that is, the distance between the platinum-iridium knife-edges against which it is bent; also for the measurement of the breadth of the plate. For the determination of the plate's thickness, the thickness measurer which the author has previously described ('Phil. Trans.,' A, 1898, vol. 191, p. 337) is admirably adapted; it affords the thickness with accuracy to the same unit as the measuring microscope, namely, the thousandth of a millimetre.

The most convenient length of plate is from 10 to 20 millims., so as to afford a length between the knife-edges of not less than 8 and upwards of 16 millims. For a 15-millim. plate a breadth of about 3 millims. and a thickness of 0·4 to 0·7 millim. are suitable.

In carrying out the determination of the distance separating the two platinum-iridium knife-edges several series of readings are obtained for the separation of the points A and C, and of B and D, and the mean taken. In case the alternative knife-edges are employed, the actual distance between the centres of the two edges can be read off directly, in addition to the separation of the end-points.

The breadth of the plate is determined for six or seven equidistant points along that portion of the plate which lies between the knife-edges, and the mean taken.

It is convenient to engrave a little cross with a fine needle at the exact centre of the plate while under the microscope, so that the platinum-iridium point of the transmitter can subsequently be readily adjusted precisely at the centre with the aid of a pocket lens.

Instead of the method of carrying out the determinations from the plane of no bending of the plate, by use of the spring tables and their gun-metal knife-edges, it may be more generally preferred to employ the method used by KOCH, of commencing with the plate slightly bent under a constant initial weight, say 50 to 100 grammes, and the apparatus lends itself admirably to this method.

Details of the modes of carrying out the determinations, together with the description of a delicate mode of feeding the balance-pan with the weight employed, are reserved, however, for a subsequent communication describing the work actually carried out with the instrument.

Conclusion.

The advantages which the apparatus now described appears to the author to possess over that of Koch, with which, however, most excellent work has been done, are as follows :—

(1.) Strictly monochromatic C-hydrogen light is employed, instead of the composite light corresponding to the two sodium D-lines, which are affected by mutual interference. Moreover, the use of auto-collimation ensures greater intensity and parallelism of the illuminating and reflected rays, and consequently greater perfection of interference.

(2.) The transmitter renders the observer independent of the nature of the surface of the plate of the substance investigated, and all necessity in the case of non-polishable and badly reflecting substances for the doubtful device of cementing a small glass plate to it is eliminated. Further, the troublesome alteration in the configuration of the bands, due to the plane surface of the plate being changed to a curved one on bending, or to increase of curvature if already more or less initially bent, is entirely avoided by the use of the transmitter, and bands of maximum excellence, suitable for adjustment between a pair of parallel micrometric spider-lines, are always obtained, owing to the same selected surfaces being employed to reflect the interfering light.

(3.) The employment of the sensitive method of a modified chemical balance for the application of the bending weight affords obvious advantages, not least among them being greater compactness of the whole apparatus, which is entirely above the supporting table, instead of being partly above and partly below.

(4.) The mode of controlling the application of the weight, and of regulating the rapidity of motion of the bands, is much more convenient and accessible.

(5.) The measuring microscope is entirely reserved for the determination of the dimensions of the plate and its setting, instead of also having to be employed for the totally different function of observing the bands. Also, increased accuracy is attained in the two rectilinear measuring movements by the provision of a novel method of eliminating backlash in the mounting of the measuring screws.

(6.) The error due to movement of the blocks supporting the plate, under the bending weight, with respect to the second reflecting surface concerned in the interference, is eliminated, together with all necessity for the application of a correction for it ; the glass disc furnishing this surface, and the knife-edges against which the plate is bent, have a common rigid support, instead of being mounted independently.

The author desires to express his thanks to the Government Grant Committee for their grant to defray the cost of the instrument. Also to record his sense of indebtedness to Mr. J. Skinner, of the firm of Messrs. Troughton and Simms, for invaluable help in designing and perfecting the instrument.

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THE MECHANICAL FORCES ACTING ON A CHARGED ELECTRIC CONDENSER MOVING THROUGH SPACE

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V. *The Mechanical Forces Acting on a Charged Electric Condenser moving through Space.*

By Professor F. T. TROUTON, *F.R.S., and* H. R. NOBLE, *B.Sc., University College, London.*

Received June 11,—Read June 18, 1903.

THE experiments described in this paper were designed with the object of investigating the behaviour of a charged electrical condenser moving through space, and to discover, if possible, whether there be a relative motion between the earth and the æther. It was previously suggested by one of us in the 'Proceedings of the Royal Dublin Soc.' (Vol. VII., Part XIV., April, 1902), in connection with an experiment of a similar nature suggested by the late Professor FITZGERALD, and mentioned in his collected papers edited by Professor LARMOR.

The idea underlying the experiments will be understood from the following considerations:—If a charged condenser be placed with its plane in the direction of the æther drift, then, on the assumption that a moving charge develops a magnetic field, there will be associated with the condenser a magnetic field perpendicular to the lines of electric induction and to the direction of the motion. When the plane of the condenser is perpendicular to the æther drift, the effects of the opposite charges will neutralise each other. Thus there is magnetic energy stored in the medium when the plane of the condenser and the direction of the drift coincide; and accordingly it is to be expected that under these circumstances the condenser, when freely suspended, would tend to move so as to take up the position with its plane perpendicular to the drift, in order to transform this energy.*

To realise this, a condenser, with its plane vertical, was suspended by a fine wire and charged. The charges were let into the plates of the condenser by means of the suspending wire, and by a wire which hung from beneath, dipping into a liquid terminal. Observations were made at different times in the day, when the plane of the condenser made various angles with the direction of the drift. If the condenser

---

* [According to the theory given by LARMOR ('FITZGERALD'S Scientific Papers,' p. 566) the longitudinal direction, being that of maximum kinetic energy, is the direction of equilibrium; the forces due to displacement from it however remain as above, if the form of the system be assumed permanent. The negative electric experimental result reached in this paper is connected with the other negative second-order results of optical experiments relating to motion through the æther, which have been obtained by MICHELSON and by RAYLEIGH. The inferences as regards molecular theory are indicated *loc. cit.*]

be hung with its plane north and south, then about 12 o'clock in the day there would be no couple tending to turn it, because the æther drift due to the earth's motion in its orbit round the sun is at right angles to the plane of the condenser; on the other hand, at any other hour, say 3 o'clock, there would be a couple making itself felt by a tendency to rotate the plane of the condenser into the position at right angles to the drift.

The effect to be looked for was an extremely small one, being a second-order effect only. In the earlier forms of the apparatus the calculated deflection was found to be entirely obscured by a number of accidental disturbing causes, and, in fact, the course of the experiments consisted mainly in eliminating these disturbances one by one.

The first difficulty arose from the preponderance of the electrostatic attractions between the suspended condenser and the walls of the containing case. To minimise these effects the condenser was protected by a metallic coating which was kept at the same potential as the case, all being earthed.

The suspending wire was made the insulated terminal, so that any electrostatic pull upon this wire could only produce a force acting through the centre of support, and thus the rotational effect would be eliminated, leaving only a translatory pull, which would not affect the result. There were still residual electrostatic actions, which were traced to the point where the suspension was fixed to the condenser. At this point there was necessarily a break in the metallic protecting coating fixed to the condenser, owing to the fact that the earthed terminal could not be brought very close to the insulated terminal without breaking down the insulation. To eliminate this effect, the protecting coating was prolonged up round the support in the form of a cylinder, about 3 centims. wide, and 6 centims. high. The pull being now between the cylinder and the wire, and therefore an internal force, there could be no rotation produced. Finally, it was found necessary, for similar reasons, to shield the wire as it passed through the top of the containing vessel (or case in which the condenser hung) by a thin brass tube 1 centim. wide, passing well into the vessel, and at the same potential as the wire. These precautions practically eliminated all electrostatic disturbances.

As it was necessary to keep the condenser charged for several minutes at a time, condensers insulated with paraffin wax were found quite useless for the high potentials required (3000 volts), any small leak probably increasing itself by melting the wax. Special condensers were then made in the following manner:—

Carefully selected mica plates, ·011 centim. thick, were individually tested to about 5000 volts. A disc of mica, 7·7 centims. diameter, was covered with tinfoil of 4·5 centims. diameter; the uncovered portion was coated with a thin layer of shellac-varnish. The disc was then dried on a hot plate. Two plates prepared in this way were ironed together with a hot iron, and the whole condenser was built up in this manner. We thus had almost perfect insulation, for when charged the potential only fell from 3000 to 2000 volts in about 5 minutes, although the outside terminal or protecting coating was wrapped round the condenser to within 1 centim. of the other terminal.

The lower contact was made by a wire dipping into a liquid, which also served the purpose of damper to the oscillations. Water was first tried, but the air in the case soon became saturated with water vapour, to the detriment of the insulation. The water was then replaced by sulphuric acid, but it was found that the acid controlled the motion of the condenser to a large extent, although thin platinum wires were used, and all damping arrangements detached. The acid was then diluted as far as was compatible with good insulation, the thin platinum wire (6 mils.) dipping into it. This has been found satisfactory, even for small controlling couples.

The last difficulty was with convection currents or draughts. Owing to the unsymmetrical shape of the suspended condenser — a flat vertical disc — air currents had powerful disturbing effects. The condenser was then fitted into a smooth spherical celluloid ball, upon which the draughts had less effect. The ball was covered with gilt paint, and earthed by means of the lower contact.

A cylindrical vessel of zinc plate, just wide enough to hold the ball, was made, inside which the condenser was hung. We thus further diminished the possibility of convection currents by limiting the space around the condenser. Around the inner zinc vessel was placed another, concentric with the first, the interspace being packed with cotton-wool. The whole of the apparatus except the suspending wire was earthed.

The final form of the apparatus is as follows (fig. 1) :—PA, the suspension, is a phosphor bronze strip 37 centims. long, the finest that could be obtained. This was soldered at its lower end A to a copper cap, fixed to the condenser protecting the projecting tin-foil tags, and making contact with them by means of fusible metal.

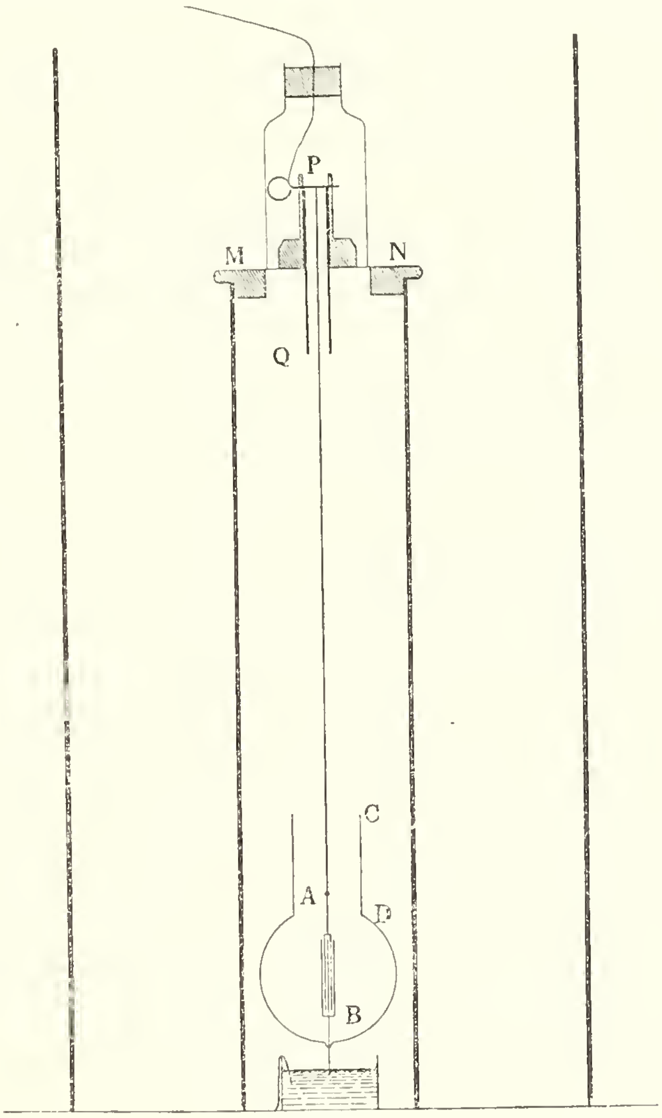

Fig. 1.

The upper end of the suspension, P, was wound on a small windlass, which was insulated by a mica plate fixed to an annular wooden ring MN, forming the lid to the inner zinc vessel.

To prevent draughts from blowing down into the apparatus, a small glass bell jar covered the windlass, contact being made by a wire passing through the small cork at the top. PQ is the small brass tube shielding the upper part of the suspension. CD is the cylinder protecting the point of support. AB indicates the position of the condenser inside the celluloid ball. Two cylindrical zinc vessels protect the apparatus; these were earthed together with the ball containing the condenser.

A plane mirror was attached to the condenser. This was viewed by means of a telescope and scale, through small mica windows in the zinc coverings.

The potential was maintained by a Wimshurst machine, to the terminals of which was attached a Kelvin-White voltmeter.

Calculation of the Effect.

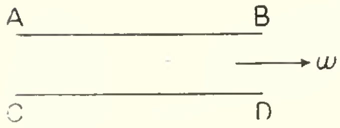

Fig. 2.

Let ABCD (fig. 2) be a given condenser charged to a surface density σ. Let it be moving in the direction AB with velocity w. We have a charge σ per unit area moving with velocity w; this is equivalent to a current σw across unit length of the plane. The opposite charge on the other plate will produce an equal and opposite current; therefore perpendicular to the plane of the paper and parallel to that of the condenser we have a magnetic field equal to $4\pi\sigma w$. The magnetic energy per unit volume is $\frac{\mu H^2}{8\pi}$, where H is the intensity of the magnetic field; this equals $2\mu\pi\sigma^2 w^2$.

The volume of the dielectric is Se, where S is the total area of one armature of the condenser and e the thickness of the dielectric. The total magnetic energy is $2\pi\mu\sigma^2 w^2 Se$. The total charge Q is $\frac{KSV}{4\pi e}$, where V is the potential difference between the plates; hence $\sigma = \frac{Q}{S} = \frac{KV}{4\pi e}$. The total magnetic energy is thus $2\pi\mu w^2 Se \frac{K^2V^2}{(4\pi)^2 e^2}$. If N be the electrostatic energy of the condenser, N is $\frac{1}{2}\left(\frac{KS}{4\pi e}\right)V^2$: so that the total magnetic energy is $\mu K N w^2$—or, if v be the velocity of electric propagation, the magnetic energy is $N\left(\frac{w}{v}\right)^2$.

Suppose now that the plane of the condenser makes an angle ψ with the direction of motion. Then magnetic energy of condenser is $N\left(\frac{w}{v}\right)^2 \cos^2\psi$.

The total energy of the system is

$$E = N\left[1 + \left(\frac{w}{v}\right)^2 \cos^2\psi\right],$$

the couple tending to increase ψ is $-\dfrac{dE}{d\psi}$, which is

$$N\left(\frac{w}{v}\right)^2 \sin 2\psi - \left[1 + \left(\frac{w}{v}\right)^2 \cos^2 \psi\right] \frac{dN}{d\psi}.$$

If we assume N independent of ψ, the couple is $N\left(\dfrac{w}{v}\right)^2 \sin 2\psi$.

If N changes so that couple is always zero, $\dfrac{dN}{d\psi} = N\left(\dfrac{w}{v}\right)^2 \sin 2\psi$ (neglecting small quantities of 4th order). Suppose u is the velocity of the earth's way through space, represented by OD (fig. 3). Let plane of condenser be yZ, and OZ the axis of suspension. Let plane ZOD cut plane xy in OH; let λ be the ZOD and μ the angle yOH.

Now component of velocity along axis of suspension cannot rotate condenser about OZ, so that effective component is $u \sin \lambda$, and the expression for the couple becomes

$$N\left(\frac{u}{v}\right)^2 \sin^2 \lambda \sin 2\mu.$$

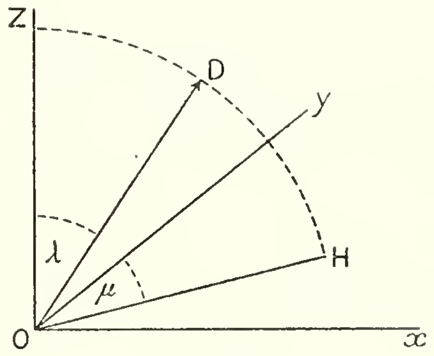

Fig. 3.

The experiment can be so arranged that $\lambda = 90°$ and $\mu = 45°$, and the couple reduces to $N\left(\dfrac{u}{v}\right)^2$.

The best Conditions for Experiment.

The following considerations show clearly the best conditions for making the experiment, in respect to time of day, time of year, and azimuth of the plane of the condenser.

(i.) The variation of the direction of drift with time of year.

Consider the celestial sphere (fig. 4). Let Σ be the position of the sun on the ecliptic $\Upsilon\Sigma$. If Q be a point such that $\Sigma Q = \frac{1}{2}\pi$, then OQ will be the direction of the drift past the earth.

Let $\Sigma NQ = \xi$.

Let $QY = \eta$, the declination of the point Q.

If w = obliquity of the ecliptic,

a = right ascension of the sun.

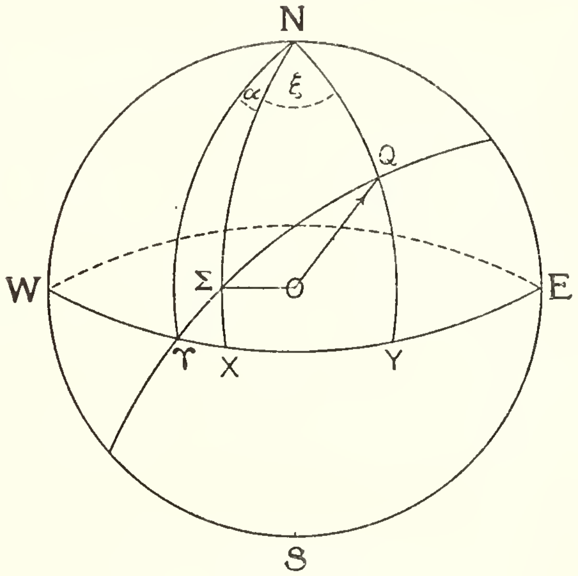

Fig. 4.

$$\text{Tan}\ \Upsilon Q \cos w = \tan \Upsilon Y$$

$$\tan \Upsilon Q = -\cot \Upsilon\Sigma, \quad \text{since} \quad \Sigma Q = \tfrac{1}{2}\pi$$

$$= -\cos w / \tan a,$$

so that $\tan \Upsilon Y = -\cos^2 w/\tan a$

$$\xi = XY = \tan^{-1}\left(-\frac{\cos^2 w}{\tan a}\right) - a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(i.)},$$

$$\text{Sin}\,\eta = \sin QY = \sin \Upsilon Q \sin w = \cos \Upsilon \Sigma \sin w$$

$$= \frac{\sin w \cos w}{\sqrt{\cos^2 w + \tan^2 a}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(ii.)}.$$

(ii.) The effective couple due to the drift.

Let sphere (fig. 5) represent the earth turning round its axis NS.

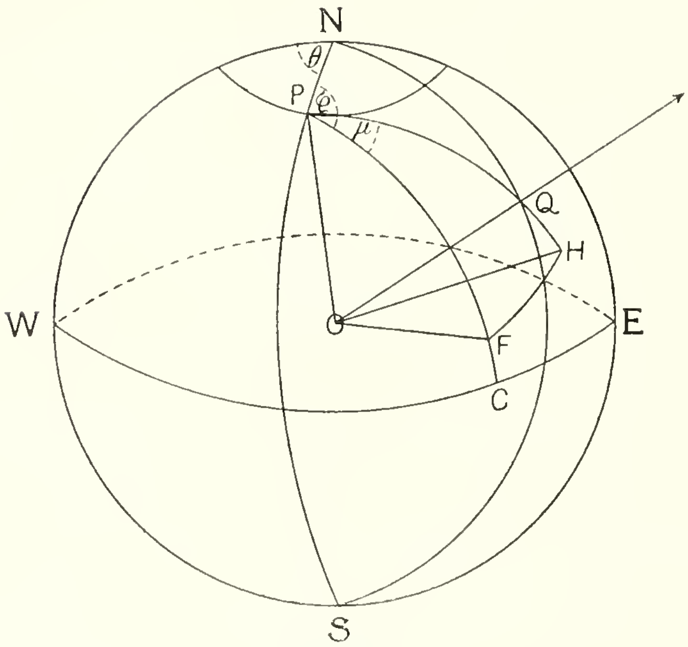

Fig. 5.

Suppose the sun to be somewhere in the plane perpendicular to the paper and passing through the centre.

Let OQ be the direction of the drift.

Then with same meaning as before for ξ and η,

$$\text{QNE} = \tfrac{1}{2}\pi - \xi, \quad \text{NQ} = \tfrac{1}{2}\pi - \eta.$$

Let P be a particular place on the earth, which for London we take the latitude $51\tfrac{1}{2}°$. Then NP $= 38\tfrac{1}{2}°$.

Let PC be plane of suspended condenser passing through centre of earth, and making angle ϕ with the meridian CPN $= \phi$.

Call WNP, the time after 6 A.M., θ.

Then PNQ $= \pi - \theta - (\tfrac{1}{2}\pi - \xi) = \tfrac{1}{2}\pi - \theta + \xi$.

Let OF be perpendicular to OP in the plane of the condenser.

With P as pole draw a great circle arc FH, meeting PQ produced at H.

Then FH $= \mu$, PQ $= \lambda$. (See fig. 3.)

Let u be the velocity of the drift along OQ.

The component along OH $= u \sin \lambda$.

So we have finally for the couple tending to rotate the condenser the value $N\,(u/v)^2 \sin^2 \lambda \sin 2\mu$.

If it be possible, let us select the time of day so that $\lambda = 90°$.

Now

$$\cos PQ = \cos NP \cos NQ + \sin NP \sin NQ \cos PNQ$$

$$\cos \lambda = \sin 51\tfrac{1}{2} \sin \eta + \cos 51\tfrac{1}{2} \cos \eta \sin (\theta - \xi) \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(iii.)}.$$

When $\lambda = 90°$, we have

$$\sin (\xi - \theta) = \tan 51\tfrac{1}{2} \tan \eta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(iv.)}.$$

Since η never exceeds $23\frac{1}{2}°$, it is always possible to choose θ so as to satisfy this condition. When θ is so chosen, we can rotate the condenser about its axis of suspension until the angle μ is 45°. The couple then becomes $N(u/v)^2$, which is the greatest possible.

The azimuth of the drift, measured as positive from the meridian easterly, is deduced from the following:—

In triangle NPQ,
$$\frac{\sin NPQ}{\sin PNQ} = \frac{\sin NQ}{\sin PQ}:$$

or, since $NPQ = \phi - \mu$, $\sin(\phi - \mu) = \frac{\cos\eta}{\sin\lambda}\cos(\xi - \theta)$.

But $\sin\lambda$ has been chosen as unity, therefore
$$\sin(\phi - \mu) = \cos\eta\cos(\xi - \theta),$$

or
$$\cos(\phi - \mu) = \frac{\sin\eta}{\cos 51\frac{1}{2}} \quad \text{. . . . .} \quad (\text{v.}).$$

The angle $(\phi - \mu)$ is the azimuth of the drift.

The dotted curve, fig. 8, shows the time of day when drift is entirely horizontal.

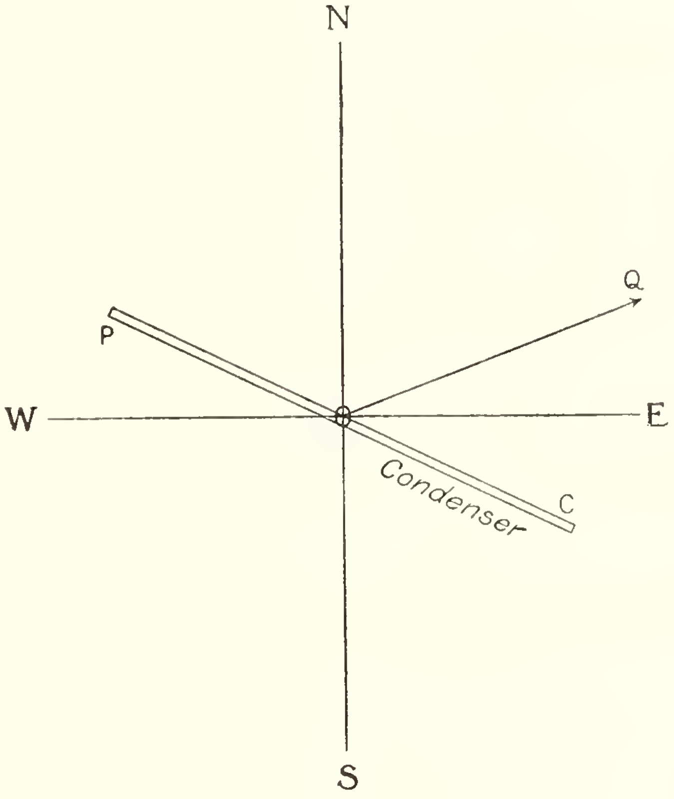

Fig. 6.

The dotted curve, fig. 9, shows the azimuth of the drift.

If the condenser be placed as in the diagram (fig. 6), then it should tend to move so as to increase the angle NOC.* That is, the motion should be in the direction E.S.W. We shall call this the positive direction. $NOC = \phi$, $QOC = \mu$.

---

* Accepting LARMOR'S Theory, the angle NOC would diminish.

Influence of the Sun's Proper Motion.

In the above we have only considered the drift due to the motion of the earth round the sun; but it is also necessary to consider the effect when the sun's proper motion is included. The magnitude of this motion has been investigated by NEWCOMB ('Astronomical Journal,' No. 457, pp. 4, 5), KAPTEYN ('Astronomische Nachrichten,' No. 3487, p. 104), CAMPBELL ('Astrophysical Journal,' vol. 13, No. 1). The result of these investigations is, that there is still considerable doubt as to the magnitude and direction of this quantity; no very exact treatment is therefore possible. We have adopted for this calculation the rough value 15 miles/sec., in a direction whose right ascension is 270° and declination $38\frac{1}{2}°$. This corresponds very nearly to the position of α Lyræ (Vega).

In the diagram (fig. 7) let OQ be the component of the drift due to the annual motion. Let V be the position of Vega, which we shall consider as having right ascension $= 270° = \frac{O\pi}{2}$ and decl. $= 38\frac{1}{2}°$; and let OD be the resultant of both components.

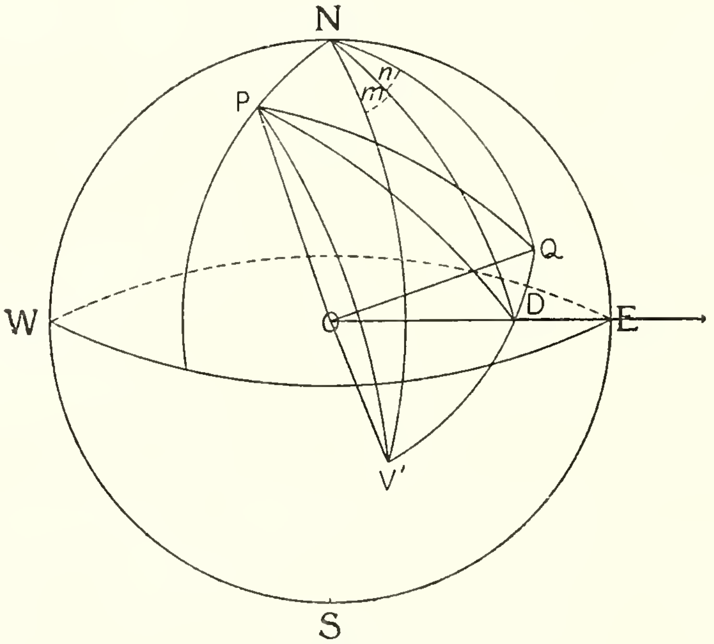

Fig. 7.

Let V' be a point diametrically opposite Vega (V). Then, if θ = time after 6 A.M.,

$$\text{PNV} = (\text{RA Vega} - \text{RA Sun}) + (\tfrac{1}{2}\pi - \theta)$$
$$= 18h - \alpha + \tfrac{1}{2}\pi - \theta = 2\pi - a - \theta,$$

$$\text{PNV}' = \text{PNV} - \pi = (\pi - \theta - a) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(i.)},$$

$$\text{NV} = (\tfrac{1}{2}\pi - 38\tfrac{1}{2}°), \quad \text{NV}' = (\tfrac{1}{2}\pi + 38\tfrac{1}{2}°) \quad . \; . \; . \; . \; . \quad \text{(ii.)},$$

OV' is the direction of drift due to the sun's proper motion, which, as we have said, we shall take as 15 miles/sec., OQ is the direction of drift due to the sun's annual motion, which we take as 19 miles/sec.

We have, therefore,

$$\frac{\sin V'D}{\sin DQ} = \tfrac{19}{15}.$$

Let $V'ND = m$, $DNQ = n$; then

$$\frac{\sin V'D}{\sin NV'} = \frac{\sin m}{\sin V'DN} \quad \text{and} \quad \frac{\sin DQ}{\sin NQ} = \frac{\sin n}{\sin NDQ}.$$

Dividing the first by the second,

$$\tfrac{19}{15}\,\frac{\cos \eta}{\cos 38\tfrac{1}{2}} = \frac{\sin m}{\sin n},$$

or

$$\frac{\cos \eta}{\cdot 618} = \frac{\sin m}{\sin n} = \frac{\sin m}{\sin (m + n - m)}.$$

Now $m + n = V'NQ = (\xi + a - \tfrac{1}{2}\pi)$, therefore

$$\frac{\cos \eta}{\cdot 618} = \frac{\sin m}{\sin (\xi + a - \tfrac{1}{2}\pi - m)} = -\frac{\sin m}{\sin (\xi + a) \sin m + \cos (\xi + a) \cos m},$$

or

$$\sin (\xi + a) + \cos (\xi + a) \cot m = -\frac{\cdot 618}{\cos \eta},$$

whence

$$\cot m = -\frac{\cdot 618}{\cos \eta \cos (\xi + a)} - \tan (\xi + a) \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}.$$

From the triangle NDV'

$$\cos ND \cos m = -\tan 38\tfrac{1}{2} \sin ND - \cot NDV' \sin m.$$

From the triangle NDQ

$$\cos ND \cos n = \tan \eta \sin ND - \cot NDQ \sin n;$$

hence, since $\cot NDV' = -\cot NDQ$,

$$\cos ND (\cos m \sin n + \cos n \sin m)$$
$$= -\sin ND (\tan 38\tfrac{1}{2} \sin n - \tan \eta \sin m),$$

or

$$\cot ND = \frac{\sin m \{\tan \eta - \tan 38\tfrac{1}{2} (\sin n/\sin m)\}}{-\cos (\xi + a)}$$

$$= \frac{\sin m}{\cos (\xi + a) \cos \eta} (\cdot 491 - \sin \eta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv.)}.$$

Now $PND = PNV' + m = (m + \pi - \theta - a)$.

Whence, taking PD = 90°,

$$0 = \cos 38\tfrac{1}{2} \cos \mathrm{ND} + \sin 38\tfrac{1}{2} \sin \mathrm{ND} \cos (m + \pi - \theta - a),$$

so that

$$\cos (\theta + a - m) = \cot 38\tfrac{1}{2} \cot \mathrm{ND} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v.)}.$$

ND is determined by the time of year from equations (iii.) and (iv.), so equation (v.) gives us the value of θ, the hour when the resultant drift is perpendicular to the axis of suspension.

The azimuth of the drift NPD is given by

$$\sin \mathrm{NPD} = \sin (\theta + a - m) \sin \mathrm{ND},$$

which reduces to

$$\cos \mathrm{NPD} = \cos \mathrm{ND} \operatorname{cosec} 38\tfrac{1}{2}^\circ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vi.)}.$$

The Best Conditions when the Drift can never be entirely Horizontal in this Latitude.

We have when PD is any angle

$$\cos \mathrm{PD} = \cos 38\tfrac{1}{2} \cos \mathrm{ND} + \sin 38\tfrac{1}{2} \sin \mathrm{ND} \cos (m + \pi - \theta - a).$$

When PD exceeds 90°, we must choose the time of day so that PD is a minimum. By differentiation we obtain the condition

$$\theta = m + \pi - a.$$

In a similar manner the azimuth of this component (viz., the one at right angles to OP) is given by

$$\sin \mathrm{NPD} = \sin (\theta + a - m) \frac{\sin \mathrm{ND}}{\sin \mathrm{PD}} = 0,$$

so that

$$\mathrm{NPD} = 180^\circ.$$

If $\mathrm{ND} = \frac{1}{2}\pi + 38\frac{1}{2} + \epsilon$; then the component utilised is, of course, given by resultant × $\cos \epsilon$. In the end table the component is given. It is also shown in fig. 9.

If we call the magnitude of the resultant drift R, then

$$\mathrm{R}^2 = 15^2 + 19^2 + 2 \times 15 \times 19 \cos \mathrm{V'Q},$$

so that

$$\mathrm{R} = 34 \cos (\tfrac{1}{2}\mathrm{V'Q}) \text{ approximately.}$$

Now

$$\cos \mathrm{V'Q} = - \sin 38\tfrac{1}{2} \sin \eta + \cos 38\tfrac{1}{2} \cos \eta \cos \mathrm{V'NQ},$$

$$\mathrm{V'NQ} = \mathrm{PNQ} - \mathrm{PNV'} = \xi + \tfrac{1}{2}\pi - \theta - \pi + \theta + a = (\xi + a - \tfrac{1}{2}\pi),$$

$$\cos \mathrm{V'Q} = - \sin 38\tfrac{1}{2} \sin \eta + \cos 38\tfrac{1}{2} \cos \eta \sin (\xi + a),$$

$$\cos \tfrac{1}{2}\mathrm{V'Q} = \sqrt{\tfrac{1}{2}(1 + \cos \mathrm{V'Q})} = \sqrt{\cdot 5 - \cdot 311 \sin \eta + \cdot 391 \cos \eta \sin (\xi + a)}.$$

Therefore

$$\mathrm{R} = 34 \sqrt{\cdot 5 - \cdot 311 \sin \eta + \cdot 391 \cos \eta \sin (\xi + a)} \quad . \quad . \quad . \quad . \quad \text{(vii.)}.$$

The time of day, when the drift is horizontal, is shown by the full line in fig. 8.

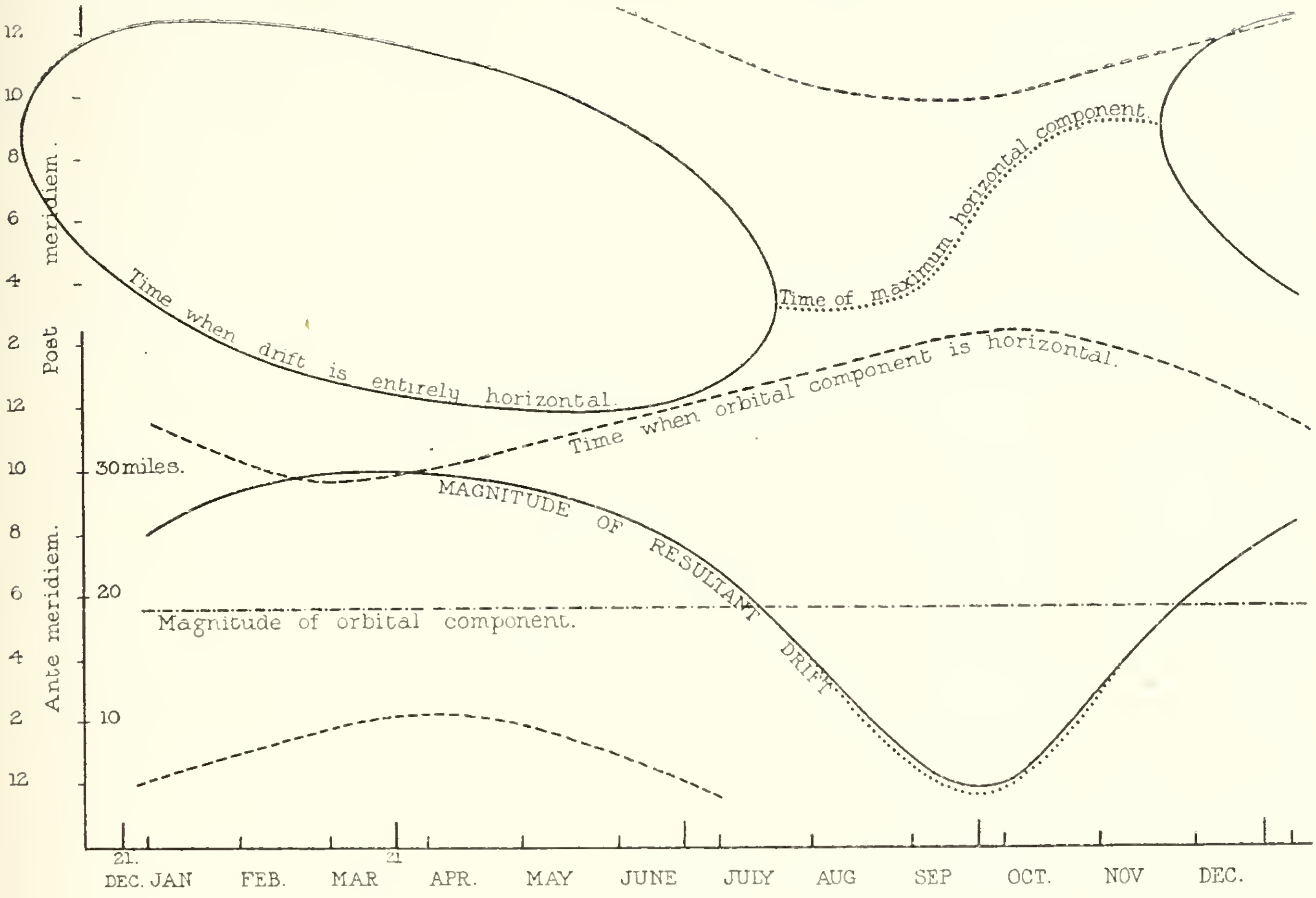

Fig. 8.

The azimuth of the drift is shown by the full line in fig. 9.

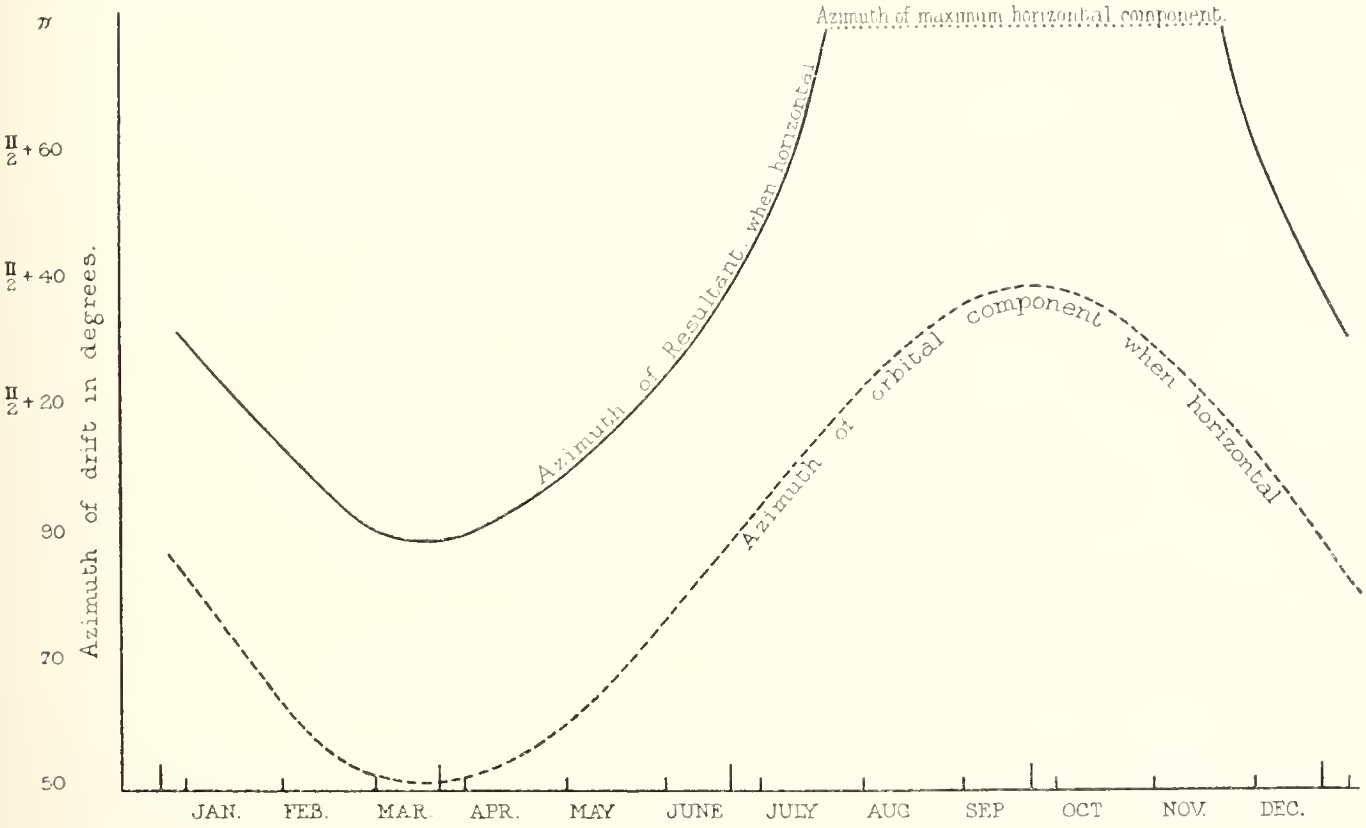

Fig. 9.

The lower curve with full line in fig. 8 shows the corresponding magnitude of the resultant drift.

The following table shows the time of day when the drift is entirely horizontal, and the azimuth of the drift at that hour, for the first day of every month in the year:—

	Orbital motion alone.		Orbital motion and sun's proper motion.		Magnitude.
	Hour of horizontal drift.	Azimuth of drift.	Hour of horizontal drift.	Azimuth of drift.	
					miles per sec.
January 1st . .	11.32 A.M.	+84°	3.31 P.M.	$+(\frac{1}{2}\pi+31^\circ)$	24·9
	12.15 ,,	−84	12.21 A.M.	$-(\frac{1}{2}\pi+31)$	
February ,, . .	10.20 ,,	+65	1.45 P.M.	$+(\frac{1}{2}\pi+14\frac{1}{2})$	27·9
	1.0 ,,	−65	12.13 A.M.	$-(\frac{1}{2}\pi+14\frac{1}{2})$	
March ,, . .	9.46 ,,	+53	12.45 P.M.	$+(\frac{1}{2}\pi+1)$	29·0
	1.48 ,,	−53	12.1 A.M.	$-(\frac{1}{2}\pi+1)$	
April ,, . .	10.2 ,,	+52	12.9 P.M.	$+(\frac{1}{2}\pi+\frac{1}{2})$	29·8
	2.12 ,,	−52	11.29 ,,	$-(\frac{1}{2}\pi+\frac{1}{2})$	
May ,, . .	10.44 ,,	+61	11.50 A.M.	$+(\frac{1}{2}\pi+11\frac{1}{2})$	27·8
	1.54 ,,	−61	10.38 ,,	$-(\frac{1}{2}\pi+11\frac{1}{2})$	
June ,, . .	11.41 ,,	+78	11.47 ,,	$+(\frac{1}{2}\pi+24\frac{1}{2})$	26·2
	12.45 ,,	−78	9.7 ,,	$-(\frac{1}{2}\pi+24\frac{1}{2})$	
July ,, . .	12.13 P.M.	$+(\frac{1}{2}\pi+5)$	12.15 P.M.	$+(\frac{1}{2}\pi+46)$	22·2
	11.46 ,,	$-(\frac{1}{2}\pi+5)$	7.3 ,,	$+(\frac{1}{2}\pi+46)$	
			Best time.	Horizontal component.	
August ,, . .	1.1 P.M.	$+(\frac{1}{2}\pi+23)$	3.2 P.M.	180°	15·3
	10.16 ,,	$-(\frac{1}{2}\pi+23)$			
September ,, . .	1.46 ,,	$+(\frac{1}{2}\pi+36)$	3.28 ,,	180	6·5
	9.46 ,,	$-(\frac{1}{2}\pi+36)$			
October ,, . .	2.15 ,,	$+(\frac{1}{2}\pi+39)$	7.6 ,,	180	4·6
	9.54 ,,	$-(\frac{1}{2}\pi+39)$			
November ,, . .	1.57 ,,	$+(\frac{1}{2}\pi+30)$	8.58 ,,	180	11·8
	10.40 ,,	$-(\frac{1}{2}\pi+30)$			
December ,, . .	12.58 ,,	$+(\frac{1}{2}\pi+14)$	6.25 P.M.	$(\frac{1}{2}\pi+63^\circ)$	19·2
	11.30 ,,	$-(\frac{1}{2}\pi+14)$	10.55 ,,	$-(\frac{1}{2}\pi+63)$	

From August to November the best time denotes the hour of the day when we obtain the maximum horizontal component. The total resultant can never be entirely horizontal during these months.

Measurement of the Capacity of the Condenser.

The capacity was measured absolutely on the apparatus designed by Dr. FLEMING and Mr. CLINTON ('Phil. Mag.,' vol. 29, 1903), and gave the value ·0037 m.f. This value was confirmed by comparison with another known capacity by DE SAUTY'S method.

Measurement of the Controlling Couple.

A piece of brass rod, of length 3·35 centims., and diameter ·97 centim., and weight 20·6 grams, was attached by its centre to the suspending strip with its long axis horizontal. The time of oscillation of this was observed, and gave the value 2 mins. 17·8 secs. The value of the couple per unit twist deduced from the above data is equal to ·0426 C.G.S.

Calculation of $N\left(\frac{u}{v}\right)^2$.

Capacity of condenser ·0037 m.f.

Couple per unit twist of wire ·0426 C.G.S.

Potential difference = 2000 volts = $\frac{20}{3}$ electrostatic units.

Electrostatic energy $= \frac{1}{2}\,\frac{\cdot 0037 \times v^2}{10^{15}}\left(\frac{20}{3}\right)^2$.

The distance of the sun from the earth is $1{\cdot}50 \times 10^{13}$ centims., so that

$$u = \frac{2\pi \times 1{\cdot}50 \times 10^{13}}{365 \times 24 \times 60 \times 60}\,\frac{\text{centim.}}{\text{sec.}} = 3 \times 10^6\,\frac{\text{centim.}}{\text{sec.}}.$$

Taking v (velocity of propagation) as 3×10^{10}, we have $(u/v)^2 = 10^{-8}$.

The couple due to the drift when the condenser is in its best position is $N \,.\, 10^{-8}$.

Let d be scale deflection at distance of 1 metre; then angular deflection is $\frac{1}{2}\,.\,\frac{d}{100}$.

Equating the balancing couples,

$$\cdot 043 \times \frac{d}{200} = 10^{-8}\,\frac{1}{2}\left(\frac{\cdot 0037 \times v^2}{10^{15}}\right)\left(\frac{20}{3}\right)^2,$$

so that d is 3·4 centims. That is to say, neglecting the proper motion of the sun, and under the best conditions, when charged to a potential of 2000 volts the deflection of the condenser should amount to 3·4 centims.

Observations.

In order to be sure that the condenser was not held in any position, it was set oscillating uncharged and readings were taken every quarter of a minute; giving the curve (fig. 10).

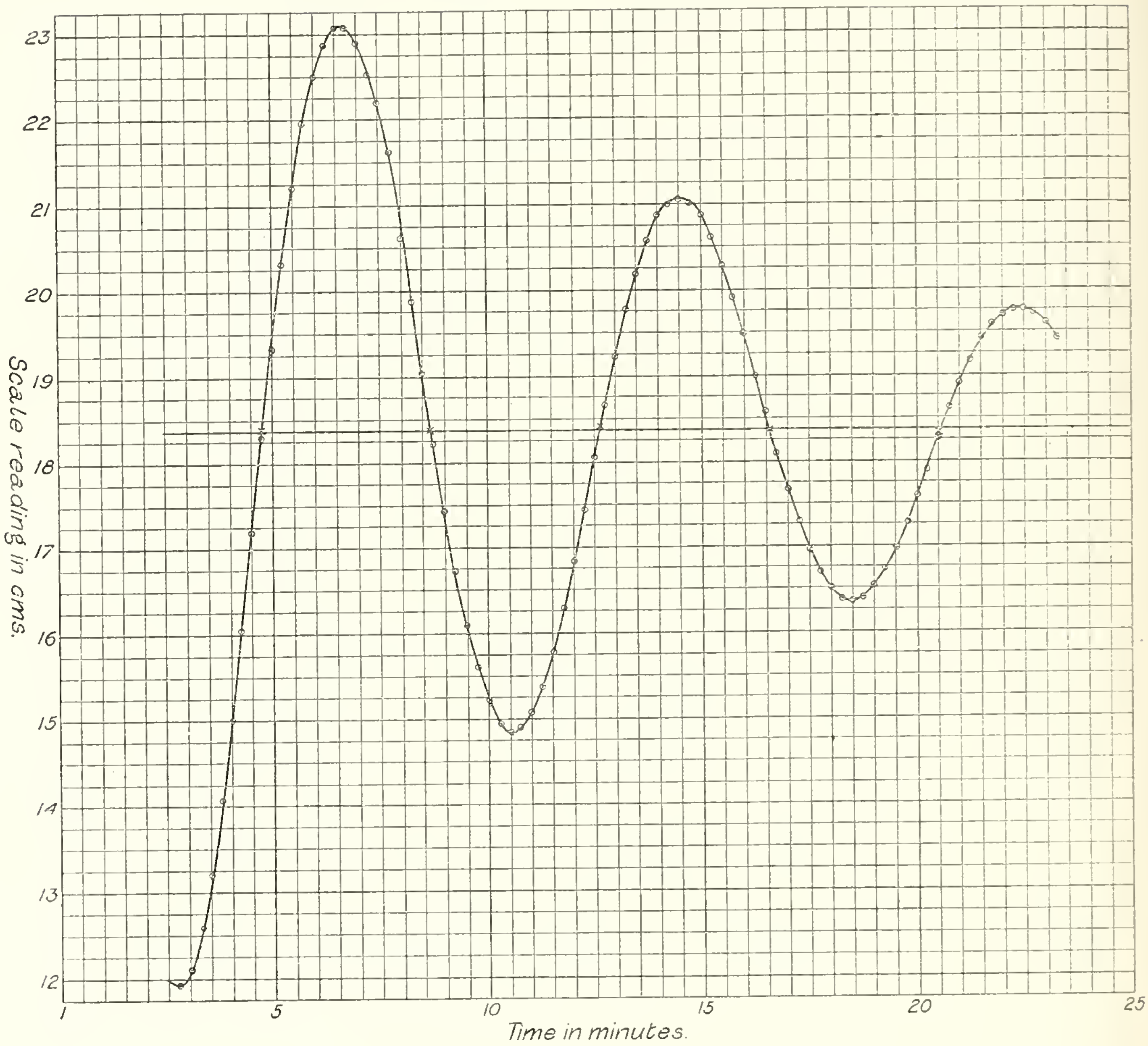

Fig. 10.

Analysis of the Curve.

Readings of extremes	Left . .		23·10		21·05		19·75
	Right .	11·99		14·85		16·37	

Amplitudes :—	Ratios :—	Amplitude × $\frac{1\cdot35}{2\cdot35}$:—
11·11		6·38
8·25	1·35	4·74
6·20	1·33	3·56
4·68	1·33	2·69
3·38	1·38	1·94
	Mean . . . 1·35	

11·99 + 6·38 = 18·37 = zero of 1st vibration.
23·10 − 4·74 = 18·36 = ,, 2nd ,,
14·85 + 3·56 = 18·41 = ,, 3rd ,,
21·05 − 2·69 = 18·36 = ,, 4th ,,
16·37 + 1·94 = 18·31 = ,, 5th ,,

Mean . . 18·36, which is mean zero.

Any irregularity would have shown itself in a corresponding change of zero as calculated from the decrement and the amplitude of any particular swing. The variations in zero do not amount to more than ·05 centim.

Observation of the Effect.

The following observation is appended as being typical :—

March 10, 1903. Time 11.45 to 12.15 mid-day.

Before Charging.

Left.	Right.	Mean.	
62·22	62·35	62·29	Zero 62·29.

Charged to 2100 *volts at pt.* 62·30.

Left.	Right.		
61·69	62·09	61·89	
61·79	61·93	61·86	
61·76	61·84	61·80	
	Mean . . .	61·85	Deflected 61·85.

Discharged at pt. 61·84.

61·80	62·35	62·08	
61·98	62·22	62·10	
	Mean . . .	62·09	Final zero.

Initial zero	62·29
Final zero	62·09
Mean zero . . .	62·19
Reading of deflection .	61·85
Deflection . . .	− ·34 centim.

The following table gives the final results obtained. These were observations taken after many months of experience with the apparatus, and were considered by us as conclusive against there being any such effect as we were seeking.

AZIMUTH of Condenser + 45°.

Date.	Time.	Potential in volts.	Deflection calculated (annual motion).	Deflection calculated (annual + proper).	Deflection observed.
			centims.	centims.	centims.
March 9 . . .	12.15 P.M.	2100	−2·6	−6·8	−0·35
,, 9 . . .	6 P.M.	2100	+0·8	0·0	−0·12
,, 10 . . .	12 (day)	2100	−2·6	−6·8	−0·34
,, 10 . . .	3 P.M.	2100	−1·2	−3·4	−0·23
,, 10 . . .	6 P.M.	2100	+0·8	0·0	−0·26
,, 12 . . .	12 (day)	2100	−2·6	−6·8	−0·36
,, 12 . . .	3 P.M.	2100	−1·2	−3·4	−0·25
,, 12 . . .	6 P.M.	2100	+0·8	0·0	−0·32
,, 13 . . .	5.30 P.M.	2100	+0·8	0·0	−0·34
,, 13 . . .	6.30 P.M.	2100	+0·8	0·0	−0·18
,, 18 . . .	3 P.M.	2000	−1·2	−3·4	−0·02

The largest observed deflection, ·36 centim., barely exceeds 5 per cent. of the calculated deflection, 6·8 centims.

The following observations, taken between March 13 and March 18, illustrate the behaviour of the apparatus as regards electrostatic effects. These justify the conclusion that the effect observed was the result of residual electrostatic action,* and could in no way be attributed to the relative motion of the earth and the æther.

The sign of the charges was reversed at times.

The insulation was good.

Date.	Potential.	Sign of suspension.	Deflection.
March 13	1100	negative	+0·05
	1100	positive	−0·01
,, 18	1100	,,	slight +
	1100	negative	+0·01
	1500	,,	+0·04
	1500	positive	+0·16
	1500	,,	+0·13
	1500	negative	+0·24
	1500	,,	+0·14
	1500	positive	−0·09

* It might be thought, at first sight, that the magnetic field produced by the moving condenser might interact with the earth's magnetic field; that no such action exists has been shown by FITZGERALD ('Scientific Papers,' p. 111). We are therefore justified in concluding that the residual action did not arise from disturbances due to the earth's magnetic field.

All the above observations were taken during the middle of the day and the afternoon.

There seems to be no change of deflection with change of sign, and by comparison with previous results there seems to be no bias one way or the other.

From experience gained with the apparatus, the deflections observed would appear to be attributable to small sparks or discharges taking place inside or over the condenser, causing slight heating and consequent perturbation of the surrounding air. This is further suggested by the fact that when the condenser employed had become damaged by falls and other vicissitudes, so that audible sparkings occurred, the perturbations became so great as to prevent all possibility of observation.

There is no doubt that the result is a purely negative one. As the energy of the magnetic field, if it exists (and from our present point of view we must suppose it does), must come from somewhere, we are driven to the conclusion that the electrostatic energy of a charged condenser must diminish by the amount N $(u/v)^2$, when moving with a velocity u at right angles to its electrostatic lines of force, where N is the electrostatic energy.

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THE SPECTRA OF NEON, KRYPTON AND XENON

BY

E. C. C. BALY,
LECTURER ON SPECTROSCOPY IN UNIVERSITY COLLEGE, LONDON.

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VI. *The Spectra of Neon, Krypton and Xenon.*

By E. C. C. Baly, *Lecturer on Spectroscopy in University College, London.*

Communicated by Sir William Ramsay, *K.C.B., F.R.S.*

Received June 12,—Read June 18, 1903.

Soon after the discovery of the new gases, neon, krypton and xenon, by Sir William Ramsay and Dr. Travers, in 1898, measurements were made of the lines of their emission spectra by means of a large prism spectrograph in University College. In view of the fact that a large Rowland grating apparatus was at that time in process of erection, it did not appear worth while to publish this first series of measurements, as I was in hopes of being able to obtain with the help of the grating far more accurate results than was possible from measurements of the photographs taken with the prism apparatus. Since the commencement of this work three series of measurements have been published, one by Runge[*] of certain lines in the krypton spectra, and two by Liveing and Dewar of the lines in the spectra of the light[†] and heavy[‡] constituents of atmospheric air respectively. All these measurements contain only the principal lines and, moreover, extend only a short distance into the ultra-violet region. Liveing and Dewar's measurements also are only given to the nearest Ångström unit. The publication of these tables of wave-lengths emphasised still more strongly in my mind the necessity for making the measurements with as high a degree of accuracy as possible, for the chief value of tables of such constants beyond the purpose of simple qualitative work, is to be found in their reliability, especially at the present time when so much work is being done upon spectral series. It is difficult to assess the accuracy which may be claimed for the measurements given below, but, judging from the values obtained for certain lines common to the spectra, the probable error may be estimated to be less than ± 0·03 Ångström unit. The specimens of the gases used were not spectroscopically pure, the neon contained traces of helium, while the krypton and xenon contained very small traces of argon; the more important spectrum lines of these impurities were generally to be found upon the photographs and were measured in due course; the wave-lengths found

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[*] 'Astrophys. Journ.,' vol. 10, p. 73, 1899.

[†] 'Roy. Soc. Proc.,' vol. 67, p. 467, 1900.

[‡] 'Roy. Soc. Proc.,' vol. 68, p. 389, 1901.

showed an extremely satisfactory agreement with RUNGE and PASCHEN's or KAYSER's determinations.

In apology for the length of time taken over the work I must urge certain unavoidable delays, of which the chief ones were due to the long exposures necessary to obtain the weaker lines and the short lives of the vacuum tubes employed; as will be explained below, these tubes will not withstand the long continued action of the electric discharge and therefore they require to be frequently refilled. One of the greatest delays arose from the fact that at one time the whole supply of xenon was used up and it became necessary to prepare a further quantity to finish this work. I take this opportunity of thanking Sir WILLIAM RAMSAY for his great kindness in undertaking this for me.

The Rowland grating has a focal length of 10 feet and is ruled with 14,438 lines to the inch; all the measurements were made in the second and third orders, with the exception of certain lines in the red region which were measured in the first order. The spectra were photographed upon LUMIÈRE's plates, the extra rapid and the A and B isochromatic series being used for the blue, green and red regions respectively. These plates possess a great advantage over other makes which were tried in that they give extremely well defined and fine grained images.

In every case the gases were illuminated by the passage of the electric discharge through them when under reduced pressure, and several forms of vacuum tubes were employed, in all of which a capillary portion was viewed "end on" through a quartz window, which was cemented on with sealing-wax or CHATTERTON's compound, neither of which give off any vapour when cold. The most satisfactory results were obtained by sealing the electrodes into side tubes on account of the peculiar action of these monatomic gases when subjected, under reduced pressure, to an electric discharge between electrodes. The latter become very hot and, unless special care has been taken in their manufacture, they rapidly disintegrate; it is therefore preferable to have them hanging down in a vertical position to guard against any possibility of their melting and falling against the glass walls of the vacuum tube. This heating of the electrodes is very noticeable under ordinary circumstances when such metals as platinum are used, but in the case of the new gases the effect is much more pronounced, for even stout aluminium wire is readily melted by a moderately strong discharge. In making the electrodes it has been found necessary to use aluminium wire of at least No. 12 B.W.G., and to carefully guard against there being any soda glass sealed to the platinum. As usually made, an electrode possesses a sheath of ordinary glass in order to protect the junction between the platinum and the aluminium, this sheath being melted on to the platinum close to the aluminium. This, however, invariably breaks when used for any of the new gases. The best way to make an electrode is as follows: some very stout aluminium wire is taken and a small hole drilled in one end into which the platinum wire is fixed. A capillary tube is made of some blue enamel glass, having a bore just sufficiently large to admit the platinum wire; this capillary tube is then joined to a piece of ordinary glass tubing which is able to slip easily over the aluminium wire. In this way a covering is made into which the electrode is placed and then the blue enamel capillary is melted on to the platinum wire, but this must not be done within half-an-inch of the platinum aluminium junction. The glass sheathing over the aluminium is cut to a convenient length and the electrode is finished off and sealed into the vacuum tube in the usual way.

The extraordinary heating of the electrodes forms a source of annoyance in working with these gases on account of the great quantity of hydrogen evolved from them. It is well known that in the process of filling a vacuum tube with any of the ordinary gases a considerable quantity of hydrogen is evolved from the electrodes, which very often masks the spectrum of the gas to be experimented with. This hydrogen can readily enough be removed by continued exhaustion while the electric discharge is passing, and, if necessary, by washing the tube out with a small quantity of the gas in question. When this has been efficiently carried out entire freedom from contamination by hydrogen is secured under ordinary circumstances. If now into a vacuum tube, which has been carefully treated in this way, a small amount of one of the new monatomic gases be introduced, a further great quantity of hydrogen will be given up by the electrodes, and it is absolutely necessary that this be removed, as otherwise the spectrum of the new gas will be entirely masked by the hydrogen spectrum. This hydrogen can only be removed by alternately exhausting and admitting small quantities of one of the monatomic gases, this being done until the spectrum lines of hydrogen begin to weaken; three or four repetitions of this with argon are generally sufficient, provided that the electrodes are not very stout. The first time a vacuum tube is filled, naturally the greatest trouble in removing the hydrogen is to be met with, although similar precautions must be taken whenever a tube is refilled.

A curious effect is to be noticed in the splashing or volatilization of the aluminium electrodes with these gases. This is common enough with platinum and similar electrodes and has been termed by Sir WILLIAM CROOKES electrical evaporation; as far as I am aware this has not been previously noticed with aluminium electrodes. It is this phenomenon which shortens the lives of the vacuum tubes containing these gases, both on account of the disintegration of the electrodes themselves and also on account of the slow absorption of the gas by the aluminium mirror deposited upon the walls of the tube immediately surrounding the electrode. This absorption of the gas when the tube is in continual use necessitates frequent refilling, especially because these gases must be illuminated under very reduced pressures, as will be presently explained.

As regards the spectra of the gases, they all consist of bright well-defined lines similar to those of argon and helium. The most striking is the spectrum of neon, which consists almost entirely of very bright lines in the orange and red regions; the colour of the electric discharge through the gas is a magnificent orange. When a

Leyden jar and a spark gap are placed in the circuit no decided change takes place in either the appearance or the spectrum of the discharge. Krypton and xenon, on the other hand, resemble argon in this respect that they both possess two spectra, one being obtained when the direct discharge is passed and the other when a Leyden jar and spark gap are placed in the circuit. The jar and spark-gap spectrum, or the second spectrum as I have called it in the tables below, is very much more complex than the first spectrum, wherein an analogy is to be found with the two spectra of argon. When the discharge is passed through krypton without the use of a jar the spectrum obtained consists of a few lines, by far the most important being the yellow and green lines and also a group in the blue. As these lines have about the same visual intensity, the colour of the discharge is rather nondescript and appears to be different to different observers. The jar and spark discharge, on the other hand, presents a fine sky-blue colour and its spectrum contains a considerable number of lines chiefly in the blue. The simple discharge through xenon is not very brilliant and is bluish in colour, being characterised by a group of blue lines less refrangible than the group in the first krypton spectrum. The second xenon spectrum is even more complex than the second krypton spectrum ; it is characterised by certain bright green lines which determine the colour of the discharge.

The time of exposure necessary for photographing the spectra depended of course upon the brightness of the discharge ; while in the case of the second xenon spectrum an exposure of two to three hours was sufficient, the lines of the first spectrum were so weak that an exposure of twenty-four hours was often required. The wave-lengths of the lines were all determined by interpolation between the lines of the arc spectrum of iron, and the wave-lengths of the principal lines in this spectrum as determined by KAYSER were adopted as standards. Many photographs were taken of the two spectra superposed upon one another, care being taken that they were both correctly placed in relation to each other. The wave-lengths of as many lines as possible were determined in this way from several plates, and the mean values of these were employed as standards in the measurements of several series of photographs taken of the new spectrum alone. In this way the wave-lengths of the fainter lines were obtained and also a certain amount of check was applied to the measurements of the standards themselves. Excepting a few lines in the red region and the fainter lines, nearly every line was measured in two orders, which ensures a correct relation between the different regions of the spectrum.

It was stated above that the spectra of the new gases are composed of bright and well defined lines ; it will be seen, however, from the tables, that certain lines are marked as being diffused, which may appear at first sight to be rather contradictory. The explanation is to be found in the fact that the distinctness of the spectrum and the definition of the lines depend to a great extent upon the pressure of the gas in the vacuum tube. If this pressure exceeds a certain small amount, the whole appearance of the spectrum is altered, for it tends to become confused, and at times indeed almost continuous. If the pressure is slowly reduced, the lines begin to appear upon a more or less continuous background, and, gradually increasing in brightness, they finally become quite sharply defined upon a black background. This effect is especially noticeable in the spectra of krypton and xenon, and in filling vacuum tubes with these gases, great care must be taken to reduce the pressure sufficiently in order to obtain good definition. When a tube has been completely exhausted according to the method described above, the connection to the exhaust pump is closed and a quantity of the gas in question, known to be in excess of that required, is admitted. The electric current is then made to pass through the gas, and the spectrum is examined through a small spectroscope; the stop-cock connecting the vacuum tube to the exhaust pump is then opened and the pressure of the gas slowly reduced until the spectrum lines appear perfectly sharp, when the tube is sealed off. All the spectrum lines do not become equally well defined at once, and the lines given in the tables as diffused are those which still remain somewhat nebulous at the pressures dealt with; these outstanding hazy lines, however, if the pressure is sufficiently reduced, tend to improve in definition, although some of them only become sharp when the pressure has been so far reduced as to very materially lessen the illumination. Since the absorption of the gases by the electrodes themselves and by the volatilized aluminium appears to be more rapid at low pressures, the necessarily low initial pressure renders imperative the frequent filling of the tubes.

In the tables given below there is a column containing the wave-lengths which have already been published by RUNGE for krypton, and by LIVEING and DEWAR for all the gases. RUNGE was unaware of the existence of xenon, and therefore certain lines belonging to the spectrum of this gas are to be found in his list of krypton lines. Another column headed "Remarks" includes memoranda concerning the individual lines, and certain points in connection with these merit some attention.

In the first place, under the second krypton spectrum, there will be found certain lines which are visible in the second or blue argon spectrum; it is interesting to note further that these lines disappear from the spectrum of argon after that gas has been fractionated by means of liquid air. In view of the discovery of these new gases in the atmosphere I made a comparison, with a glass prism spectroscope of considerable dispersion, between the blue spectra of ordinary atmospheric argon and of the same gas after fractionation by means of liquid air.* Both the spectra were completely measured, but the list of wave-lengths is not worth publishing in its entirety on account of the very slightly different values found from those already given by KAYSER and by EDER and VALENTA; certain lines however were measured which do not appear in these lists, and they are given in Table I. In Table II. are given the wave-lengths of the lines which are removed from the spectrum of argon by the process of fractionation. Three of these lines at $\lambda = 4488{\cdot}14$, $4199{\cdot}97$ and $4047{\cdot}38$

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* I take this opportunity of expressing my thanks to Messrs. W. L. ST. J. ALTON and A. C. CARTER for their valuable help in this investigation.

have not been measured before; the remainder must be deleted from KAYSER's and EDER and VALENTA's lists.

Out of the 16 lines in Table II., three apparently belong to the second krypton spectrum, but the origin of the others could not be traced; they undoubtedly are present in unfractionated argon, and are removed by fractionation. It is curious that only three of the weakest krypton lines should be visible in the argon spectra; a careful search was made for the stronger lines, but no trace of them could be detected.

The first or red spectra of the two samples of argon were similarly investigated, but no difference whatever could be found, nor were any new lines observed beyond those already known.

TABLE I.—Additional Lines Measured in the Blue Spectrum of Argon.

Wave-length.	Intensity.	Wave-length.	Intensity.
4537·82	3	4198·40	2
4510·07	1	4169·08	1
4445·92	1	4130·68	1
4440·40	1	4127·56	1
4405·06	1	4127·22	1
4385·16	2	4116·50	3
4338·40	1	4031·50	1
4217·50	1		

TABLE II.—Lines to be Omitted from the Blue Spectrum of Argon.

Wave-length.	Intensity.	Wave-length.	Intensity.
4488·14	2	4098·33	1
4443·545	1	4089·041	1
4408·095	1	4065·171	1
4343·904	1	4047·38	1
4229·015	1	4023·730	3
4199·97	1	4017·986	1
4183·106	2	4010·052	1
4146·761	1	3960·591	2

A further interesting fact in connection with the second spectra of krypton and xenon, is to be found in the existence of a number of lines of weak intensity common to the two spectra. Since these lines are equally weak in both spectra, it is impossible to say whether they in reality belong to krypton or xenon, and I have therefore credited them to both. On the other hand it may be that they are due to some common impurity, possibly a still heavier element of the same family; the evidence of the periodic table of elements is against this, but of course such evidence cannot be considered to be conclusive, and we may perhaps look forward to the discovery of such an element at a not very distant date. Experiments are at present being carried out in this direction.

The wave-lengths of these lines are given in Table III., the values obtained in both gases being given.

TABLE III.—Lines Common to the Second Spectra of Krypton and Xenon.

Wave-lengths.		Intensity.	Wave-lengths.		Intensity.
In krypton.	In xenon.		In krypton.	In xenon.	
5562·45	5562·46	2	2844·59	2844·60	3
5143·25	5143·24	1	2941·10	2941·10	1
4857·36	4857·37	1	2811·81	2811·81	3
3942·28	3942·29	1	2756·66	2756·64	1
3768·10	3768·08	1	2733·38	2733·36	4
3765·98	3765·99	4	2732·46	2732·48	1
		(much weaker	2696·71	2696·73	4
		in krypton)	2691·94	2691·92	1
3751·81	3751·80	1	2690·35	2690·33	1
3564·38	3564·40	4	2670·78	2670·80	2
3428·95	3428·95	1	2648·80	2648·79	1
3396·72	3396·72	2	2624·63	2624·65	1
3387·26	3387·26	1	2616·80	2616·79	1
3379·18	3379·20	2	2581·84	2581·84	1
3360·22	3360·20	2	2572·44	2572·46	2
3315·80	3315·80	1	2513·50	2513·52	1
3222·40	3222·40	1	2494·10	2494·11	3
3175·78	3175·80	3	2468·56	2468·54	2
3044·93	3044·91	2	2425·15	2425·18	2
2960·92	2960·93	2			

In addition to the above, there remains what is probably only a chance coincidence at $\lambda = 4577·36$ and $\lambda = 4577·40$ in the xenon and krypton spectra respectively; mention should also be made of the bright lines at $\lambda = 3330·90$ and $\lambda = 3330·88$ in the two spectra.

As regards LIVEING and DEWAR's values for the wave-lengths of these gases, it will be seen from the tables that there is in general a complete agreement in the fourth significant figure between the two sets of measurements. A great number of lines which do not appear in LIVEING and DEWAR's lists have been measured; this is only to be expected from the fact that these observers in all probability were not dealing with perfectly pure gases. The relative intensities of the lines are about the same in the two series of measurements, but of course the general average of intensity in LIVEING and DEWAR's measurements is the weaker. These observers give in their tables of the krypton and xenon spectra a few lines which do not appear on any of my plates, and which therefore it is probable do not belong to these spectra. LIVEING and DEWAR's list of the wave-lengths of the lines in the spectra of the most volatile constituents of the atmosphere contains 162 lines, which, as far as I can judge, do not belong to neon. The neon used for this work was undoubtedly perfectly pure, and as the lines measured both by LIVEING and DEWAR and by myself are generally very much brighter on my plates, and as further I have observed a number of lines not observed by LIVEING and DEWAR, the only conclusion to be drawn is that the outstanding lines in the latter case are not due to neon.

TABLE IV.—Neon Spectrum.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
6717 ·20	1		6716, L. & D.	6189 ·30	1		
6599 ·16	4		6601, L. & D.	6182 ·37	10		6183, L. & D.
6533 ·10	4		6535, L. & D.	6179 ·90	1		
6506 ·72	6		6508, L. & D.	6175 ·15	2		6176, L. & D.
6444 ·90	1		6446, L. & D.	6173 ·02	1		
6409 ·90	1			6166 ·81	1		
6402 ·40	10		6404, L. & D.	6163 ·79	10		6163, L. & D.
6401 ·26	1			6157 ·12	1		
6383·15	8		6382, L. & D.	6150 ·49	1		
6352 ·04	1			6143 ·28	10		6144, L. & D.
6331 ·13	1			6128 ·63	8		6128, L. & D.
6328 ·38	6		6334, L. & D.	6118 ·22	2		
6313 ·94	1			6096 ·37	10		6097, L. & D.
6304 ·99	8		6304, L. & D.	6074 ·52	10		6075, L. & D.
6294 ·04	1			6064 ·36	1		
6273 ·26	1			6046 ·06	1		
6266 ·66	10		6266, L. & D.	6043 ·24	1		
6259 ·06	1			6032 ·32	2		6031, L. & D.
6247 ·00	1		? 6244, L. & D.	6030 ·20	10		
6217 ·50	8		6217, L. & D.	6026 ·03	1		
6214 ·13	2			6024 ·40	1		
6206 ·01	1			6001 ·00	1		6001, L. & D.
6199 ·34	1			5991 ·72	2		5991, L. & D.

TABLE IV.—Neon Spectrum—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
5988 ·00	4		5987, L. & D.	4710 ·21	2		
5981 ·94	1			4709 ·00	4		4710, L. & D.
5975 ·78	8		5976, L. & D.	4704 ·56	4		4704, L. & D.
5974 ·73	6			4540 ·48	1		4540, L. & D.
5965 ·50	4		5964, L. & D.	4537 ·39	1		4538, L. & D.
5961 ·64	1			4510 ·86	1		
5949 ·51	1			4459 ·68	1		4460, L. & D.
5944 ·91	10		5945, L. & D.	4431 ·14	1		4431, L. & D.
5939 ·44	1			4430 ·33	1		4429, L. & D.
5919 ·08	1		5919, L. & D.	4426 ·15	2		
5913 ·82	1		5914, L. & D.	4425 ·57	1		
5906 ·54	2		5905, L. & D.	4424 ·98	2		4424, L. & D.
5902 ·57	4			4422 ·69	2		4422, L. & D.
5882 ·04	8		5882, L. & D.	4414 ·44	1		4413, L. & D.
5873 ·04	1			4259 ·53	6		4258, L. & D.
5852 ·65	20	Extraordinarily brilliant	5852 ·7, L. & D.	4201 ·03	4		
5820 ·29	4		5820, L. & D.	4198 ·71	4		4198, L. & D.
5804 ·57	1		5804, L. & D.	4191 ·44	2		
5764 ·54	8		5763, L. & D.	4190 ·86	2		
5764 ·20	1			4182 ·00	2		
5760 ·72	1			4158 ·68	4		
5748 ·44	4		5747, L. & D.	3899 ·21	1		3900, L. & D.
5719 ·42	1		5718, L. & D.	3886 ·26	1		

5689·96	2	5689, L. & D.	
5662·76	1	5662, L. & D.	
5656·80	4	5656, L. & D.	
5652·67	1		
5562·96	2	5561, L. & D.	
5433·86	1	5432, L. & D.	
5400·77	4	5400, L. & D.	A pair.
5400·50	4		
5343·41	1	5341, L. & D.	A pair.
5341·25	4		
5332·33	4	5330, L. & D.	
5278·50	1		
5271·50	1		
5218·30	1		
5204·12	1	5204, L. & D.	
5188·79	1	5188, L. & D.	
5145·15	1	5145, L. & D.	
5116·72	1	5116, L. & D.	
5080·54	1	5080, L. & D.	
5037·95	1	5038, L. & D.	Strong line.
4837·54	1	4838, L. & D.	
4806·24	1		
4789·07	1	4791, L. & D.	
4752·88	1	4754, L. & D.	
4715·49	4	4715, L. & D.	
4713·51	2		
4712·23	2		

3879·49	1	
3754·31	2	3754, L. & D.
3701·30	6	3701, L. & D.
3685·84	4	3686, L. & D.
3682·33	4	3683, L. & D.
3633·78	6	3634, L. & D.
3609·27	2	3609, L. & D.
3606·61	1	
3600·24	4	3600, L. & D.
3593·67	10	3593, L. & D.
3588·60	1	
3587·52	1	3587·5, a pair, L. & D.
3587·24	1	
3586·62	1	
3567·73	1	
3554·39	1	
3532·30	1	
3529·95	1	
3522·92	1	
3520·57	8	3521, L. & D.
3515·30	6	3515, L. & D.
3510·87	2	3510, L. & D.
3501·34	6	3500, L. & D.
3498·19	6	3498, L. & D.
3481·94	1	3481, L. & D.
3472·70	8	3473, L. & D.
3466·72	6	3467, L. & D.

TABLE IV.—Neon Spectrum—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
3464·48	6		3464, L. & D.	3375·72	1		3374? L. & D.
3460·67	6		3460, L. & D	3370·01	6		3370, L. & D.
3454·30	6		3454, L. & D.	3148·76	1		
3450·87	4		3451, L. & D.	3126·33	1		
3447·83	8		3447·7, ? He, L. & D.	3092·84	1		
3438·66	1			3080·05	1		
3424·05	2		3424, L. & D.	3077·08	1		
3418·05	8		3418, L. & D.	3057·50	1		

TABLE V.—First Krypton Spectrum, without Leyden Jar and Spark Gap.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
6456·65	1		6458, L. & D. Intensity 1.	4792·80	1		
6421·32	1		6420, L. & D. Intensity 4.	4734·32	4		
6236·61	1			4697·17	4		
6223·00	1			4691·12	2		
6083·08	1		6082, L. & D. Intensity 1.	4671·40	10		4671·42, RUNGE. Intensity 2.
6075·50	1			4624·48	10		4624·46, RUNGE. Intensity 1.
6056·32	2		6056, L. & D. Intensity 2.				
6012·34	1		6011, L. & D. Intensity 2.	4612·07	1		

5994·02	2	. . . .	5992, L. & D. Intensity 3.
5880·06	1		
5871·12	10	Visible in second krypton spectrum . .	5871·071, RUNGE. Intensity 8. 5871, L. & D. Intensity 10.
5866·94	1		
5832·94	1		
5827·28	1		
5756·96	1		
5718·59	1		
5701·06	2		
5695·58	1		
5660·37	3		
5649·85	1		
5580·64	1	Equal intensity in second krypton spectrum.	
5570·50	10	Visible in second krypton spectrum, probably the green aurora line.	5570·417, RUNGE. Intensity 8. 5571, L. & D. Intensity 10.
5562·45	6	Visible in second krypton spectrum . .	5562·363, RUNGE. 5563, L. & D. Intensity 3.
5520·74	1	Equal intensity in second krypton spectrum.	
5519·61	4		
5500·90	1		
5498·24	3		
5491·11	1		
5475·49	2		
5423·44	1	. . . .	? 5424, L. & D. Intensity 1.
4829·90	3		
4807·22	4		
4582·90	4	. . . .	4583, L. & D. Intensity 4.
4524·82	4		
4502·56	9	Visible in second krypton spectrum . .	4502·43, RUNGE. Intensity 4. ? 4505, L. & D. Intensity 2.
4501·13	7		
4463·88	10	Visible in second krypton spectrum . .	4463·82, RUNGE. Intensity 5. 4464, L. & D. Intensity 3.
4454·12	10	Visible in second krypton spectrum. .	4454·07, RUNGE. Intensity 4. 4454, L. & D. Intensity 1.
4425·32	1		
4418·89	1		
4410·49	1		
4400·11	6	. . . .	4400·05, RUNGE. Intensity 1. 4400, L. & D. Intensity 1.
4385·87	1		
4384·01	1		
4376·33	10	Visible in second krypton spectrum . .	4376·24, RUNGE. Intensity 3. 4376, L. & D. Intensity 3.
4364·58	1		
4362·83	9	Visible in second krypton spectrum. .	4362·76, RUNGE. Intensity 2. 4363, L. & D. Intensity 2.
4358·43	1		
4355·67	1	Second krypton spectrum	4355·62, RUNGE. Intensity 5. 4356, L. & D. Intensity 12.
4351·48	3		
4319·76	10	Visible in second krypton spectrum. .	4319·760, RUNGE. Intensity 4. 4320, L. & D. Intensity 8.

TABLE V.—First Krypton Spectrum, without Leyden Jar and Spark Gap—(continued).

Wave-length.	Intensity.	Remarks.	Other observers.
4318·74	8	Visible in second krypton spectrum.	4318·70, RUNGE. Intensity 2. 4319, L. & D. Intensity 3.
4300·67	1	Second krypton spectrum	4301, L. & D. Intensity 7.
4286·64	1		
4283·17	4	Visible in second krypton spectrum.	4283, L. & D. Intensity 3.
4274·15	10	Visible in second krypton spectrum.	4274·09, RUNGE. Intensity 4. 4274, L. & D. Intensity 4.
4046·60	1		
3800·71	2		
3797·05	1		
3773·59	3		
3679·58	4		
3668·74	2	Equal intensity in second krypton spectrum	
3665·43	3		
3650·21	2		
3615·57	2		
3522·79	1		
3502·69	2		

TABLE VI.—Second Krypton Spectrum, with Leyden Jar and Spark Gap.

Wave-length.	Intensity.	Remarks.	Other observers.
5871·12	1	First krypton spectrum	5871, L. & D. Intensity 10.
5771·60	1		5771, L. & D. Intensity 2.
5753·19	1		5753, L. & D. Intensity 2.
5690·56	3		5690, L. & D. Intensity 5.
5682·15	5		5682, L. & D. Intensity 5.
5674·70	1		
5672·94	1		
5229·67	1		5229, L. & D. Intensity 1.
5224·72	1		
5217·59	1		5218, L. & D. Intensity 1. 5215, L. & D. Not seen.
5208·50	3		5208·57, RUNGE. 5209, L. & D. Intensity 5.
5200·36	1		5203, L. & D. Intensity 1.
5187·17	1		5186, L. & D. Intensity 1.

5650·56	1	. . . .	5650, L. & D. Intensity 1.
5649·76	1	. . . .	
5633·17	6	. . . .	5632, L. & D. Intensity 2.
5597·47	1		
5580·64	1	Equal intensity in first krypton spectrum.	
5570·50	3	First krypton spectrum	5570·417, Runge. 5571, L. & D. Intensity 10.
5568·84	2		
5562·45	2	First krypton spectrum	5562·363, Runge. 5563, L. & D. Intensity 3.
5553·15	1	Diffused	5553, L. & D. Intensity 1. 5544, L. & D. Not seen.
5523·75	1	. . . .	5523, L. & D. Intensity 2.
5523·13	2	. . . .	
5520·74	1	Equal intensity in first krypton spectrum.	
			5506, L. & D. Not seen.
5499·73	1	. . . .	5500, L. & D. Intensity 2.
			5483, L. & D. Not seen.
5468·31	2	Diffused.	
5446·51	2	. . . .	5446, L. & D. Intensity 2.
5438·84	1		
5418·55	1	. . . .	5429 5424 L. & D. Not seen.
5333·55	2	. . . .	5403, L. & D. Not seen.
5323·15	1		
5317·56	1	. . . .	5319, L. & D. Intensity 1.
5308·84	1	. . . .	5208·57, Runge. Intensity 1. 5305, L. & D. Not seen.
5276·69	1	. . . .	5278, L. & D. Intensity 1.

5168·33	1	. . . .	5172, L. & D. Not seen.
5166·95	1	. . . .	5166, L. & D. Intensity 5.
5143·25	1	*Cf.* Xenon II., 5143·24. Intensity 1.	5143, L. & D. Intensity 4.
5125·88	2	. . . .	5126, L. & D. Intensity 6.
5123·35	1		
5086·67	1	. . . .	5087, L. & D. Intensity 3.
5077·37	1	. . . .	5078, L. & D. Intensity 1.
5072·71	1	. . . .	5073, L. & D. Intensity 2.
5065·74	1		
5054·61	1	. . . .	5057, L. & D. Not seen.
5046·51	1		
5033·95	1	. . . .	5034, L. & D. Intensity 1.
5028·48	1		
5022·57	2	. . . .	5023, L. & D. Intensity 4.
5022·01	1		
5016·58	1		
5013·42	3	. . . .	5014, L. & D. Intensity 2.
5009·49	1		
4982·95	1		
4979·00	3	. . . .	4980, L. & D. Intensity 1.
4960·44	1	. . . .	4960, L. & D. Intensity 1.
4948·67	1		
4945·75	2	. . . .	4946, L. & D. Intensity 1.
4933·32	1		
4916·11	1		4903, L. & D. Not seen.
4889·16	1		
4870·23	1		

TABLE VI.—Second Krypton Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.
4857·36	1	*Cf.* Xenon II., 4857·37. Intensity 1.	
4816·76	4	Diffused	4847, L. & D. Intensity 2.
4815·79	1	. . . .	4815, L. & D. Intensity 2.
4836·75	2		
4833·89	1		
4832·26	4	Diffused	4832·22, RUNGE. Intensity 2. 4833, L. & D. Intensity 5.
4826·21	1		
4825·37	3	Diffused	4825·38. RUNGE. Intensity 1. 4826, L. & D. Intensity 3.
4811·91	4	. . . .	4812, L. & D. Intensity 3.
4803·16	<1		
4796·48	2	Diffused.	
4789·89	1		
4788·93	<1		
4778·57	1	Diffused.	
4773·16	2		
4765·90	6	. . . .	4766, L. & D. Intensity 10.
4762·60	5	. . . .	4762·66, RUNGE. Intensity 2. 4763, L. & D. Intensity 3.
4754·63	2		
4752·14	3	Diffused.	
4739·16	7	. . . .	4739·13, RUNGE. Intensity 5. 4739, L. & D. Intensity 10.
4729·88	1		
4614·67	2		
4613·93	1		
4610·79	3	. . . .	4610, L. & D. Intensity 3.
4607·03	<1		
4604·16	2		
4598·64	2	. . . .	4598, L. & D. Intensity 1.
4592·94	3	Diffused	4593, L. & D. Intensity 2.
4583·03	4	. . . .	4583, L. & D. Intensity 4.
4577·40	6	A line occurs in Xenon II. at 4577·36. Intensity 6.	4577·31, RUNGE. Intensity 4. 4577, L. & D. Intensity 8.
4575·87	1		
4573·52	2		
4556·77	4		
4537·45	1		
4536·67	1	Diffused.	
4523·32	5	. . . .	4525, L. & D. Intensity 3.
4518·82	1		
4502·56	1	First krypton spectrum	? 4505, L. & D. Intensity 2.
4490·04	4	. . . .	4490, L. & D. Intensity 2.
4475·18	7	. . . .	4475, L. & D. Intensity 6.
4463·88	1	First krypton spectrum	4464·11, RUNGE. Not seen. 4464, L. & D. Intensity 3.
4460·18	1		

4727·81	1		
4710·68	1		
4699·82	2	. . . .	4702·73, Runge. Not seen.
4695·82	2		
4694·59	4	. . . .	? 4694·82, Runge. Intensity 2. 4694, L. & D. Intensity 3.
4693·83	1		
4691·46	2		
4689·95	1		
4687·46	1		
4686·43	1		
4680·57	4	. . . .	4680·67, Runge. Intensity 3. 4680, L. & D. Intensity 5.
4673·96	1		
4672·22	<1		
4659·04	5	. . . .	4659, L. & D. Intensity 8.
4655·94	<1		
4650·33	2	. . . .	4650, L. & D. Intensity 1.
4638·53	2		
4634·05	5	. . . .	4634·07, Runge. Intensity 4. 4635, L. & D. Intensity 6.
4621·58	1		
4620·21	<1		
4619·31	6	. . . .	4619·30, Runge. Intensity 5. 4620, L. & D. Intensity 8.
4615·46	5	. . . .	4615·48, Runge. Intensity 4. 4615, L. & D. Intensity 6.

4457·42	2		
4454·55	1		
4454·12	1	First krypton spectrum	4454, L. & D. Intensity 1.
4453·38	3		
4443·87	1		
4443·46	2		
4436·98	4	. . . .	4436·96, Runge. Intensity 2. 4437, L. & D. Intensity 6.
4431·85	4	. . . .	4432, L. & D. Intensity 6.
4422·86	4	. . . .	4423, L. & D. Intensity 2.
4417·40	2		
4408·10	2	This line is visible in the spectrum of atmospheric argon, but disappears after fractionation.	4408·095, Kayser in the blue argon spectrum. Intensity = 1.
4404·47	1		
4400·98	1		
4399·57	1	. . . .	4400, L. & D. Intensity 1.
4389·87	1		
4386·69	4	. . . .	4387, L. & D. Intensity 3.
4385·39	1		
4381·71	3		
4377·89	2		
4376·33	1	Diffused . . . . First krypton spectrum	4376·24, Runge. 4376, L. & D. Intensity 3.
4376·20	1		
4369·86	4		
4367·27	<1		
4366·43	<1		

TABLE VI.—Second Krypton Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
4362 ·83	1	Krypton spectrum first	4362·76, RUNGE. 4363, L. & D. Intensity 2.	4179 ·67	2	Diffused.	
4355 ·84	1			4172 ·63	2		
4355 ·67	10	Visible in first krypton spectrum . .	4355·62, RUNGE. Intensity 5. 4356, L. & D. Intensity 12.	4171 ·97	2	. . . .	4172, L. & D. Intensity 1.
4355 ·14	2			4160 ·37	1		
4352 ·76	<1			4159 ·13	1		
4351 ·20	2	Diffused.		4154 ·62	4		
4344 ·42	1			4145 ·28	6	. . . .	4145·27, RUNGE. Intensity 3. 4145, L. & D. Intensity 8.
4344 ·05	<1			4139 ·28	4	Very diffused	4140, L. & D. Intensity 2.
4341 ·50	<1			4138 ·12	4		
4333 ·50	2			4134 ·72	3		
4323 ·16	4	. . . .	4323, L. & D. Intensity 2.	4133 ·81	<1		
4319 ·76	1	First krypton spectrum	4319·760, RUNGE. 4320, L. & D. Intensity 8.	4131 ·48	4		
4319 ·30	1	. . . .	4319, L. & D. Intensity 3.	4118 ·28	2	Diffused	4119, L. & D. Intensity 3.
4318 ·74	1	First krypton spectrum	4318·70, RUNGE. } 4318, L. & D. Intensity 3.	4113 ·90	1		
4317 ·98	5	. . . .	4318·22, RUNGE. Intensity 2	4109 ·38	6	. . . .	4109, L. & D. Intensity 6.
4305 ·37	2			4098 ·89	7	. . . .	4099, L. & D. Intensity 8.
4301 ·71	3	. . . .	}4301, L. & D. Intensity 7.	4088 ·48	8	. . . .	4088·53, RUNGE. Intensity 6. 4089, L. & D. Intensity 8.
4300 ·67	5	Visible in first krypton spectrum . .		4082 ·58	4	. . . .	A line occurs in the blue spectrum of argon of wave-length 4082·535 (KAYSER), but which does not disappear on fractionation. Intensity = 2.
4295 ·35	1						
4294 ·99	2						

4293 ·10	6	. . . .	4293·10, Runge. Intensity 5. 4293, L. & D. Intensity 10.
4283 ·17	2	First krypton spectrum	4283, L. & D. Intensity 3.
4281 ·65	<1		
4280 ·77	1	Diffused.	
4274 ·15	2	First krypton spectrum	4274·09, Runge. 4274, L. & D. Intensity 4.
4273 ·65	<1		
4268 ·97	3	. . . .	4269, L. & D. Intensity 3.
4268 ·72	2	. . . .	
4259 ·60	3	. . . .	4260, L. & D. Intensity 1.
4254 ·98	3	. . . .	4256, L. & D. Intensity 1.
4252 ·87	2		
4250 ·76	4	. . . .	4251, L. & D. Intensity 5.
4244 ·32	1		
4237 ·11	2	. . . .	4237, L. & D. Intensity 4.
4236 ·81	3	. . . .	
4228 ·98	1	This line is visible in the spectrum of atmospheric argon, but disappears after fractionation.	4429·015, Kayser in the blue argon spectrum. Intensity = 1.
4226 ·75	3		
4226 ·09	3		
4225 ·50	1		
4223 ·22	<1		
4222 ·36	1		
4201 ·84	1		
4201 ·55	<1		
4185 ·29	2	Diffused	4185 L. & D. Intensity 3.
4069 ·97	4	Diffused.	
4067 ·53	5		
4065 ·22	8	. . . .	4065·19, Runge. Intensity 3. 4065, L. & D. Intensity 7.
4059 ·02	4	Diffused	. . . . . . 4058, L. & D. Intensity 6.
4057 ·17	8	. . . .	4057·16, Runge. Intensity 2
4054 ·43	1		
4050 ·62	5	Diffused.	
4046 ·30	1		
4044 ·80	5	. . . .	4045, L. & D. Intensity 4.
4037 ·96	4	. . . .	4038, L. & D. Intensity 2.
4035 ·53	2		
4026 ·38	1	Diffused.	
4024 ·72	2	Diffused.	
4008 ·60	2	Diffused	4008, L. & D. Intensity 2.
4008 ·21	3	. . . .	
4005 ·70	3	Diffused	4005, L. & D. Intensity 1.
4002 ·73	3		
3998 ·10	5	. . . .	3997, L. & D. Intensity 3.
3996 ·81	<1		
3994 ·98	6	. . . .	3994, L. & D. Intensity 6.
3992 ·08	2		
3990 ·79	2	Diffused.	
3987 ·93	4	. . . .	3988, L. & D. Intensity 2.
3987 ·22	1	Diffused.	
3965 ·02	4	. . . .	3965, L. & D. Intensity 1.

TABLE VI.—Second Krypton Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.
3962·46	1		
3957·82	4		
3954·90	5		3955, L. & D. Intensity 2.
3953·71	3		
3952·16	3	Diffused.	
3947·76	1		
3945·60	1		
3942·78	2	Diffused.	
3942·28	1	*Cf.* Xenon II., 3942·29. Intensity I.	
3941·03	1	Diffused.	
3938·98	2		3939, L. & D. Intensity 1.
3938·62	1		
3934·29	3	Diffused.	
3932·80	4	Diffused	?
3929·34	3	Diffused	3928, L. & D. Intensity 3.
3924·91	1	Diffused.	
3921·81	2	Diffused.	
3920·29	8		3920·59, RUNGE. Intensity 1. 3921, L. & D. Intensity 8.
3917·76	6		3918, L. & D. Intensity 2.
3917·03	1		
3914·04	1		
3913·01	1		
3821·93	1	Diffused.	
3817·23	3		3817, L. & D. Intensity 2.
3814·70	2	Diffused.	
3809·30	2		
3806·46	1		3806, L. & D. Intensity 2.
3806·28	1		
3804·80	4		3805, L. & D. Intensity 3.
3793·35	1		
3792·82	4		
3791·22	2	Diffused.	
3788·26	2	Very diffused.	
3785·76	1	Diffused.	
3783·28	10		3783·40, RUNGE. Intensity 4. 3784, L. & D. Intensity 10.
3780·70	1		
3778·23	10		3778·29, RUNGE. Intensity 4. 3779, L. & D. Intensity 8.
3776·66	1	Diffused.	
3775·68	1		
3773·20	2		
3771·46	4		3772, L. & D. Intensity 4.
3768·10	1	Diffused. *Cf.* Xenon II., 3768·08. Intensity I.	

3912 ·69	5	. . . .	3913, L. & D. Intensity 6. 3912 ·36, Runge. Intensity 1.
3906 ·37	8	. . . .	3907, L. & D. Intensity 6.
3901 ·28	2	. . . .	3901, L. & D. Intensity 1.
3898 ·83	3		
3894 ·83	5	. . . .	3896, L. & D. Intensity 3.
3884 ·04	1		
3883 ·77	1		
3875 ·95	2	. . . .	3876, L. & D. Intensity 7.
3875 ·56	7	. . . .	
3874 ·15	2		
3873 ·38	2	Diffused.	
3863 ·99	5	Diffused.	3862, L. & D. Intensity 1.
3860 ·58	5	. . . .	3859, L. & D. Intensity 1.
3858 ·90	2	Diffused	3859, L. & D. Intensity 1.
3857 ·44	3		
3850 ·23	2	Diffused.	
3847 ·93	1	Diffused.	
3847 ·63	1		
3846 ·99	1	. . . .	3847, L. & D. Intensity 1.
3844 ·55	2	Diffused	3844, L. & D. Intensity 2.
3842 ·98	1	Diffused.	
3842 ·40	3	. . . .	3842, L. & D. Intensity 1.
3839 ·49	1	. . . .	3839, L. & D. Intensity 1.
3836 ·64	3	. . . .	3837, L. & D. Intensity 2.
3835 ·47	1		
3835 ·10	2	Diffused.	
3765 ·98	1	Diffused. *Cf.* Xenon II., 3765 ·99. Intensity 4.	
3759 ·04	2	Diffused	3759, L. & D. Intensity 2.
3755 ·92	1	Diffused.	
3754 ·35	5	. . . .	3755, L. & D. Intensity 6.
3751 ·81	1	*Cf.* Xenon II., 3751 ·80. Intensity 1.	
3749 ·77	3	Diffused.	
3744 ·95	9	. . . .	3746, L. & D. Intensity 6.
3741 ·83	10	. . . .	3741 ·85, Runge. Intensity 3. 3742, L. & D. Intensity 6.
3740 ·87	2		
3740 ·37	1		
3735 ·91	5	. . . .	3736, L. & D. Intensity 3.
3733 ·09	2	A line of wave-length 3733 ·122 is given by Kayser in the blue argon spectrum. Intensity = 1.	3734, L. & D. Intensity 4.
3732 ·77	3	. . . .	
3731 ·82	1		
3728 ·13	2	Diffused.	
3726 ·45	2		
3721 ·50	7	. . . .	3722, L. & D. Intensity 5.
3718 ·79	8	. . . .	3719, L. & D. Intensity 10.
3718 ·17	10	. . . .	
3716 ·28	1		
3715 ·18	3	. . . .	3715, L. & D. Intensity 1.
3708 ·23	1	Diffused.	
3696 ·84	1		
3690 ·80	5	. . . .	3691, L. & D. Intensity 1.

TABLE VI.—Second Krypton Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.
3686·30	6	. . . .	3686·26, RUNGE. Intensity 1. 3687, L. & D. Intensity 5.
3680·64	1	. . . .	3681, L. & D. Intensity 7.
3680·52	7	. . . .	
3678·77	2		
3674·37	1		
3670·38	1		
3669·16	9	. . . .	3670, L. & D. Intensity 7.
3668·74	2	Equal intensity in first krypton spectrum	3667, L. & D. Intensity 1.
3666·15	3	. . . .	
3663·57	4	. . . .	3664, L. & D. Intensity 3.
3661·15	4	. . . .	3661, L. & D. Intensity 3.
3660·20	1		
3654·11	10	. . . .	3654·11, RUNGE. Intensity 3. 3654, L. & D. Intensity 10.
3648·74	5	. . . .	3649, L. & D. Intensity 3.
3644·36	1		
3641·48	4		
3637·63	4	. . . .	3638, L. & D. Intensity 4.
3634·54	2	Diffused.	
3633·69	2		
3632·62	1		
3535·48	6	*Cf.* Argon, 3535·514. Intensity = 4 (KAYSER).	
3527·53	1		
3524·93	1		
3521·27	1		
3517·52	1		
3514·68	3		
3507·58	9		
3503·38	6	. . . .	3503, L. & D. Intensity 2.
3498·63	1	Diffused.	
3497·29	3		
3493·16	2		
3492·94	2		
3488·74	8	. . . .	3489, L. & D. Intensity 2.
3487·61	1		
3478·04	1		
3474·79	7		
3471·52	<1		
3471·16	1		
3470·19	7	. . . .	3470, L. & D. Intensity 1.
3465·54	1	Diffused.	
3460·24	6	. . . .	3460, L. & D. Intensity 3.
3448·87	4		

3632·02	10	. . . .	3632, L. & D. Intensity 10.
3627·20	1		
3623·74	4	. . . .	3624, L. & D. Intensity 1.
3615·97	3		
3611·21	1		
3608·02	9	. . . .	3608, L. & D. Intensity 6.
3604·10	1		
3602·26	1	Diffused.	
3600·05	6	. . . .	3600, L. & D. Intensity 6.
3599·35	4		
3598·14	1		
3596·99	1		
3589·79	7	. . . .	3590, L. & D. Intensity 3.
3586·40	2		
3580·11	1		
3577·74	1		
3572·82	3	Diffused	3574, L. & D. Intensity 1.
3567·88	2		
3564·38	4	*Cf.* Xenon II., 3564·40. Intensity 4.	
3563·48	1		
3562·23	1		
3555·69	2	Very diffused.	
3553·61	4	. . . .	3554, L. & D. Intensity 2.
3549·57	3		
3548·86	2		
3544·69	5	. . . .	3545, L. & D. Intensity 6.
3544·29	5	. . . .	
3447·01	3		
3446·66	7	Diffused.	
3445·43	1		
3443·01	1		
3439·60	6		
3439·03	1		
3431·85	1		
3431·15	2		
3428·95	1	*Cf.* Xenon II., 3428·95. Intensity 1.	
3427·84	4		
3423·87	3		
3414·95	1		
3405·28	7		
3396·72	2	*Cf.* Xenon II., 3396·72. Intensity 2.	
3389·80	1		
3389·06	3		
3387·26	1	*Cf.* Xenon II., 3387·26. Intensity 1.	
3385·35	1		
3381·24	2	. . . .	A line is given by Eder and Valenta in the blue argon spectrum at 3381·27. This line was not seen by Kayser nor myself.
3379·18	1	*Cf.* Xenon II., 3379·20. Intensity 2.	
3375·09	4		
3360·22	2	*Cf.* Xenon II., 3360·20. Intensity 2.	
3352·07	6		
3349·61	3	Diffused.	

TABLE VI.—Second Krypton Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
3348 ·28	2			3177 ·09	1	Very diffused.	
3342 ·59	5			3175 ·78	2	Diffused.	
3341 ·70	1	Diffused.		3171 ·06	3	*Cf.* Xenon II., 3175 ·80. Intensity 3.	
3340 ·61	2	Diffused.		3151 ·88	3		
3337 ·99	1	Diffused.		3151 ·06	5		
3336 ·84	1	Diffused.		3144 ·90	1		
3332 ·61	3			3144 ·47	2		
3330 ·88	7	*Cf.* Xenon II., 3330 ·90. Intensity 6.		3142 ·01	5		
3329 ·86	1	Diffused.		3141 ·48	6		
3328 ·34	1	Diffused.		3139 ·71	3		
3325 ·84	9			3138 ·49	1	Possibly Xenon II., 3138 ·46. Intensity 6.	
3324 ·33	1	Very diffused.		3136 ·33	2		
3321 ·26	1			3135 ·24	1		
3320 ·39	1	Diffused.		3124 ·52	6		
3319 ·48	1			3122 ·61	3		
3315 ·80	1	*Cf.* Xenon II., 3315 ·80. Intensity 1.		3120 ·73	4		
3311 ·59	6			3112 ·36	5		
3308 ·28	4			3105 ·48	1		
3305 ·79	1	Diffused.		3101 ·85	1		
3304 ·87	5			3097 ·27	4		
3301 ·97	1			3096 ·59	3	Diffused.	
3294 ·02	1			3095 ·24	1	Diffused.	
3286 ·01	4						

3285·36	1	
3282·21	1	
3271·77	4	
3268·61	7	
3264·94	8	
3261·70	1	Diffused.
3248·16	1	Very diffused.
3247·14	1	Diffused.
3246·74	2	
3245·82	10	
3240·55	6	
3239·64	6	
3237·94	1	
3235·29	1	
3224·99	3	
3223·66	1	Diffused.
3222·40	1	*Cf.* Xenon II., 3222·40. Intensity 1.
3220·76	4	
3216·39	1	
3211·04	1	
3208·39	3	
3207·91	4	
3205·40	1	Diffused.
3202·67	1	Diffused.
3200·53	3	
3191·33	6	
3189·23	7	
3063·26	5	
3062·55	1	
3060·99	2	Diffused.
3056·86	4	
3056·14	2	
3049·83	2	
3047·07	5	
3044·92	1	*Cf.* Xenon II., 3044·91. Intensity 1.
3024·57	4	
3022·43	3	
3017·78	2	Diffused.
3013·36	1	
3008·57	2	
3002·39	1	
2999·99	3	Diffused.
2996·77	2	
2992·36	3	
2986·02	1	
2983·22	1	
2979·95	3	
2979·01	3	
2976·44	1	
2976·06	1	
2974·18	3	
2971·90	1	
2968·44	2	
2967·37	5	

TABLE VI.—Second Krypton Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
2963·26	1			2803·32	4		
2961·19	2			2801·25	1	Very diffused.	
2960·92	2	*Cf.* Xenon II., 2960·93. Intensity 2.		2795·92	5		
2960·27	3	Diffused.		2790·31	1		
2958·48	2	Diffused.		2779·63	1		
2956·44	1			2779·23	3		
2954·40	2			2778·34	1		
2952·69	4			2774·70	1		
2952·23	1			2772·73	2		
2950·33	3			2761·87	1		
2949·67	2			2759·16	1	Diffused.	
2948·27	1			2756·66	1	*Cf.* Xenon II., 2756·64. Intensity 1.	
2940·05	1			2752·33	1		
2938·70	1			2751·71	1	Diffused.	
2935·36	2			2750·49	1		
2934·13	1			2748·18	1		
2931·03	1			2742·67	4		
2930·72	1			2742·13	1		
2927·69	1			2733·38	4	*Cf.* Xenon II., 2733·36. Intensity 4.	
2917·81	1			2732·46	1	*Cf.* Xenon II., 2732·48. Intensity 1.	
2915·88	1			2730·55	1		
2915·40	1			2730·02	1		
2913·35	1			2729·58	4		

2909 ·30	2	
2908 ·74	1	
2900 ·19	3	
2893 ·81	4	
2892 ·30	5	
2873 ·84	1	
2872 ·99	1	
2870 ·73	4	
2851 ·29	3	
2847 ·51	4	
2844 ·59	3	*Cf.* Xenon II., 2844 ·59. Intensity 3.
2841 ·10	1	*Cf.* Xenon II., 2841 ·10. Intensity 1.
2838 ·92	3	
2836 ·08	1	
2835 ·49	2	Diffused.
2833 ·11	6	
2830 ·55	1	Diffused.
2829 ·60	1	
2822 ·75	1	
2817 ·00	4	
2816 ·58	6	
2814 ·62	2	Possibly Xenon II., 2814 ·62. Intensity 6.
2814 ·09	1	
2811 ·81	2	*Cf.* Xenon II., 2811 ·81. Intensity 3.
2806 ·21	1	
2803 ·71	1	
2720 ·03	1	Diffused.
2716 ·27	3	
2715 ·31	1	
2714 ·61	1	
2712 ·50	8	
2711 ·22	1	
2710 ·37	1	
2701 ·45	3	
2700 ·73	1	
2698 ·20	1	
2697 ·41	4	
2696 ·71	4	*Cf.* Xenon II., 2696 ·73. Intensity 4.
2695 ·81	4	
2694 ·93	3	
2692 ·65	1	
2691 ·94	1	*Cf.* Xenon II., 2691·92. Intensity 1.
2691 ·31	1	
2690 ·35	1	*Cf.* Xenon II., 2690·33. Intensity 1.
2688 ·44	1	
2683 ·66	3	
2681 ·29	4	
2680 ·80	1	
2680 ·44	3	
2679 ·73	2	
2677 ·30	2	Possibly Xenon II., 2677·29. Intensity 8.
2676 ·10	1	

TABLE VI.—Second Krypton Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
2675 ·41	1			2558 ·08	1		
2670 ·78	2	*Cf.* Xenon II., 2670·80. Intensity 2.		2556 ·44	2		
2664 ·10	2	Diffused.		2556 ·01	2		
2661 ·34	1			2555 ·23	2		
2661 ·09	2	Diffused.		2554 ·35	2		
2656 ·49	2	Diffused.		2553 ·26	1		
2654 ·07	1			2548 ·68	1		
2649 ·84	1	Diffused.		2544 ·79	1		
2649 ·38	3			2538 ·43	2	Diffused.	
2648 ·80	1	*Cf.* Xenon II., 2648·79. Intensity 1.		2537 ·67	1		
2648 ·55	1			2535 ·97	1		
2648 ·26	4			2528 ·51	1		
2643 ·18	3			2527 ·26	2	Diffused.	
2642 ·19	1			2525 ·56	1	Diffused.	
2640 ·84	1			2525 ·07	2		
2639 ·86	4			2519 ·38	1		
2634 ·52	1			2518 ·02	1		
2630 ·76	2			2515 ·50	1		
2629 ·00	3			2513 ·50	1	*Cf.* Xenon II., 2513·52. Intensity 1.	
2628 ·19	1			2513 ·03	1		
2627 ·86	2			2511 ·83	1		
2627 ·34	1			2506 ·97	1		
2624 ·90	1	Diffused.		2506 ·66	2	Diffused.	

2624·63	1	*Cf.* Xenon II., 2624·65. Intensity 1.
2620·54	4	
2616·80	2	*Cf.* Xenon II., 2616·79. Intensity 1.
2611·08	3	
2604·72	1	
2604·59	1	
2602·23	2	
2597·80	2	
2596·83	1	Diffused.
2595·44	1	Diffused.
2594·49	1	
2592·57	5	
2591·33	1	
2590·83	1	
2589·19	4	
2584·21	1	
2581·84	1	Diffused. *Cf.* Xenon II., 2581·84. Intensity 1.
2574·87	1	
2572·44	1	*Cf.* Xenon II., 2572·46. Intensity 2.
2572·14	2	
2571·30	1	
2570·54	1	
2565·72	1	
2563·32	2	
2562·05	1	
2559·20	2	
2503·97	3	Diffused.
2500·72	1	
2498·84	1	
2497·81	1	
2497·51	1	Diffused.
2494·10	2	*Cf.* Xenon II., 2494·11. Intensity 3.
2489·51	3	
2487·75	2	
2487·58	2	
2486·40	2	
2485·68	2	
2483·71	2	
2483·32	2	
2483·09	1	
2478·97	4	
2474·99	2	
2474·79	2	
2474·06	1	
2473·39	1	
2472·24	1	
2470·50	2	
2468·56	2	*Cf.* Xenon II., 2468·54. Intensity 2.
2467·00	2	
2465·91	2	
2464·87	8	
2459·74	1	
2457·79	2	

TABLE VI.—Second Krypton Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.
2456·16	6		
2455·42	1		
2454·19	1		
2453·37	2		
2452·38	3		
2446·56	2		
2442·68	1		
2440·96	1		
2439·64	1		
2439·32	2		
2428·44	3		
2426·46	3		
2425·15	1	*Cf.* Xenon 2425·18, a very diffused line of intensity 2.	
2420·30	1		
2418·13 &c.	1		

TABLE VII.—First Xenon Spectrum, without Leyden Jar and Spark Gap.

Wave-length.	Intensity.	Remarks.	Other observers.
6198·70	1		
6182·92	3	. . . .	6183, L. & D. Intensity = 1.
6180·16	1	. . . .	6181, L. & D. Intensity = 1.
6178·80	2		
6164·30	2	. . . .	? 6166, L. & D. Intensity = 1.
6112·58	1		
			5935, L. & D. Intensity = 1. Not seen.
5895·20	1	. . . .	5895, L. & D. Intensity = 1.
4807·19	6	Visible in second xenon spectrum . .	4807, L. & D. Intensity = 1.
4792·77	1		
4734·30	8	Visible in second xenon spectrum . .	4734, L. & D. Intensity = 1.
4697·17	7	. . . .	Band of close lines. L. & D.
4691·13	1	. . . .	
4683·83	1	. . . .	
4671·42	10	Visible in second xenon spectrum . .	
4668·32	1	. . . .	

5875·30	1	. . . .	5876, L. & D. Intensity = 1.
			5856, L. & D. Intensity = 1. Not seen.
5824·98	1	. . . .	5825, L. & D. Intensity = 2.
5824·08	1	. . . .	
5716·20	2	Very diffused.	
5696·68	1		
5695·96	2		
5688·59	1		
5649·77	<1		
5619·07	2		
5612·84	<1		
5581·96	1		
5580·60	1		
5579·48	<1		
5563·83	2		
5552·59	2		
5488·73	<1		
5440·16	1	Diffused.	
5394·84	1		
5392·94	2		
5363·74	<1		
5028·42	2		
			5025, L. & D. Intensity = 1. Not seen.
4923·28	6	. . . .	4924, L. & D. Intensity = 4.
4916·63	6	. . . .	4917, L. & D. Intensity = 4.
4843·44	2		
4829·87	4	. . . .	4820, L. & D. Intensity = 1.
4658·94	1		
4624·46	15	Visible in second xenon spectrum . .	4624, L. & D. Intensity = 2.
4612·06	2		
4582·89	5		
4524·83	6	. . . .	4525, L. & D. Intensity = 5.
4501·13	10	Visible in second xenon spectrum . .	4500, L. & D. Intensity = 1.
4385·97	1	. . . .	4386, L. & D. Intensity = 3.
4384·12	2		
4376·35	3	. . . .	4375, L. & D. Intensity = 4.
4358·51	3		
4203·87	2	. . . .	4204, L. & D. Intensity = 1.
4193·70	8	. . . .	4193, L. & D. Intensity = 6.
4193·19	1	. . . .	
4135·27	1		
4116·25	7		
4109·84	5		
4078·94	10	. . . .	4079, L. & D. Intensity = 1.
4046·71	3		
3985·39	3		
3974·61	3		
3967·74	10		
3951·16	10	. . . .	3951, L. & D. Intensity = 6.
3948·93	1		
3948·38	3		
3826·99	2	Equal intensity in second xenon spectrum.	3826, L. & D. Intensity = 1.
3823·86	1		

TABLE VII.—First Xenon Spectrum, without Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.
3810·01	2		
3804·96	3		
3801·54	1		
3796·47	3		
3773·58	1		
3745·54	1		
3693·69	3		
3686·08	3		
3679·77	1		
3670·10	1		
3665·53	1		
3663·52	<1		
3655·03	1		
3650·36	4		
3610·47	2		
3554·16	2		
3549·99	2		
3506·90	1		
3472·48	<1		
3469·95	<1		
3341·65	1		
3132·01	2		
3131·66	1		
3125·85	2	Equal intensity in second xenon spectrum.	
3022·09	1		
2536·58	2		

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap.

Wave-length.	Intensity.	Remarks.	Other observers.
6097·80	7	. . . .	6097, L. & D. Intensity 6.
6051·36	7	. . . .	6051, L. & D. Intensity 6.
6036·40	6	. . . .	6036, L. & D. Intensity 5.
5976·67	7	. . . .	5976, L. & D. Intensity 6.
5619·18	1		
5616·99	6	. . . .	5617, L. & D. Intensity not given.
5613·14	1		
5607·18	1	. . . .	5609, L. & D. Intensity 1.

5971·32	1		5972, L. & D. Intensity not given.
5915·71	1		5946, L. & D. Intensity 2.
			5935, L. & D. Not seen.
5917·73	1		
5905·40	1		5906, L. & D. Intensity 1.
5893·59	1		? 5895, L. & D. Intensity 1.
5816·21	1		5817, L. & D. Intensity 1.
5776·64	3		5777, L. & D. Intensity 4.
5758·92	4		5759, L. & D. Intensity 4.
5754·38	1	Diffused.	
5752·79	1		
5751·28	5		5751, L. & D. Intensity 5.
5748·95	1		
5727·15	5		5727, L. & D. Intensity 4.
5719·83	6		5720, L. & D. Intensity 4.
5716·36	1		
5708·74	1		
5701·48	1		L. & D. give a line at 5700. Intensity 6. This was not seen.
5699·80	1		
5686·73	1		
5675·41	1		
5671·15	3		
5667·85	6		5668, L. & D. Intensity 4.
5659·67	5		5660, L. & D. Intensity 1.
5633·32	1		
5625·18	1		
5604·66	1		
5595·32	2	Very diffused indeed.	
5591·96	1		
5584·00	2	Very diffused	5583, L. & D. Intensity 1.
5582·30	2	Diffused	
5572·48	2		5573, L. & D. Intensity 1.
5570·60	1		
5553·08	1		
5548·40	1		
5531·33	7		5532, L. & D. Intensity 4.
5525·81	2		
5524·63	1		
5518·96	1		
5507·72	1		
5495·20	1		
5481·38	3	Diffused.	
5472·90	7		5473, L. & D. ? Intensity 3.
5469·81	1		
5460·63	6		5461, L. & D. Intensity 3.
5453·33	1		
5451·22	1		
5450·71	5		5451, L. & D. Intensity 1.
5445·70	2		
5439·19	8		5439, L. & D. Intensity 3.
5419·40	10		5420, L. & D. Intensity 10. 5419·38, RUNGE, as a weak krypton line.
5415·64	1		

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
5413 ·74	2			4978 ·49	4	Diffused.	
5401 ·23	3			4971 ·85	1		4972, L. & D. Intensity 2.
5386 ·90	1			4923 ·40	1		
5372 ·62	8		5372, L. & D. Intensity 6.	4921 ·68	6		4922, L. & D. Intensity 8.
5368 ·30	3		5368, L. & D. Intensity 1.	4919 ·85	4		
5367 ·29	1			4916 ·71	1		
5363 ·47	2			4890 ·24	5		4890, L. & D. Intensity 3.
5339 ·56	9		5339, L. & D. Intensity 6.	4887 ·47	5		4887, L. & D. Intensity not given.
5328 ·10	1			4884 ·36	1		4884, L. & D. Intensity 4.
5314 ·15	8		5313, L. & D. Intensity 1.	4883 ·68	6		4883, L. & D. Intensity not given.
5311 ·15	1			4876 ·68	7		4876, L. & D. Intensity 4.
5309 ·49	4		5309, L. & D. Intensity 1.	4869 ·60	3		
5292 ·40	10		5292, L. & D. Intensity 10. 5292 ·37, RUNGE, as a weak krypton line.	4862 ·69	8		
5268 ·50	1			4857 ·37	1	*Cf.* Krypton II., 4857 ·36. Intensity 1.	
5262 ·16	5		5262, L. & D. Intensity 2.	4853 ·90	2		
5260 ·65	5		5260, L. & D. Intensity 2.	4844 ·50	10		4844, L. & D. Intensity 10. 4844 ·58, RUNGE as a weak krypton line.
5260 ·10	1						
5247 ·98	1			4832 ·46	2		
5239 ·14	2		5240, L. & D. Intensity not given.	4829 ·23	1		4830, L. & D. Intensity 1.
5226 ·84	1		5227, L. & D. Intensity 1.	4825 ·23	1		
5223 ·85	1			4823 ·47	6		4823, L. & D. Intensity 3.

5206·52	1			
5201·64	1	. . . .	5202, L. & D.	Intensity 1.
5192·36	1	. . . .	5192, L. & D.	Intensity 6.
5191·60	5	. . . .		
5188·28	4	. . . .	5189, L. & D.	Intensity 3.
5184·68	2	. . . .	5185, L. & D.	Intensity 3.
5179·02	3	. . . .	5179, L. & D.	Intensity 3.
5143·24	1	*Cf.* Krypton II., 5143·25. Intensity 1.		
5125·94	3	. . . .	5126, L. & D.	Intensity 3.
5122·65	3	. . . .	5123, L. & D.	Intensity 1.
5107·58	3	. . . .	5107, L. & D.	Intensity 3.
5099·96	1			
5092·22	3			
5080·88	7	. . . .	5080, L. & D.	Intensity 2.
			5068, L. & D. Not seen.	Intensity 5.
5052·74	1	. . . .	5052, L. & D.	Intensity 1.
5045·09	3	. . . .	5045, L. & D.	Intensity 6.
5041·62	1			
5028·62	1	. . . .	? 5025, L. & D.	Intensity 1.
5013·04	1	Diffused.		
5008·74	1			
5001·20	1	Diffused.		
4994·27	1			
4993·22	1			
4991·36	2	Diffused.		
4988·22	2	. . . .	4988, L. & D.	Intensity 4.

4818·15	4			
4817·30	1			
4807·19	1	First xenon spectrum	4807, L. & D.	Intensity 1.
4796·66	1	Diffused.		
4794·61	2	. . . .	4793, L. & D.	Intensity 1.
4792·72	1	. . . .		
4787·95	4	. . . .	4787, L. & D.	Intensity 2.
4786·83	1	Very diffused.		
4779·33	1	. . . .	4779, L & D.	Intensity 2.
4775·85	1			
4775·33	1			
4773·34	2	Diffused.		
4769·21	4	. . . .	4769, L. & D.	Intensity 2.
4757·48	1			
4749·10	3			
4744·04	1			
			4740, L. & D.	Not seen.
4734·30	1	First xenon spectrum	4734, L. & D.	Intensity 1.
4732·53	1			
4731·35	3	Diffused	4731, L. & D.	Intensity 1.
4723·74	2	. . . .	4723, L. & D.	Intensity 1.
4715·31	3	. . . .	4714, L. & D.	Intensity 1.
4712·78	3	. . . .		
4698·20	5	. . . .	4698, L. & D.	Intensity 3.
4693·50	<1			
4683·76	5			

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—*continued*.

Wave-length.	Intensity.	Remarks.	Other observers.
4677 ·00	1	Diffused	Band of close lines. L. & D.
4676 ·61	3	Diffused	
4674 ·78	3		
4673 ·91	4		
4672 ·40	2		
4671 ·88	1		
4671 ·41	2	First xenon spectrum	
4668 ·72	3		
4666 ·48	2	Very diffused	
4659 ·10	1		
4658 ·06	3	*Cf.* argon blue spectrum 4658 ·08 (KAYSER).	
4653 ·23	3		
4652 ·15	6		4652, L. & D. Intensity 4.
4641 ·64	2		
4637 ·42	1		
4633 ·49	3		4634, L. & D. Intensity 2.
4632 ·83	<1		
4631 ·67	1	Diffused.	
4624 ·47	2	Diffused. First xenon spectrum	4624, L. & D. Intensity 2.
4620 ·60	<1		
4617 ·66	2	Diffused.	
4615 ·72	5		4616, L. & D. Intensity 3.
4472 ·12	<1		4471, L. & D. Intensity 1.
4468 ·34	<1		
4462 ·38	20		4462, L. & D. Intensity 10.
4460 ·75	<1		
4453 ·81	3		
4448 ·28	10		4449, L. & D. Intensity 6.
4441 ·08	3	Diffused	4440, L. & D. Intensity 1.
4434 ·35	6		4434, L. & D. Intensity 2.
4418 ·10	2		
4416 ·21	3	Diffused	4415, L. & D. Intensity 8.
4415 ·00	7		
4413 ·23	3		
4406 ·99	5	Diffused	4407, L. & D. Intensity 3.
4395 ·91	10		4396, L. & D. Intensity 4.
4395 ·30	1		
4393 ·34	10		4393, L. & D. Intensity 4.
4387 ·65	1		
4386 ·19	1		4386, L. & D. Intensity 3.
4385 ·08	3		
4373 ·87	3	Diffused	4375, L. & D. Intensity 4.
4369 ·34	4		4369, L. & D. Intensity 4.
4367 ·15	1	Diffused.	

4603 ·21	10	. . . .	4602, L. & D. Intensity 8.
4600 ·20	1	Diffused.	
4593 ·90	1		
4592 ·22	6	Diffused	4592, L. & D. Intensity 3.
4585 ·65	10	. . . .	4586, L. & D. Intensity 5.
4580 ·81	1	Very diffused.	
4577 ·36	6	A line occurs in Krypton II. at 4577 ·40 of intensity = 6.	4577, L. & D. Intensity 3. 4577 ·31, RUNGE. As krypton line.
4572 ·16	1	Diffused.	
4571 ·85	1	Diffused.	
4569 ·29	1		
4556 ·08	3	Diffused	4556, L. & D. Intensity 2.
4550 ·90	1		
4545 ·34	8	. . . .	4545, L. & D. Intensity 3.
4541 ·03	8	. . . .	4541. L. & D. Intensity 3.
4537 ·51	3	. . . .	4535, L. & D. Intensity 2.
4537 ·02	1	. . . .	
4532 ·67	5	. . . .	
4524 ·38	5	. . . .	4525, L. & D. Intensity 5.
4521 ·98	3	Diffused	4522, L. & D. Intensity 1.
4507 ·32	1		
4503 ·64	2		
4501 ·14	2	First xenon spectrum.	4500, L. & D. Intensity 1.
4486 ·12	2	. . . .	4486, L. & D. Intensity 1.
4481 ·01	7	Diffused	4481, L. & D. Intensity 5.
4474 ·10	<1	Diffused.	
			4356, given by L. & D. No doubt the Krypton II. line 4355 ·67, which is easily visible in xenon when only small traces are present.
			4343, L. & D. Intensity 1. Not seen
4337 ·14	2	Diffused	4337, L. & D. Intensity 3.
4335 ·95	1		
4330 ·63	15	. . . .	4331, L. & D. Intensity 10.
4321 ·95	4	. . . .	4322, L. & D. Intensity 3.
4310 ·69	2	Diffused	4311, L. & D. Intensity 3.
4310 ·54	2	Diffused	
4309 ·46	2		
4308 ·16	3		
4305 ·99	<1		
4296 ·97	<1		
4296 ·52	5	. . . .	4297, L. & D. Intensity 3.
4293 ·85	2		
4286 ·86	1		
4286 ·04	4	. . . .	4286, L. & D. Intensity 3.
4272 ·74	4	. . . .	4272, L. & D. Intensity 3.
4270 ·00	3	. . . .	4269, L. & D. Intensity 3.
4267 ·97	<1		
			4263, L. & D. Not seen.
4251 ·68	4	Diffused	4251, L. & D. Intensity 3.
4245 ·54	10	. . . .	4245, L. & D. Intensity 10.
4244 ·56	4	. . . .	

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.
4244 ·04	1		
4240 ·41	3		
4238 ·37	10		4239, L. & D. Intensity 8.
4227 ·12	2		4227, L. & D. Intensity 1.
4223 ·14	5	Diffused	4223, L. & D. Intensity 5.
4216 ·88	1		
4215 ·77	5		4215, L. & D. Intensity 10.
4214 ·85	1		
4214 ·17	5		
4213 ·80	5		4214, L. & D. Intensity 6.
4209 ·75	4		4209, L. & D. Intensity 8.
4209 ·53	4		
4208 ·61	6		
4204 ·06	2		4204, L. & D. Intensity 1.
4203 ·35	1		
4201 ·38	1		4201, L. & D. Intensity 1
4197 ·92	1		4198, L. & D. Intensity 1.
4196 ·85	<1		
4195 ·02	2		
4193 ·25	8		4193, L. & D. Intensity 6.
4181 ·28	<1		
4180 ·20	10		4181, L. & D. Intensity 10.
4179 ·83	1		
4083 ·07	<1		
4082 ·79	2		
4078 ·85	2		4079 L. & D. Intensity 1.
4078 ·33	1	Diffused.	
4073 ·62	1		
4072 ·62	4	Diffused	4074 L. & D. Intensity 1.
4070 ·30	1		
4066 ·67	1		
4062 ·27	<1		
4061 ·30	1		
4061 ·06	2		
4060 ·60	3		4060 L. & D. Intensity 1.
4057 ·55	5	Diffused	4058 L. & D. Intensity 6.
4056 ·22	<1	Diffused.	
4053 ·75	2		
4051 ·79	1		
4051 ·36	<1	Diffused.	
4050 ·19	6		4050 L. & D. Intensity 6.
4047 ·45	1	Diffused.	
4046 ·29	1	*Cf.* 4046 ·30 Krypton II. spectrum.	
4044 ·96	2		4044 L. & D. Intensity 1.
4044 ·09	1		
4043 ·73	<1		

4176·65	3		4176, L. & D. Intensity 1.
4171·08	1	Diffused	4172, L. & D. Intensity 1.
4162·25	3		4163, L. & D. Intensity 3.
4158·14	5		4159, L. & D. Intensity 3.
4156·27	<1	Diffused.	
4155·70	<1		
4154·76	1		
4152·12	1		
4145·85	5		4146 L. & D. Intensity 3.
4142·12	2		4142 L. & D. Intensity 1.
4133·08	1		
4132·52	1		3132 L. & D. Intensity 2.
4131·11	1		
4122·01	1		4121 L. & D. Intensity 1.
4113·34	<1		
4112·25	2	Diffused	4112 L. & D. Intensity 2.
4110·53	1		
4110·18	1		
4109·20	6		4109 L. & D. Intensity 6.
4106·25	1		4106 L. & D. Intensity 3.
4105·10	2		
4103·19	1		
4100·48	2		4100 L. & D. Intensity 2.
4099·01	4		4099 L. & D. Intensity 3.
4095·04	3		4093 L. & D. Intensity 1.
4087·38	<1		
4083·48	<1	Diffused.	
4043·38	3		4043 L. & D. Intensity 1.
4039·39	<1		
4037·70	2		4037 L. & D. Intensity 6.
4037·43	3		
4033·02	<1		
4030·69	2		
4028·72	3		4029 L. & D. Intensity 1.
4028·10	3		
4025·32	1		4025 L. & D. Intensity 3.
4021·76	1		4021 L. & D. Intensity 1.
4018·05	1		
4014·27	1		
4003·71	<1		
4002·51	2		4002 L. & D. Intensity 3.
4001·32	1		
4000·66	1		
3998·67	1	Diffused.	
3997·18	<1		
3994·55	1		3994 L. & D. Intensity 2.
3992·98	5		3991 L. & D. Intensity 3.
3990·40	3	Diffused.	
3986·10	3		3986 L. & D. Intensity 1.
3981·69	2		3981 L. & D. Intensity 1.
3979·35	2		
3976·47	1		3975 L. & D. Intensity 1.
3975·73	<1		
3974·14	<1		

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.
3972·69	2	Diffused	3973, L. & D. Intensity 2.
3970·04	1		
3965·59	1		
			3957, L. & D. Not seen.
			3955. L. & D. Not seen.
3951·73	<1		
3950·70	8		3951, L. & D. Intensity 6.
3943·73	3		3944, L. & D. Intensity 3.
3942·29	1	*Cf.* Krypton II., 3942·28. Intensity 1.	
3939·05	2		3939, L. & D. Intensity 1.
3932·63	2		
3929·73	1		
			3926, L. & D. Not seen. Possibly argon, 3925·90.
3923·56	2	Diffused	3923, L. & D. Intensity 6.
3922·67	10		
3918·71	3		
3917·28	1	Diffused.	
3915·46	3		3915, L. & D. Intensity 1.
3912·23	<1		
3911·77	1		
3908·00	7		3908, L. & D. Intensity 4.
3906·02	3		3906, L. & D. Intensity 1.
3847·57	2		
3846·43	1		
3842·05	5		3842, L. & D. Intensity 4.
3841·68	7		
3839·13	1		
3837·87	1		
3829·90	1		3829, L. & D. Intensity 1.
3828·49	2		
3828·15	1		
3826·99	2	Equal intensity in first xenon spectrum	3826, L. & D. Intensity 1.
3826·33	1		
3823·34	1		3824, L. & D. Intensity 1.
3816·93	1		
3815·32	1		3815, L. & D. Intensity 1.
3811·93	1		
3811·19	4		3811, L. & D. Intensity 3.
3808·14	1		
3807·42	1		3807, L. & D. Intensity 1.
3801·86	2		3801, L. & D. Intensity 1.
3801·13	1		
3792·46	1		
3791·82	5		3792, L. & D. Intensity 1.
3787·46	1		3787, L. & D. Intensity 1.

3905 ·71	1		
3903 ·82	2		3903, L. & D. Intensity 1.
3903 ·30	1		
3897 ·88	1		
3895 ·18	6		3894, L. & D. Intensity 3.
3894 ·17	<1		
3893 ·59	<1		
3892 ·51	1		
3891 ·73	1		
3887 ·14	1		
3886 ·88	2		
3385 ·54	1		
3885 ·15	4		3885, L. & D. Intensity 3.
3882 ·81	1		
3880 ·60	6		3880, L. & D. Intensity 3.
3879 ·35	1		
3877 ·95	8		3877, L. & D. Intensity 3.
3877 ·12	1		
3869 ·79	2		3870, L. & D. Intensity 2.
3866 ·80	1	Diffused.	
3862 ·71	<1		
3861 ·19	4		3862, L. & D. Intensity 2.
3858 ·67	2		3858, L. & D. Intensity 2.
3856 ·20	<1		
3854 ·44	4		3855, L. & D. Intensity 1.
3849 ·97	3	Diffused	3850, L. & D. Intensity 2.
3848 ·75	2		3849, L. & D. Intensity 1.

			3783, L. & D. Probably 3783 ·28 Krypton II.
3781 ·13	10		3781, L. & D. Intensity 6.
3776 ·46	7		3776, L. & D. Intensity 3.
3774 ·38	<1		
3772 ·68	5		3773, L. & D. Intensity 1.
3771 ·05	1		3770, L. & D. Intensity 1.
3768 ·08	1	*Cf.* Krypton II., 3768·10. Intensity 1.	
3765 ·99	4	*Cf.* Krypton II., 3765·98. Intensity 1.	3766, L. & D. Intensity 1.
3763 ·52	2		3763, L. & D. Intensity 2.
3762 ·43	4		3762, L. & D. Intensity 1.
3758 ·13	1		
3757 ·03	1		3757, L. & D. Intensity 1.
3756 ·14	1		
3751 ·80	1	*Cf.* Krypton II., 3751·81. Intensity 1.	
3750 ·86	4		
3745 ·85	5		3746, L. & D. Intensity 3.
3738 ·04	3		3737, L. & D. Intensity 1.
3736 ·15	1		
3731 ·33	1		3731, L. & D. Intensity 2.
3730 ·29	3		
3728 ·33	1		
3727 ·45	1		
3720 ·93	4		3721, L. & D. Intensity 2.
			3717, L. & D. Not seen, possibly argon 3717.
3715 ·73	1	*Cf.* argon 3715.	

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
3712 ·04	3		3712, L. & D. Intensity 2.	3607 ·58	1		3607, L. & D. Intensity 4.
3711 ·78	2			3607 ·17	5		
3709 ·88	1			3606 ·22	3		
3709 ·07	2			3602 ·03	2		3602, L. & D. Intensity 1.
3708 ·29	3		3708, L. & D. Intensity 1.	3601 ·21	3		
3706 ·32	1			3596 ·75	5		3597, L. & D. Intensity 3.
3698 ·87	1			3595 ·53	2		
3692 ·75	<1			3593 ·61	1		
3689 ·96	1		3689, L. & D. Intensity 1.	3592 ·14	1		
3676 ·75	7		3677, L. & D. Intensity 3.	3591 ·34	1		
3672 ·68	2		3673, L. & D. Intensity 2.	3589 ·40	<1		
3669 ·28	5			3587 ·84	2		
3666 ·90	5			3587 ·45	1		
3665 ·26	1			3584 ·68	1		
3664 ·60	1			3583 ·79	6		3584, L. & D. Intensity 8.
3664 ·05	3		3664, L. & D. Intensity 1.	3579 ·85	6		3580, L. & D. Intensity 8.
3662 ·99	1			3578 ·71	1		
3662 ·44	1			3578 ·14	1		
3661 ·79	2		3662, L. & D. Intensity 2.	3576 ·80	5		
3658 ·97	<1			3575 ·08	1		
3658 ·59	1		3658, L. & D. Intensity 1.	3574 ·56	1		
3658 ·32	<1			3574 ·26	1		

3657 ·88	1			3570 ·31	1		
3654 ·75	5		3655 L. & D. Intensity 2.	3569 ·67	1		
3653 ·27	2			3565 ·35	4		3565, L. & D. Intensity 8.
3649 ·71	4		3650 L. & D. Intensity 1.	3564 ·40	4	*Cf.* Krypton II., 3564 ·38. Intensity 4	
3648 ·47	2			3563 ·15	1		
3646 ·83	<1			3562 ·37	3		
3645 ·05	2		3645 L. & D. Intensity 6.	3561 ·53	3		
3644 ·58	2			3558 ·12	1		
3644 ·29	2			3556 ·64	2		3556, L. & D. Intensity 3.
3641 ·15	4		3641 L. & D. Intensity 2.	3556 ·00	1		
3636 ·17	2			3554 ·60	1		
3635 ·49	1			3553 ·42	1		
3634 ·34	1			3552 ·29	6		3553, L. & D. Intensity 5.
3633 ·87	1	Diffused.		3550 ·21	1		
3632 ·30	4		3632 L. & D. Intensity 2.	3549 ·39	1		
3631 ·44	1			3548 ·35	1		
3628 ·69	2			3547 ·04	1		
3624 ·21	8		3624 L. & D. Intensity 10.	3545 ·04	2		
3623 ·28	5			3542 ·50	6		3543, L. & D. Intensity 6.
3621 ·75	1			3540 ·09	3		
3620 ·18	2			3537 ·56	3		
3619 ·03	2			3533 ·39	1		
3616 ·02	3		3616 L. & D. Intensity 1.	3531 ·93	1		
3614 ·59	1			3531 ·43	1		
3612 ·52	3		3613 L. & D. Intensity 4.	3530 ·76	1		
3612 ·16	1			3530 ·40	1		
3609 ·60	5		3610 L. & D. Intensity 2.	3528 ·14	1		

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
3527·39	1			3438·28	1		
3526·04	<1			3437·96	1		
3522·98	5		3523, L. & D. Intensity 4.	3437·68	2		
3519·26	3			3435·91	2		
3518·12	1			3435·17	1		
3516·92	1			3432·18	1		
3516·38	1			3431·71	4		
3515·53	1			3430·62	1		
3513·72	3			3429·13	1		
3511·83	1			3428·95	1	*Cf.* Krypton II., 3428·95. Intensity 1.	
3511·60	1			3428·61	1		
3509·05	1		3510, L. & D. Intensity 2.	3428·20	1		
3506·74	1			3426·61	1		
3503·99	1		3504, L. & D. Intensity 1.	3424·88	1		
3501·86	3		3501, L. & D. Intensity 4.	3420·89	4		
3500·53	2			3418·11	<1		
3498·33	1			3413·34	1	Diffused.	
3498·04	4			3409·60	<1	Diffused.	
3495·00	1			3407·76	1		
3494·69	2			3407·25	1		
3488·34	1			3405·62	1		
3483·39	1			3404·06	3		
3479·82	1			3400·02	1		

3479·29	1		
3475·43	1		
3474·42	1		
3472·59	3		
3471·47	1		
3470·73	1		
3470·27	1		
3469·31	1		
3468·35	5	. . . .	3648, L. & D. Intensity 2.
3467·37	5	. . . .	
3463·63	<1		
3462·69	<1		
3461·44	3	. . . .	3641, L. & D. Intensity 1.
3458·90	6		
3455·87	1		
3454·41	7	. . . .	3454, L. & D. Intensity 1.
3452·13	1		
3450·86	1		
3450·19	1		
3446·52	1		
3445·01	1		
3444·61	1		
3444·38	4		
3443·49	1		
3442·08	1	Diffused.	
3440·91	1	Diffused.	
3438·88	1	Diffused.	

3397·65	1	
3396·72	2	*Cf.* Krypton II., 3396·72. Intensity 2.
3395·68	1	
3394·92	2	
3392·73	4	
3390·78	3	
3390·13	1	
3387·26	1	*Cf.* Krypton II., 3387·26. Intensity 1.
3386·89	4	
3385·85	1	
3384·28	3	
3384·07	2	
3381·81	1	
3380·24	3	
3379·20	2	*Cf.* Krypton II., 3379·18. Intensity 1.
3377·17	1	
3374·11	1	
3370·81	1	
3367·64	1	
3366·87	3	Diffused.
3364·82	1	
3363·64	1	
3362·93	1	
3360·20	2	*Cf.* Krypton II., 3360·22. Intensity 2.
3358·13	4	
3356·09	2	
3354·51	1	

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.
3350·53	1	Diffused.	
3349·91	3		
3345·11	1		
3344·41	1		
3340·85	1		
3340·54	3		
3340·23	2		
3339·67	1		
3339·37	1		
3339·17	3		
3339·00	2		
3334·38	1		
3332·97	5		
3331·80	5		
3330·90	6	*Cf.* Krypton II., 3330·88. Intensity = 7.	
3328·45	1		
3327·64	1		
3322·30	6		
3320·21	2		
3319·69	1		
3319·15	1		
3318·76	1		
3317·59	1		
3284·81	1		
3283·75	<1	Diffused.	
3281·33	1		
3280·94	<1		
3280·66	4		
3279·31	<1		
3278·61	3		
3277·41	3		
3276·55	3		
3275·07	2		
3273·89	3		
3273·06	3		
3271·35	1		
3269·57	<1		
3269·11	5		
3268·31	2		
3267·52	1		
3267·19	4		
3266·21	1		
3264·76	4		
3262·18	1		
3260·81	<1		
3260·42	<1		

3316 ·47	1			3259 ·57	4		
3315 ·80	1	*Cf.* Krypton II., 3315 ·80. Intensity 1.		3258 ·04	1		
3315 00	1			3256 ·79	3		
3314 ·41	1			3256 ·39	3		
3313 ·64	1	Diffused.		3253 ·38	5		
3313 ·01	1			3250 ·70	3		
3312 ·34	<1			3249 ·14	<1		
3311 ·95	<1			3248 ·98	<1		
3310 ·52	5			3248 ·76	1		
3306 ·94	3			3247 ·80	5		
3306 ·04	4			3246 ·99	4		
3304 ·19	2			3245 ·17	<1		
3303 ·47	2			3244 ·30	3		
3301 ·65	3			3242 ·98	7		
3300 ·38	1	Diffused.		3241 ·26	1		
3298 ·85	1			3239 ·41	6		
3298 ·06	<1			3237 ·50	1		
3296 ·07	4			3236 ·97	5		
3295 ·63	2			3235 ·85	4		
3294 ·70	<1	Diffused.		3235 ·49	<1		
3294 ·09	1			3234 ·69	1		
3293 ·17	<1			3234 ·36	1		
3291 ·72	1	Diffused.		3233 ·56	<1		
3290 ·44	<1			3233 ·39	1		
3288 ·03	5			3231 ·83	5		
3286 ·17	1			3230 ·80	<1		
3285 ·93	8			3230 ·12	1		

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.
3229 ·21	1		
3227 ·32	4		
3225 ·65	4		
3225 ·26	2		
3223 ·91	1		
3223 ·52	2		
3223 ·14	4		
3222 ·40	1	*Cf.* Krypton II., 3222·40. Intensity = 1.	
3221 ·45	1		
3221 ·18	2		
3219 ·97	<1		
3218 ·13	<1		
3216 ·92	<1	Diffused.	
3214 ·66	1		
3214 ·30	4		
3212 ·68	<1		
3212 ·46	1		
3210 ·40	3		
3209 ·54	4		
3206 ·49	1		
3206 ·21	<1		
3202 ·81	1		
3202 ·17	2		
3168 ·77	<1		
3167 ·67	<1		
3166 ·92	<1		
3166 ·26	1		
3164 ·63	2		
3164 ·43	1		
3163 ·10	2		
3160 ·82	2		
3159 ·97	1		
3156 ·85	2		
3155 ·66	3		
3153 ·58	3		
3153 ·14	4		
3151 ·98	5		
3151 ·11	6		
3150 ·86	6		
3149 ·11	1		
3148 ·17	1	Very diffused.	
3146 ·84	<1		
3145 ·17	1		
3143 ·77	2		
3142 ·69	1		
3141 ·77	2		

3201 ·94	<1	
3201 ·67	3	
3199 ·87	1	
3199 ·39	1	
3198 ·75	4	
3196 ·68	3	
3196 ·37	5	
3195 ·10	<1	
3193 ·86	<1	
3193 ·35	2	
3188 ·80	<1	
3187 ·91	<1	
3187 ·60	2	
3186 ·93	1	
3185 ·93	<1	
3185 ·35	5	
3184 ·74	3	
3184 ·42	2	
3181 ·57	1	
3180 ·62	<1	
3179 ·40	5	
3177 ·27	2	
3176 ·18	3	
3175 ·80	3	*Cf.* Krypton II., 3175·78. Intensity 2.
3175 ·38	5	
3173 ·15	1	Diffused.
3170 ·81	1	
3139 ·21	1	
3138 ·87	1	
3138 ·46	6	
3134 ·86	1	
3132 ·87	1	
3130 ·48	2	Very diffused.
3126 ·90	1	
3125 ·86	2	Equal intensity in first xenon spectrum.
3125 ·12	<1	
3124 ·75	1	
3124 ·15	1	
3122 ·32	1	
3122 ·00	8	
3121 ·15	1	
3119 ·34	1	
3116 ·88	1	
3114 ·56	4	
3113 ·69	<1	
3112 ·87	3	
3108 ·72	1	Diffused.
3107 ·91	2	Very diffused.
3106 ·50	5	
3105 ·75	1	
3104 ·60	3	
3103 ·64	2	
3103 ·38	<1	
3102 ·88	1	

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
3102 ·54	<1			3032 ·63	<1		
3101 ·68	2	Diffused.		3031 ·97	1	Diffused.	
3100 ·04	3			3029 ·91	2		
3098 ·68	1			3029 ·05	1	Diffused.	
3098 ·33	1			3028 ·49	<1		
3097 ·03	1			3027 ·77	1		
3094 ·91	1			3027 ·41	1		
3094 ·69	2			3026 ·66	3		
3093 ·55	1	Diffused.		3023 ·99	5		
3092 ·57	2			3023 ·83	5		
3091 ·22	5			3020 ·47	1		
3090 ·15	3			3019 ·96	<1		
3089 ·07	1			3017 ·89	<1		
3085 ·74	<1			3017 ·58	4		
3083 ·70	6			3015 ·91	1		
3083 ·05	1			3015 ·57	2		
3082 ·74	2			3014 ·77	3		
3080 ·61	3			3014 ·32	2		
3079 ·86	4			3013 ·53	1		
3077 ·82	1			3013 ·05	<1		
3075 ·47	1			3012 ·45	<1		
3073 ·62	4			3011 ·44	<1		
3073 ·31	1			3010 ·85	3		

3071 ·49	3	
3070 ·19	2	
3068 ·71	1	
3067 ·43	4	
3066 ·69	1	
3065 ·33	6	
3063 ·49	2	
3061 ·71	3	
3057 ·16	<1	
3056 ·63	3	
3055 ·42	2	
3054 ·62	4	
3051 ·41	1	
3051 ·14	1	
3049 ·04	1	
3048 ·31	1	
3047 ·93	1	Diffused.
3046 ·40	3	
3045 ·42	3	
3044 ·91	2	*Cf.* Krypton II., 3044 ·92. Intensity 1.
3044 ·36	2	
3042 ·22	3	
3037 ·47	1	
3037 ·00	2	Diffused.
3034 ·36	3	
3033 ·86	1	
3033 ·22	2	
3009 ·16	3	
3004 ·81	1	
3004 ·48	4	
3004 ·11	3	
3002 ·01	3	
3001 ·70	3	
3000 ·12	<1	
2999 ·44	2	
2999 ·24	2	Diffused.
2997 ·69	2	
2995 ·11	1	
2994 ·86	2	
2993 ·07	5	
2991 ·91	<1	
2991 ·65	2	
2991 ·42	3	
2990 ·74	1	
2990 ·48	1	
2987 ·00	2	
2986 ·32	3	
2985 ·72	4	
2984 ·77	4	
2982 ·39	3	
2981 ·47	2	
2980 ·26	<1	
2979 ·48	6	
2976 ·95	<1	

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
2976·58	3			2928·20	<1		
2974·97	2			2927·74	<1		
2973·65	3			2927·30	1		
2972·48	1			2926·27	4		
2971·40	2			2925·58	<1		
2971·08	1			2925·11	<1		
2970·65	3			2924·56	1		
2970·29	1			2924·12	3		
2969·95	2			2923·68	4		
2969·63	1			2922·62	<1		
2969·42	1			2922·10	<1		
2968·74	3			2921·74	<1		
2967·11	3			2920·05	3		
2965·13	3			2918·74	<1		
2964·35	3			2917·76	4		
2963·59	3			2916·81	3		
2961·69	1			2915·87	<1		
2960·93	2	*Cf.* Krypton II., 2960·93. Intensity 2.		2915·22	1		
2960·53	3			2914·28	4		
2959·55	4			2912·56	5	Diffused.	
2957·77	5			2912·06	5		
2956·05	1			2911·63	1		
2955·08	<1			2911·38	<1		

2954 ·84	1		
2954 ·27	3		
2954 ·08	1		
2951 ·73	1		
2950 ·91	<1		
2949 ·88	2	Very diffused.	
2948 ·23	4		
2947 ·69	5		
2946 ·52	1		
2945 ·71	2		
2945 ·41	5		
2944 ·78	1		
2943 ·59	2		
2943 ·07	1		
2942 ·25	4		
2941 ·55	3		
2940 ·37	5		
2939 ·89	3		
2939 ·29	4		
2938 ·38	<1		
2937 ·61	<1		
2936 ·03	6		
2934 ·98	1		
3932 ·92	4		
2932 ·27	3		
2930 ·44	5		
2929 ·41	1		

2910 ·54	1		
2907 ·35	4		
2906 ·71	5		
2905 ·26	<1	Diffused.	
2904 ·79	<1		
2904 ·32	1		
2902 ·84	1		
2902 ·47	1		
2900 ·59	1		
2899 ·56	<1		
2898 ·97	<1		
2893 ·65	1		
2898 ·19	1		
2897 ·85	1		
2896 ·79	4		
2896 ·20	<1		
2895 ·40	4		
2891 ·86	4		
2890 ·81	<1		
2890 ·14	2		
2889 ·22	2		
2888 ·74	<1		
2887 ·29	2		
2886 ·86	3		
2884 ·39	<1		
2883 ·89	2		
2879 ·94	1		

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
2877 ·87	1			2827 ·06	2	Diffused.	
2873 ·65	2			2826 ·18	4		
2872 ·91	1			2824 ·25	1		
2871 ·85	4			2822 ·67	2		
2871 ·43	3			2822 ·36	1		
2871 ·27	5			2820 ·22	1		
2869 ·71	<1			2819 ·87	2		
2868 ·61	1			2817 ·51	3		
2867 ·55	1			2816 ·10	5		
2866 ·96	1			2814 ·62	6		
2864 ·92	4	Diffused.		2811 ·81	3	*Cf.* **Krypton II., 2811 ·81.** Intensity 2.	
2864 ·32	1			2810 ·67	2		
2864 ·00	<1			2810 ·00	<1		
2862 ·56	3			2809 ·68	1		
2862 ·06	1			2809 ·23	3		
2858 ·03	1			2808 ·77	1		
2857 ·29	<1	Diffused.		2807 ·39	4		
2856 ·80	1			2806 ·83	<1		
2855 ·92	1			2805 ·24	1		
2855 ·42	<1			2804 ·82	1		
2854 ·70	4	Diffused.		2803 ·15	2		
2853 ·78	1			2800 ·37	5		
2853 ·28	<1			2798 ·01	2		

2852·55	2	Diffused.
2851·10	1	
2850·41	1	
2847·81	4	
2846·63	2	Diffused.
2846·07	2	
2845·26	2	
2844·60	3	*Cf.* Krypton II., 2844·59. Intensity 3.
2844·28	1	
2841·46	<1	
2841·10	1	*Cf.* Krypton II., 2841·10. Intensity 1.
2840·22	<1	
2839·75	2	
2838·99	2	
2838·55	1	
2837·03	<1	
2836·32	<1	
2835·16	<1	
2833·32	2	
2833·08	1	
2832·59	<1	
2832·19	<1	
2829·35	1	
2828·84	1	
2828·37	1	
2828·01	1	
2827·62	4	
2797·74	1	
2797·29	3	
2796·73	2	
2795·00	5	
2789·64	1	
2785·95	1	
2785·53	1	
2785·10	1	
2783·49	4	
2782·86	2	
2782·45	1	
2780·86	1	
2780·02	1	
2779·78	2	
2778·11	3	
2777·10	4	
2774·99	3	
2774·02	1	
2773·68	2	
2772·51	4	
2770·56	1	
2769·35	2	
2767·96	1	
2767·71	1	
2766·33	2	
2766·10	1	
2763·71	<1	

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
2763 ·18	1			2703 ·58	4		
2762 ·90	2			2702 ·48	3		
2761 ·73	4			2701 ·99	1		
2760 ·88	3			2701 ·71	1		
2759 ·87	<1			2699 ·29	1	Diffused.	
2759 ·36	3			2697 ·70	1		
2758 ·55	1			2696 ·72	4	*Cf.* Krypton II., 2696 ·71. Intensity 4.	
2758 ·02	3	Diffused.		2696 ·08	1		
2757 ·76	1	Diffused.		2695 ·52	1		
2756 ·64	1	*Cf.* Krypton II., 2765 ·66. Intensity 1.		2695 ·28	1		
2755 ·08	3			2694 ·27	2		
2754 ·80	2			2691 ·92	1	*Cf.* Krypton II., 2691 ·94. Intensity 1.	
2754 ·05	<1			2691 ·63	1		
2751 ·09	1			2691 ·41	1		
2748 ·96	<1	Diffused.		2690 ·33	1	*Cf.* Krypton, 2690 ·35. Intensity 1.	
2748 ·02	3			2689 ·82	1	Diffused.	
2744 ·26	1			2687 ·12	3		
2743 ·71	<1			2685 ·73	1		
2743 ·24	1	Diffused.		2685 ·49	<1		
2740 ·93	3			2682 ·84	1	Very diffused.	
2739 ·91	1			2680 ·12	1		
2739 ·40	1			2679 ·57	<1		
2737 ·18	2			2678 ·70	2		

2734 ·31	5	Diffused.
2734 ·11	1	
2733 ·36	4	Diffused. *Cf.* Krypton II., 2733 ·38. Intensity 4.
2732 ·48	1	*Cf.* Krypton II., 2732 ·46. Intensity 1.
2731 ·61	1	
2728 ·37	2	
2727 ·38	3	
2725 ·45	2	
2724 ·71	<1	
2723 ·56	<1	
2723 ·09	1	
2720 ·41	1	
2718 ·92	<1	
2717 ·47	7	
2715 ·91	1	
2715 ·07	4	
2714 ·20	<1	
2713 ·50	1	
2712 ·06	1	
2711 ·69	2	Diffused.
2711 ·16	1	
2708 ·65	3	
2707 ·49	2	Very diffused.
2707 ·15	1	
2706 ·89	2	
2704 ·61	1	

2677 ·29	8	*Cf.* Krypton II., 2677 ·30. Intensity 2.
2676 ·22	<1	
2675 ·51	<1	
2673 ·95	2	Very diffused.
2672 ·35	3	
2670 ·80	2	*Cf.* Krypton II., 2670·78. Intensity 1.
2670 ·40	1	
2669 ·12	4	
2668 ·14	3	
2665 ·30	1	
2664 ·97	1	
2664 ·61	<1	Diffused.
2663 ·43	2	
2662 ·60	<1	Diffused.
2661 ·99	<1	
2661 ·14	2	
2659 ·51	1	
2658 ·37	2	
2655 ·57	1	
2653 ·47	<1	
2652 ·93	1	
2652 ·28	2	Diffused.
2651 ·69	1	
2650 ·34	1	
2649 ·76	1	
2648 ·79	1	*Cf.* Krypton II., 2648·80. Intensity 1.
2643 ·89	1	Very diffused.

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.	Wave-length.	Intensity.	Remarks.	Other observers.
2643·56	1			2581·84	1	Diffused. *Cf.* Krypton II., 2581·81 Intensity 1.	
2642·68	1			2578·80	2		
2641·25	3			2578·51	3		
2639·30	2			2577·11	3		
2637·63	3			2574·18	1	Very diffused.	
2636·95	2			2573·06	1		
2636·58	2			2572·46	2	*Cf.* Krypton II., 2572·14. Intensity 1.	
2635·78	1			2570·41	1		
2635·20	<1			2569·53	1		
2634·33	3			2568·94	2		
2634·05	1			2567·62	<1		
2633·53	<1			2567·25	1		
2630·56	2			2565·09	<1		
2629·70	3	Diffused.		2564·12	1		
2627·10	1			2561·04	2		
2626·12	1			2560·11	1		
2624·65	1	*Cf.* Krypton II., 2624·63. Intensity 1.		2557·91	1		
2623·31	1	Diffused.		2556·30	1		
2621·88	1			2551·85	2		
2621·52	1			2550·70	1		
2620·07	<1			2549·92	3		
2619·83	1			2549·05	1		
2617·06	1			2546·89	<1		

2616 ·79	1	*Cf.* Krypton II., 2616·80. Intensity 2.
2615 ·83	1	
2615 ·54	1	
2614 ·13	3	
2612 ·61	1	Diffused.
2611 ·17	1	
2610 ·73	1	
2609 ·04	3	
2607 ·68	1	
2607 ·09	2	
2605 ·69	10	
2600 ·29	3	
2599 ·77	<1	
2598 ·59	3	Diffused.
2597 ·14	4	Diffused.
2595 ·19	1	
2595 ·81	1	
2593 ·70	<1	
2591 ·84	2	
2591 ·26	1	
2590 ·59	3	
2588 ·52	1	
2587 ·72	1	
2585 ·45	1	
2584 ·04	1	
2583 ·90	1	
2582 ·74	1	

2546 ·57	1	Diffused.
2544 ·27	1	
2542 ·03	1	
2541 ·22	<1	
2539 ·08	1	
2538 ·16	1	
2537 ·04	2	
2536 ·08	2	
2533 ·47	2	
2531 ·45	1	Diffused.
2530 ·33	1	
2527 ·10	4	
2526 ·97	4	
2524 ·58	2	
2524 ·13	2	
2521 ·58	1	
2520 ·28	1	
2519 ·17	3	Diffused.
2517 ·21	1	Diffused.
2515 ·26	1	
2514 ·85	<1	
2514 ·70	<1	
2514 ·16	1	Diffused.
2513 ·52	1	Diffused. *Cf.* Krypton II., 2513 ·50. Intensity 1.
2511 ·43	1	Diffused.
2510 ·65	2	

TABLE VIII.—Second Xenon Spectrum, with Leyden Jar and Spark Gap—continued.

Wave-length.	Intensity.	Remarks.	Other observers.
2509 ·89	<1		
2505 ·05	1		
2501 ·16	2		
2498 ·20	1		
2495 ·27	1		
2494 ·11	3	*Cf.* Krypton II., 2494 ·10. Intensity 2.	
2493 ·60	<1		
2493 ·18	1		
2492 ·69	<1		
2491 ·93	2	Diffused.	
2490 ·89	4	Diffused.	
2490 ·23	4	Diffused.	
2486 ·86	1		
2486 ·46	4		
2485 ·13	1		
2483 ·59	1		
2479 ·98	1		
2479 ·25	1		
2476 ·02	10		
2472 ·50	1		
2471 ·42	2		
2470 ·30	2		
2469 ·57	2	Diffused.	
2468 ·54	2	*Cf.* Krypton II., 2468 ·56. Intensity 2.	
2463 ·72	1		
2463 ·14	1		
2455 ·19	1		
2454 ·40	1	Diffused.	
2452 ·76	2		
2451 ·50	1		
2451 ·02	1		
2449 ·16	1		
2448 ·63	1		
2447 ·79	1		
2447 ·21	1		
2446 ·23	1		
2436 ·63	1		
2435 ·59	1	Diffused.	
2433 ·75	1		
2432 ·87	1		
2429 ·11	1		
2425 ·18	2	Very diffused. *Cf.* Krypton II., 2425 ·16. Intensity 1.	
2423 ·08	1		
2422 ·28	3		
2421 ·36	1		
2418 ·83	1		
2418 ·47	1		
2416 ·86	1		
2414 ·88 &c.	1		

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ON THE DISCHARGE OF ELECTRICITY FROM HOT PLATINUM

BY

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VII. *On the Discharge of Electricity from Hot Platinum.*

By Harold A. Wilson, *D.Sc., B.A., Fellow of Trinity College, Cambridge.*

Communicated by C. T. R. Wilson, *F.R.S.*

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The following paper contains an account of the results obtained in a series of experiments on the loss of electricity from hot platinum in several gases at various pressures. I shall begin by giving a brief account of some of the results obtained by previous workers on this subject, confining myself to those results which appear to bear more or less directly on the present investigation. Further information on the results of the earlier investigations may be found in Wiedemann's 'Elektrizität,' vol. 4, in J. J. Thomson's 'Recent Researches,' in Stark's 'Die Elektrizität in Gasen,' and in the papers referred to.

Elster and Geitel ('Wied. Ann.,' vol 37, p. 315, 1889) found that hot platinum, in air and oxygen, produces positive electrification of the surrounding gas and bodies immersed in it, except at low pressures, when negative electrification is obtained. In hydrogen they found the electrification is always negative.

J. J. Thomson ('Phil. Mag.' [5], vol. 29, pp. 358-441, 1890) measured the current due to a constant P.D. between two parallel platinum plates immersed in various gases and vapours at a bright red heat. He found that the current depends very greatly on the nature of the gas. Gases which dissociate into atoms when heated, such as HCl and salt vapours, conduct very much better than gases such as air and ammonia, which do not dissociate into atoms. Unless both electrodes are hot enough to glow, very little current can be obtained.

Arrhenius ('Wied Ann.,' vol. 42, p. 18, 1891) measured the current between two parallel platinum plates immersed in a Bunsen flame, by which they were kept at a bright red heat. He found that the current with increasing P.D. increases at first proportionately to the P.D., but when the P.D. is more than one or two volts, the curve connecting the current and P.D. bends over, and then becomes nearly parallel to the axis of P.D. The current is greatly increased when an alkali salt vapour is introduced into the flame. He investigated the relative conductivities due to various salts, but it is not necessary to describe here the results he obtained, since they do not bear directly on the present investigation.

The results obtained by Arrhenius were confirmed and extended in a research by

Professor A. SMITHELLS, Dr. H. M. DAWSON, and the writer ('Phil. Trans.,' A, vol. 193, pp. 89–128). Using as electrodes two concentric cylinders of platinum, it was found that the current was much greater when the outer cylinder was made the kathode than when it was made the anode. Also when the electrodes were simply connected to the galvanometer a current was observed from the inner to the outer cylinder through the flame. Phenomena of this kind have been known for a long time to occur when metal electrodes are immersed in a flame. They are evidently closely analogous to the effects described by ELSTER and GEITEL, referred to above.

The discharge of electricity from platinum immersed in a Bunsen flame was further investigated by the writer ('Phil. Trans.,' A, vol. 192, pp. 499–528). In this paper it is shown that the ions concerned in the discharge between hot platinum electrodes immersed in a flame are nearly all produced at the surface of the platinum, and that the negative ions have a much greater velocity, due to an electric field, than the positive ions. Consequently, nearly all the current is carried by negative ions which start at the negative electrode. These results enable the polar properties of the conductivity of flames to be very simply explained. Hot platinum in a flame consequently discharges negative electricity very much more readily than positive electricity.

In the 'Phil. Mag.' for December, 1899, J. J. THOMSON gave an account of some experiments on the ratio of the charge (e) to the mass (m) of the negative ions emitted by a hot carbon filament in a vacuum. He found that it is impossible to obtain consistent results unless precautions are taken to ensure that the filament is in an atmosphere of pure hydrogen. The cause of this is the gas evolved by the filament when it is heated. He found that by heating the filament for a long time, and repeatedly pumping out the apparatus and letting in pure hydrogen, regular results could be obtained. When this had been done, the filament only lost negative electricity, whereas before it lost sometimes only positive and sometimes only negative, and sometimes both. He found that e/m was equal to about 10^7, which is nearly the same as e/m for kathode rays, so that it is clear that the filament emits negatively charged corpuscles or electrons. The importance of taking such precautions as those described by Professor THOMSON, in experiments on the leak from hot wires at low pressures, is very great. Unless this is done, the gases evolved by the wire fill the apparatus, and the leak observed is very irregular in its behaviour. It is probable that the gas evolved by platinum wires is mainly composed of hydrogen, which, as will be shown below, has a very large effect on the leak, even when present in very small quantities.

A further investigation of the leak from hot platinum was published by the writer in 1901 ('Phil. Trans.,' A, vol. 197, pp. 415–441). In this paper it is shown that hot platinum in air at atmospheric pressure in general discharges positive more readily than negative electricity, and that the rate of discharge at constant temperature falls off gradually with the time and ultimately becomes very small compared with its original value. The current between platinum electrodes in air with a constant P.D. increases rapidly with rise of temperature. If x_1 is the current (due to a small P.D.) at the absolute temperature θ_1, and x_2 that at θ_2, and Q the energy required to produce a gramme molecular weight of positive and negative ions, then it is shown that

$$Q\left\{\frac{1}{\theta_1}-\frac{1}{\theta_2}\right\}=2\log\frac{x_2^2\theta_1}{x_1^2\theta_2};$$

and Q is found to be nearly independent of the temperature, so that we may put $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/4\theta}$, where A is a constant quantity. This formula is deduced on the assumption that the air close to the surface of the platinum dissociates into ions.* The value found for Q is 60,000 small calories. This gives 2·6 volts for the P.D., through which the ionic charge must fall to obtain enough energy to ionize one molecule of air in contact with hot platinum. [When a large P.D. is used, so that the current is the maximum, the appropriate formula is $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$, p. 259 *infra.*]

It is also shown in this paper that the maximum current between hot platinum electrodes immersed in a stream of an alkali salt vapour is equal to the current required to electrolyse in a solution the amount of salt passing between the electrodes.† It is therefore clear that the leak is due to the ionization of the salt in contact with the platinum.

Professor McClelland, in 1902, published the results of some experiments on the leak from hot platinum in air at comparatively low pressures ('Proc. Camb. Phil. Soc.,' vol. 11, Part IV., p. 296). A fine platinum wire surrounded by a cylindrical electrode could be heated by passing a current through it. The current from the wire to the electrode was measured with various differences of potential between them. It was found that, at pressures below 1 millim., the current is much greater when the wire is negatively charged than when it is positively charged. The current with the wire positively charged is nearly independent of the P.D. between the limits 40 and 200 volts, but above 200 volts it rises rapidly with the P.D. When the wire is negatively charged, the current at $\frac{2}{3}$ millim. always rises rapidly with the P.D., but at $\frac{1}{10}$ millim. the rate of rise diminishes as the P.D. increases. These results can be explained by supposing that the ions coming from the wire produce others by colliding with the gas molecules when the electric intensity is large enough. This effect was discovered by Professor Townsend‡ for the ions produced in air by Röntgen rays, and it was shown by him that the negative ions produce others by collisions when the electric intensity is comparatively small. The intensity required to make the positive ions produce others by collisions is probably nearly that required to start an ordinary discharge through the gas, but in McClelland's

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* No assumption need be made as to the nature of the ions; they may be molecules, atoms or corpuscles carrying the ionic charge $e = 3 \times 10^{-10}$ E.S. unit.

† See also "The Laws of Electrolysis of Alkali Salt Vapours," 'Phil. Mag.,' August, 1902.

‡ 'Phil. Mag.,' February, 1901.

experiments the electric intensity near the fine wire approaches this value even when the P.D. is only 100 volts or less.

McClelland states in this paper that the negative leak from the wire is nearly independent of the air pressure from $\frac{1}{25}$ millim. to $\frac{1}{240}$ millim., and he suggests that the negative leak at low pressures is caused by the escape of negative ions from the metal.

Mr. O. W. Richardson ('Proc. Camb. Phil. Soc.,' vol. 11, Part IV., 1902, p. 286) has published the results of a series of measurements of the negative leak from hot platinum in gas at low pressures. He finds that the variation of the leak with the temperature can be represented by a formula of the type $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$. This formula Richardson deduces from the assumption that the platinum contains negative corpuscles which can only get through the surface layers when their velocity exceeds a definite value. The value he obtains for Q corresponds to a fall of the ionic charge through 4·1 volts, which does not differ much from the value 2·6 volts found by the writer in air at atmospheric pressure. According to Richardson's theory, Q is the energy required to drive a gramme molecular weight of the corpuscles out of the metal through the surface layers. It is shown below that the formula $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$ can be deduced without making any further assumption than that ions are produced at the surface of the metal, so that the agreement of the experimental results obtained with this formula cannot be regarded as evidence in favour of any particular theory with regard to the way in which the ions are produced. Richardson also shows that on his theory it is possible to deduce from the constant A in the above equation the number (n) of corpuscles in a cubic centimetre of the platinum. He obtains $n = 1{\cdot}3 \times 10^{21}$, which is of nearly the same order of magnitude as the values of n deduced from experiments* on the variation of the electrical resistance of platinum in a magnetic field. Richardson has recently read a paper† before the Royal Society on this subject, in which he has examined the negative leak from some other metals besides platinum in gas at low pressures. The results with platinum described in that paper are the same as those just referred to. In all these experiments the positive leak was very small compared with the negative leak.

W. Wien ('Annalen der Physik,' vol. 8, 1902, p. 244) has described some experiments on the leak from hot platinum wires in high vacua. He finds that even in a very good vacuum a hot wire can still discharge electricity to a distant small electrode if it is charged to a rather high potential. In the best vacuum the P.D. necessary was 800 volts for negative electricity and 3000 volts for positive.

According to C. D. Child ('Phys. Review,' Nos. 4 and 5, 1902) the negative leak from a hot platinum wire, using a large P.D., increases very rapidly with diminishing pressure from one atmosphere down to a small fraction of a millimetre of mercury. It will be shown below that this large increase is due to ionization by collisions with

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* Patterson, 'Phil. Mag.,' June, 1902.

† See 'Phil. Trans.,' A, vol. 201, 1903.

the gas molecules, and that below a certain pressure the leak in air diminishes with the pressure unless the P.D. used is too small to produce ions by collisions.[*]

In the following paper the results are given of experiments on the variation of the leak from hot platinum wires with the temperature of the wire, the pressure of the gas, and the nature of the gas. Some results are also given on the leak from a hot palladium wire. The rest of the paper is divided into the following sections:—

(1.) Description of apparatus, &c.
(2.) The leak in air, nitrogen and water vapour.
(3.) The variation of the negative leak with the temperature.
(4.) The leak in hydrogen.
(5.) The leak from palladium in hydrogen.
(6.) Summary of principal results.
(7.) Conclusion.

(1.) *Description of Apparatus, &c.*

The apparatus used is shown in fig. 1. The leak was measured from a platinum wire PP to a thin cylinder of platinum AB surrounding it. The cylinder was

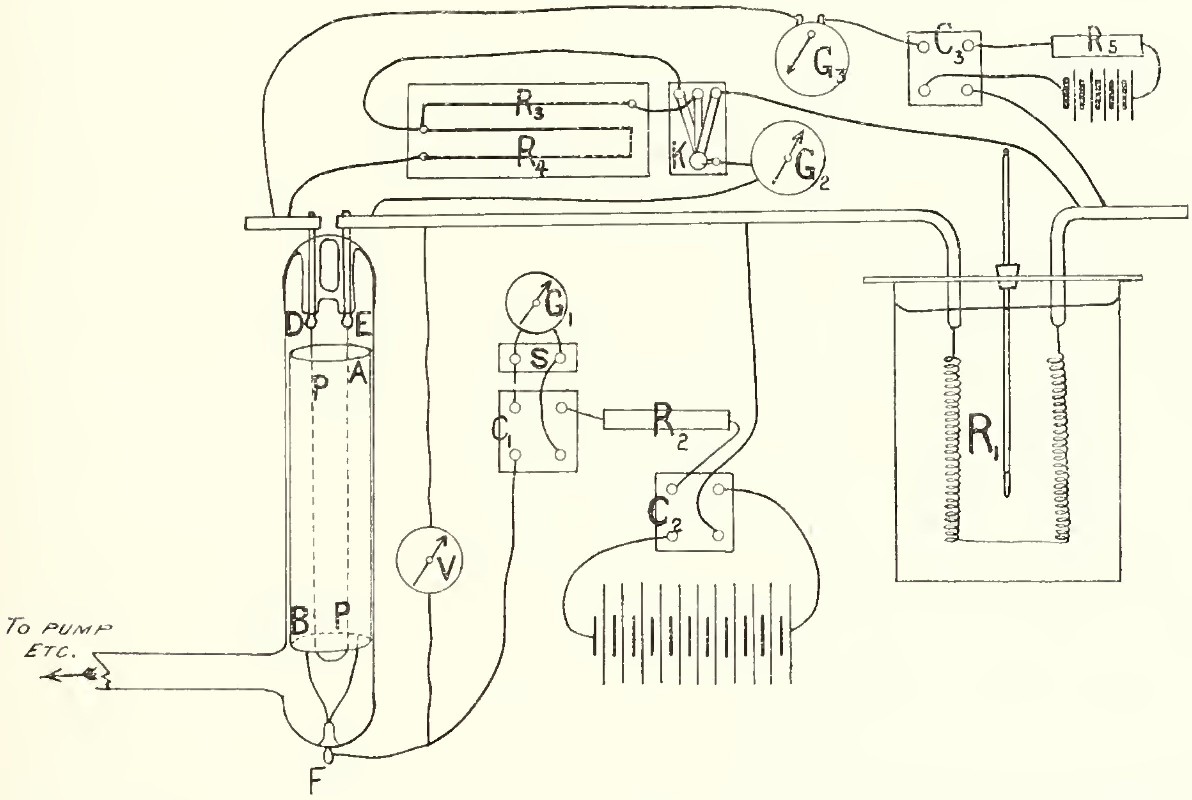

Fig. 1. PP, platinum wire; V, voltmeter; $C_1C_2C_3$, commutators; R_5, rheostat; G_3, ammeter; AB, cylinder; K, key; $R_1R_2R_3R_4$, resistances; G_1G_2, galvanometers; S, shunt.

1·4 centim. in diameter and 5 centims. long. The wire PP was in the form of a loop hanging vertically downwards. The cylinder was contained in a glass tube which

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[*] Child also made measurements in hydrogen and found the leaks greater in hydrogen than in air. He did not measure the temperature of his wire, so that his results are purely qualitative.

fitted it loosely and was welded to two platinum wires sealed through the end of the tube at F. The loop was welded to two platinum wires D and E, which were sealed through the other end of the tube as shown. These wires were each 1 millim. thick and 2 centims. long, and the current used to heat the loop entered through them.

The cylinder was connected through a reversing commutator to an Ayrton-Mather galvanometer G_1, and then through a liquid resistance of about 10^5 ohms and another reversing commutator to one pole of a battery of small secondary cells, the other pole of which was connected to the loop. The P.D. between the loop and cylinder was measured by means of an electrostatic voltmeter V.

The resistance of the loop was measured by means of a Wheatstone's bridge arrangement. The loop was connected in series with a resistance coil R_1 of thick German silver wire spirals immersed in a jar of paraffin oil, the temperature of which was indicated by a normal thermometer.

The coil R_1 and the loop formed two arms of the bridge, and for the other two arms the coils of a P.O. box were used. The coil R_1 had a resistance of about 1·3 ohms, and 1000 or 200 ohms was usually used for the adjacent arm in the box. The fourth arm then had a value, usually several thousand ohms, depending on the resistance of the loop. The current through the loop, which nearly all passed through the coil R_1, was supplied by a battery of from 4 to 10 secondary cells, and was measured by means of a Weston ammeter. Another Ayrton-Mather galvanometer was used with the bridge arrangement, and was connected to the wire E and the opposite corner of the bridge. A key was used with this galvanometer, which closed first the two arms of the bridge in the P.O. box and then the galvanometer circuit. In this way the current only passed through the coils in the box when the key was pressed down. The resistance of these coils was so large compared with that of R_1 and the loop that no appreciable change in the current through the loop occurred when the key was pressed down. A rheostat in the battery circuit enabled the current through the loop to be varied, and the method used was to give the resistance of the variable arm of the bridge the desired value, and then by altering the current through the loop by means of the rheostat balance the bridge. At high temperatures the bridge was very sensitive and the resistance of the loop could easily be kept constant to one part in 5000 by adjusting the rheostat. When it was desired to measure the resistance of the loop cold, a single Leclanché cell in series with a resistance of 10 ohms was substituted for the secondary cells, and the variable arm of the bridge adjusted till a balance was obtained. This measurement could be made to one part in a thousand. The temperature of the loop was got in this case by a thermometer placed close to the tube, and whenever possible this measurement was made with the apparatus filled with gas at atmospheric pressure, because at low pressures a very small current is sufficient to heat the loop appreciably. The current through the loop in this case, therefore, was only kept on for a few seconds at a time, in order to prevent the loop from being heated above the surrounding temperature.

The resistance of 0° C. was calculated from the resistance at the temperature of the room, using the known value (0·0038) of the temperature coefficient at low temperatures of the wire used. The loop and wires D and E were made from pure platinum supplied by Messrs. JOHNSON, MATTHEY and Co.

The temperature of the loop was deduced from its resistance in the following manner. The temperature coefficient of the wire used was determined by measuring the resistance of a piece of the wire cold and at the melting-point of pure K_2SO_4, which, according to HEYCOCK and NEVILLE, is 1066° C. The wire was hung horizontally, and screened from air currents, and a minute particle of K_2SO_4 put on it and observed through a microscope. It was then heated by passing a current through it until the particle of K_2SO_4 just began to melt, and its resistance when this occurred was measured by the bridge arrangement just described. This was done with a particle at several points along the wire, and the mean of the resistances when the particles melted, which were all very nearly the same, was taken to be the resistance at 1066° C.

The following are the results of one experiment of this kind:—

Resistance in variable arm of bridge required to balance resistance of 18 centims. of wire, 0·2 millim. in diameter, at 19° C., 1014 ohms.

Resistances required at 1066° C.: (1) 4098, (2) 4100, (3) 4102; Mean 4100 ohms.

Resistance at 0° C. $= \frac{1014}{1 + 19 \times 0 \cdot 0038} = 945 \cdot 7$.

Hence mean temperature coefficient of the wire between 0° C. and 1066° C. is

$$\frac{3154 \cdot 3}{1066 \times 945 \cdot 7} = 0 \cdot 003129 \text{ ohm per ohm at } 0^\circ \text{ C.}$$

The "platinum temperature" of the wire loop in any experiment was first calculated from its resistances at 0° C. and at the required temperature by means of the formula $R = R_0 (1 + \alpha pt)$, where R_0 is the resistance at 0° C., R that at the required temperature (pt), and α the coefficient 0·003129. The "platinum temperatures" so determined were corrected to the centigrade scale by means of a table of corrections. These corrections were obtained by determining the resistance of the wire at the melting-point of platinum, which was taken to be 1820° C. This was done by heating a wire loop in the apparatus described above until it just melted. The wire was heated in a vacuum and the current increased (very gradually when close to the melting-point), and the resistance measured until the wire just melted. This method gave sufficiently concordant results. The following are the numbers obtained in two experiments of this kind:—

(1) Balancing resistance at 15° C. for wire 0·1 millim. in diameter and about 13 centims. long, 1320 ohms.

Ditto when just on point of melting, 7615 ohms.

$$\text{Hence } R_0 = \frac{1320}{1 + 15 \times 0 \cdot 0038} = 1248 \cdot 8 \text{ ohms},$$

$$pt = \frac{R - R_0}{R_0 \alpha} = \frac{6366}{1249 \times 0 \cdot 003129} = 1629^\circ \text{ on the platinum scale used.}$$

(2) Balancing resistance at 18° C. for wire 0·2 millim. in diameter and about 13 centims. long, 694 ohms.

Ditto when just melting, 4000 ohms.

$$\text{Hence } R_0 = \frac{694}{1 + 18 \times 0 \cdot 0038} = 650 \cdot 4 \text{ ohms},$$

$$pt = \frac{3349 \cdot 6}{650 \cdot 4 \times 0 \cdot 003129} = 1647^\circ \text{ on the platinum scale used.}$$

The mean of these two results, 1638°, was taken to be the melting-point of platinum on the platinum scale used. The correction to the centigrade scale at the melting-point of platinum is therefore 1820 − 1638 = + 182°.

The correction at other temperatures was calculated from this by means of a parabolic difference formula as used by CALLENDAR and GRIFFITHS,

$$t - pt = A\left(\frac{t}{1066} - 1\right)\frac{t}{1066},$$

where t = temperature centigrade, pt = temperature on platinum scale used, A = a constant.

The constant A is given by the equation $182 = A\,(\frac{1820}{1066} - 1)\,\frac{1820}{1066}$, which gives A = 151. The following table gives the values of the correction at several temperatures :—

Temperature.	Correction.	Temperature on platinum scale.
° C.	°	°
1066	0	1066
1100	5	1095
1200	22	1178
1300	40	1260
1400	62	1338
1500	87	1413
1600	114	1486
1700	143	1557
1800	176	1624
1820	182	1638

A curve was plotted from these numbers giving the correction in terms of the temperature on the platinum scale. The following table gives some values of the correction taken from this curve :—

Temperature on platinum scale.	Correction.	Temperature.
°	°	° C.
1066	0	1066
1100	6	1106
1200	26	1226
1300	50	1350
1400	83	1483
1500	120	1620
1600	164	1764
1638	182	1820

The temperatures so determined in this way are subject to an error due to the ends of the wire being cooled by the thicker electrodes to which they are welded. There is also an error due to the resistance of these electrodes being measured along with the wire and changing with the temperature. These errors are, however, almost entirely eliminated by the method of standardising the wire adopted, for the wire was standardised under nearly the same conditions as it was used under in the experiments, consequently these errors are reduced to almost zero at 1066° and at 1820°, and are therefore very small at the intermediate temperatures. The numbers obtained consequently represent very nearly the temperature of the wire at some distance from the electrodes. There was no appreciable error due to thermo-electric effects.

It was found that after a wire had been just fused, as described above, the whole length of the wire, except about 1 centim. at each end, showed signs of fusion, although as soon as any part of the wire fused completely it broke, and so stopped the current. The wires used were always about 13 centims. long, but in calculating the leak per sq. centim. of platinum surface, their length was taken as 1 centim. less than their actual length to allow for the cooling of the ends near the electrodes. This amounts to counting the 1 centim. of wire at each end as leaking half as much per unit area as the rest of the wire.

The tube containing the platinum wire was sealed on to a tube which communicated with a Töpler pump and McLeod gauge. The connecting tubes between the different parts of the apparatus were made short to enable the gas to get into equilibrium as quickly as possible.

The methods used for preparing and purifying the different gases used will be described in the following sections.

(2.) *The Leak from Hot Platinum in Air, Nitrogen, and Water Vapour.*

The results obtained with air will first be described. The air was passed slowly through tubes containing soda-lime and calcium chloride and then let into the apparatus through a good mercury-sealed tap. A bulb containing phosphorus pentoxide was sealed on to the apparatus near the tube containing the hot wire. The P_2O_5 used was a specially good sample, which was found to be quite free from lower oxides and contained no lumps of meta-phosphoric acid. In some of the earlier experiments a small tube packed tightly with gold leaf was put in between the hot wire tube and the rest of the apparatus to absorb mercury vapour. About 50 gold leaves were packed into a tube 1 centim. in diameter and 3 centims. long, and it was found that the gold near the end of the tube next the pump and gauge became amalgamated, whereas the rest of the gold remained for months perfectly bright. I believe that such a tube entirely prevents the diffusion through it of mercury vapour, and that previous failures in using this method of absorption are due to too few gold leaves having been used and not sufficiently tightly packed. Of course, such a tube does not allow very free communication between its ends, so that some little time has to be allowed to elapse after changing the pressure in the apparatus before making any measurements. It was found that the leak was very little affected by the absorption of the mercury vapour, so that in the later experiments this gold-leaf tube was abandoned. Some of the experiments in which the gold leaf was used will be described in the section on the leak in hydrogen.

In the earlier experiments very inconsistent results were often obtained. This was found to be due to gas, probably mostly hydrogen, given off by the wire when heated. A very small quantity of hydrogen has a very large effect on the leak, as will be shown in Section (4). When the platinum wire is welded to its electrodes it is heated in a blow-pipe flame, and probably absorbs some hydrogen, which is afterwards given out when the wire is heated in a vacuum. A new wire was generally found to give very large leaks, which varied in an irregular manner with the time. Long-continued heating in a good vacuum ultimately nearly gets rid of these irregularities, but long continued heating also causes the wire to disintegrate, and its surface becomes roughened and covered with a network of deep cracks. It was found that the irregular behaviour of the wire could be entirely got rid of without long continued heating by the simple process of boiling it in strong nitric acid, after welding it to its electrodes and sealing them into the tube. The tube was about half filled with pure nitric acid and boiled over a spirit lamp for a few minutes, the acid then poured out, and the process repeated two or three times. The tube was then washed out with distilled water. If the platinum loop had been bent by the boiling process, it was straightened by a clean platinum wire hook introduced through the side tube, and then the tube was sealed on to the pump and gauge, &c. The apparatus was then pumped out and filled up with air several times, and then on heating the wire the negative leak at once took up an almost steady value. The positive leak was very small, and did not fall off with the time after the first few seconds. The process of filling the apparatus with air and pumping out several times with the wire kept hot all the time was repeated at frequent intervals to ensure that the apparatus should only contain pure dry air.

Fig. 2 shows the way in which the leak from the hot wire varies with the P.D. at pressures of 766, 211, and 27 millims. of mercury, the wire being negatively charged. When the P.D. is small, the current is nearly independent of the P.D., but with larger P.D.'s the current rises rapidly with the P.D., the rate of rise being greater the lower the pressure. The temperature of the wire in this case was 1648° C., and the wire was 13 centims. long and 0·1 millim. in diameter.

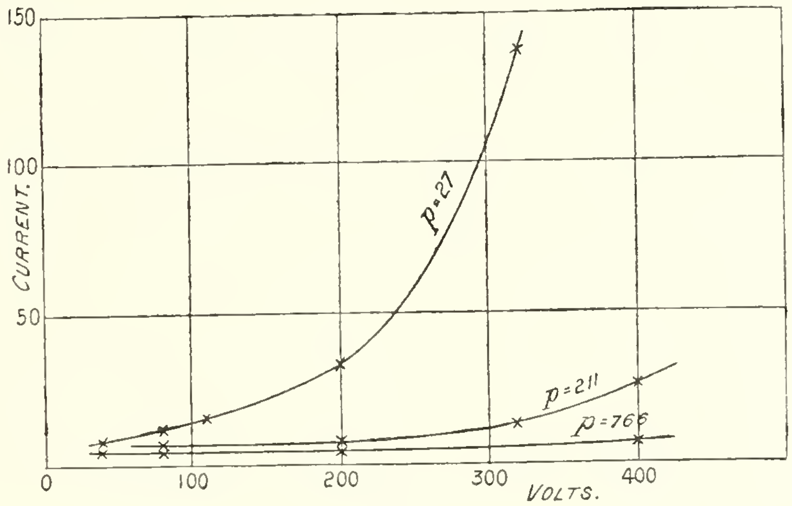

Fig. 2.

Fig. 3 shows the variation of the negative leak with the P.D. at pressures of 0·0036, 0·18, 0·29, 0·49, 0·81, and 12·1 millims. of mercury. At these pressures the rise of current with the P.D. is more rapid the higher the pressure. The temperature of the wire in this case was 1483° C.

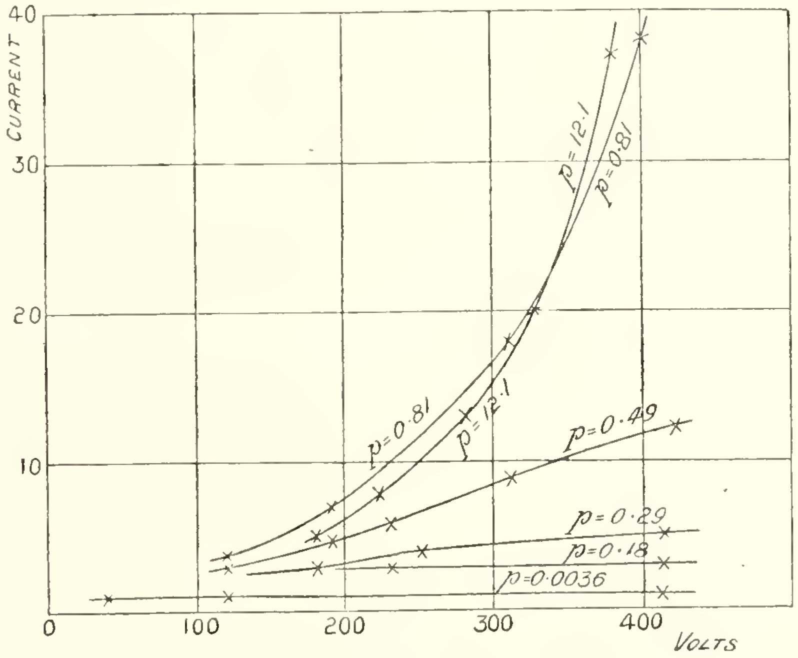

Fig. 3.

Fig. 4 shows the variation of the negative leak with the pressure, using constant P.D.'s of 250 and 40 volts. With 40 volts the current is quite independent of the pressure, but with 250 volts it rises rapidly to a maximum value at nearly 3 millims., and then falls with increasing pressure. The temperature in this case was 1483° C.

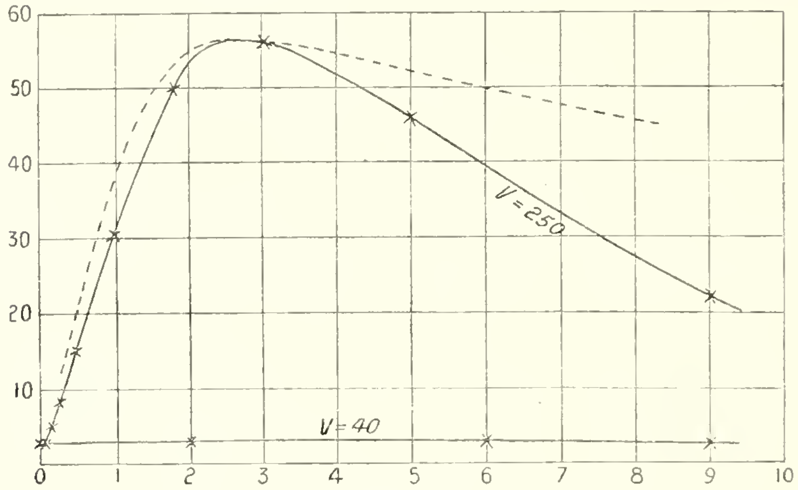

Fig. 4.

The above results on the variation of the current with the P.D. and pressure can be explained if it is assumed—

(1.) That the number of negative ions coming from the surface of the platinum per second is independent of the air pressure and so remains constant during each series of measurements, and

(2.) That the negative ions can produce ionization by collisions with the air molecules when moving with sufficiently great velocities.

It has been shown by Professor TOWNSEND[*] that negative ions produced in air and other gases at low pressures produce ionization by collisions with the molecules when moving under the influence of a sufficiently large electric intensity. He finds that if α is the number of negative ions produced by one negative ion in going 1 centim., then $\alpha = pf(X/p)$,[†] where p is the pressure, X is the electric intensity, and f denotes a function whose values he has determined.

The following table gives the values of $f(X/p)$ for air found experimentally by TOWNSEND ('Phil. Mag.,' vol. 5, 1903, p. 395) for several values of X/p:—

$\frac{X}{p}$.	$f\left(\frac{X}{p}\right) = \frac{\alpha}{p}$.	$N\epsilon^{-\frac{NEp}{X}}$.
70	0·25	0·07
100	0·73	0·33
200	2·5	2·2
400	5·8	5·8
600	7·9	8·0
800	9·4	9·4
1400	12	11·6

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[*] 'Phil. Mag.,' February, 1901, June, 1902, April, 1903, and 'Electrician,' April 3, 1903.

[†] TOWNSEND has determined a large number of values of α with various values of p and X, and he finds that they can be very accurately represented by an equation of this form.

When X/p is greater than about 200, α/p is given (as TOWNSEND shows) by the formula $\alpha/p = N\epsilon^{-NEp/X}$, where $N = 15{\cdot}2$ and $E = 25$ volts. The values of $N\epsilon^{-NEp/X}$ are given in the third column of the above table, and it can be seen that they agree with the experimentally determined values of α/p. X is measured in volts per centimetre and p in millimetres of mercury. Thus when X/p is large, α/p is nearly equal to $15{\cdot}2$.

If V is the P.D. between the wire loop and cylinder, and r the distance from the centre of the wire, then approximately near the wire $X = \dfrac{V}{r \log b/a}$, where b is the radius of the cylinder and a that of the wire. In the experiments just described $b = 0{\cdot}7$ centim. and $a = 0{\cdot}005$ centim., so that $\log b/a = 4{\cdot}94$ and $X = V/4{\cdot}94r$. Hence X at the surface of the wire is equal to 40 V.

Let n_r denote the number of negative ions, crossing a cylinder of radius r coaxial with the hot wire, per second. Then we have

$$dn_r = n_r\alpha\, dr\,;\ \text{also}\ \alpha = Np\epsilon^{-NEp/X},\ \text{and}\ X = \frac{V}{r \log b/a},\ \text{so that}\ dn_r = n_r N p \epsilon^{-(NEpr/V)\log b/a}\, dr.$$

Integrating, we get $\log n_b/n_a = \dfrac{V}{E \log b/a}\{\epsilon^{-(NEpa/V)\log b/a} - \epsilon^{-(NEpb/V)\log b/a}\}$. This equation should therefore be capable of approximately representing the variations of the current with the pressure and P.D. at constant temperature, when the P.D. is large enough to drag all the corpuscles which escape away from the wire. The value of N or the maximum number of negative ions produced by a corpuscle in going 1 centim. in air at 1 millim. pressure is equal, according to TOWNSEND's results (*loc. cit.*), to the number of collisions with air molecules made by the corpuscle. N should, therefore, be proportional to the number of molecules present at 1 millim. pressure, that is, it should be inversely proportional to the absolute temperature of the air.

The following table contains values of n_b/n_a taken from the curve in fig. 2 at 27 millims. pressure and those calculated by the formula taking $N = 3{\cdot}04$ and $E = 17{\cdot}7$, which values were obtained from the observed values of n_b/b_a at 150 and 300 volts.

V.	n_b/n_a found ($n_a = 5$).	n_b/n_a (calculated).
100	2·2	2·5
150	3·9	4·0
200	6·8	6·4
250	11·7	11·0
300	21·2	21·0
320	26·1	27·2

If N varies inversely as the absolute temperature, then, the value of N being 15 at 20° C., N at 1648° C. should be $2{\cdot}3$. The number 3 obtained is rather larger than this, as was to be expected, because the air near the wire must be cooler than the wire itself. It seems therefore that the results obtained are consistent with the view that N varies inversely as the absolute temperature.

The dotted curve in fig. 4 was calculated by means of the expression

$$\log n_b/n_a = \frac{\mathrm{V}}{\mathrm{E} \log b/a} \left\{ \epsilon^{-(\mathrm{NE}\,pa/\mathrm{V}) \log b/a} - \epsilon^{-(\mathrm{NE}\,pb/\mathrm{V}) \log b/a} \right\},$$

taking N = 8·04 and E = 16·55. These values were obtained by making the maximum on the calculated curve coincide with the observed maximum. Below 4 millims. pressure the observed and calculated curves agree fairly well, but at the higher pressures the calculated current is too large. At high pressures most of the ionization by collisions takes place near the wire where the gas is very hot, so that the value of N ought really to be taken smaller at the higher pressures, consequently the calculated currents are too large.

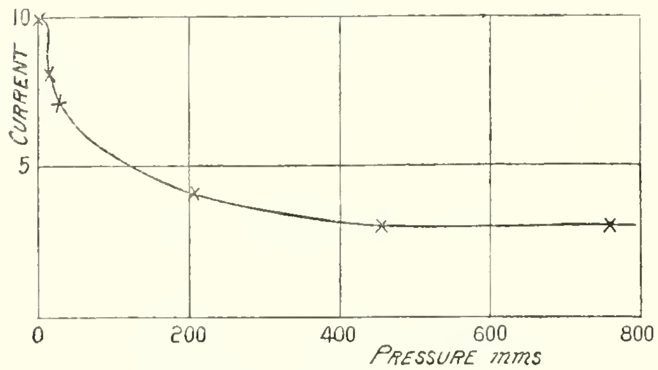

Fig. 5.

Fig. 5 shows the variation of the negative leak with the pressure using 40 volts only, so that practically no ions are produced by collisions. The current falls off as the pressure increases. This is probably due to the presence of the gas hindering the escape of the negative corpuscles from the surface of the wire.

Some measurements of the negative leak were also made in nitrogen and in water-vapour. The nitrogen was prepared from KNO_2 and NH_4Cl and passed over H_2SO_4 before admitting it into the apparatus. The last traces of oxygen were removed from it by sodium electrolysed into the apparatus through hot glass. The details of this process will be described in Section (4). The leak in nitrogen at pressures up to several millims. was nearly equal to that in a good vacuum from similarly treated wires, provided the P.D. used was not large enough to produce ionization by collisions. The effects with large P.D.'s were similar to those obtained in air.

The leak in water-vapour at temperatures below 1500° C. with a pressure of about 15 millims. was also very nearly equal to that in a good vacuum at the same temperature. The tube containing the wire was connected to a three-way tap, which was also connected to a tube leading to the pump and to a small bulb containing water. The tube and the bulb were exhausted separately and then connected together, several times, so that the tube containing the wire was filled with water-vapour. The current obtained was 25 divisions at 1446° C. The corresponding current in a vacuum was 27 divisions, using a wire which had been treated in a similar way.

The positive leak in air and other gases is very small at low pressures. When a platinum wire which has not been specially cleaned is first heated in a vacuum or in air at low pressures, it can discharge positive electricity to an extent appreciable on a galvanometer, but the current rapidly falls off and in a few seconds becomes inappreciable. A wire which has been cleaned by boiling HNO_3 usually only shows this effect to a very slight extent or not at all.

In air at high pressures the permanent positive leak is, of course, appreciable on a galvanometer. It increases with the pressure at constant temperature. In pure air at atmospheric pressure, using a wire cleaned with HNO_3 in the way described, the positive leak is about double the negative leak when the temperature is about 1550° C. The two leaks are nearly equal at a pressure of about 200 millims. at the same temperature.

(3.) *The Variation of the Negative Leak from Hot Platinum with the Temperature.*

The results in the preceding section show that the number of negative ions or corpuscles which start from the platinum is independent of the air pressure, provided that this is not more than a few millims., or that if the pressure is large the P.D. used is sufficient to drag away all the corpuscles which get out. In the present section the variation of the number of these corpuscles which escape from the platinum with the temperature will be considered.

The wire used was 13·0 centims. long and 0·1 millim. in diameter, and it was well cleaned with HNO_3 after it had been mounted as described above. The apparatus was filled with pure air and pumped down to a low pressure several times with the wire red hot. When it was thought that all gases evolved by the wire were got rid of, the apparatus was pumped down and the measurements made. If these precautions were not taken, the leaks were always much larger and very irregular.

The following table contains the results obtained with a particular wire treated in this way. Balancing resistances in P.O. box at 18·5° C. before experiments 1000 and 1669 ohms, and after the experiments 1000 and 1669 ohms.*

Balancing resistances 200 ohms and	Negative leak in galvanometer scale divisions. V = 40 volts.		
	$p = 0 \cdot 1$ millim.	$p = 0 \cdot 2$ millim.	Mean.
1600	(1) 5·0	(8) 5·0	5
1625	(2) 11·0	(9) 11·0	11
1650	(3) 25	(10) 23	24
1675	(4) 50	(11) 48	49
1700	(5) 108	(12) 100	104
1725	(6) 207	(13) 202	205
1750	(7) 412	(14) 410	411

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* In making a series of measurements, it is necessary to measure the resistance of the wire when cold from time to time, because at high temperatures the wire disintegrates and its resistance consequently rises with long continued heating.

The leak is the same at 0·2 millim. as at 0·1 millim., and it was verified carefully that no change occurred even on pumping down to 0·001 millim. The numbers in brackets refer to the order in which the measurements were made. The following table gives the values of the leaks in ampères and the temperatures deduced from the above numbers :—

Temperature on platinum scale.	Temperature on Centigrade scale.	Leak in ampères.	Ampères per square centimetre of platinum.
(1) 1319°	1375°	$5 \cdot 8 \times 10^{-9}$	$1 \cdot 57 \times 10^{-8}$
(2) 1344·5	1408·5	$12 \cdot 7 \times 10^{-9}$	$3 \cdot 43 \times 10^{-8}$
(3) 1370	1442	$27 \cdot 6 \times 10^{-9}$	$7 \cdot 46 \times 10^{-8}$
(4) 1395·5	1476	$56 \cdot 4 \times 10^{-9}$	$15 \cdot 2 \times 10^{-8}$
(5) 1421	1510·5	$119 \cdot 6 \times 10^{-9}$	$32 \cdot 3 \times 10^{-8}$
(6) 1446·5	1545	236×10^{-9}	$63 \cdot 8 \times 10^{-8}$
(7) 1472	1580	473×10^{-9}	$128 \cdot 0 \times 10^{-8}$

It will be observed that as the temperature increases by nearly equal increments the current increases by nearly equal factors.

A theoretical proof of the formula $x = \mathrm{A}\theta^{\frac{1}{2}}\epsilon^{-\mathrm{Q}/2\theta}$ will now be given, and then it will be shown that the above results can be represented by this formula. The emission of negative corpuscles by hot platinum is analogous to the evaporation of a liquid, and whether the corpuscles come out of the metal or are produced at its surface, the number produced per second per unit area of platinum surface may be regarded as analogous to the number of molecules emitted per second by unit area of a liquid.

If p is the vapour pressure of a liquid at the absolute temperature θ, and L its latent heat of evaporation per gramme molecular weight, then $\mathrm{L} = (v_2 - v_1)\theta\, dp/d\theta$, where v_2 = volume of vapour and v_1 = volume of liquid. Neglecting v_1 and putting $v_2 = \mathrm{R}\theta/p$ we get $\mathrm{L} = \mathrm{R}\theta^2/p \,.\, dp/d\theta$. Let the internal work done in evaporating the liquid be Q and suppose $\mathrm{Q} = \mathrm{Q}_0 + a\theta$, where a is some constant, then $\mathrm{L} = \mathrm{Q} + pv$, so that we have

$$\mathrm{Q}_0 + a\theta + \mathrm{R}\theta = \mathrm{R}\theta^2/p \,.\, dp/d\theta$$

or

$$\frac{\mathrm{Q}_0 + (\mathrm{R} + a)\theta}{\theta^2}\, d\theta = \frac{\mathrm{R}\, dp}{p}.$$

Hence if p_1 is the vapour pressure at a temperature θ_1, and p_2 that at θ_2,

$$\log \frac{\theta_1^{\mathrm{R}+a}}{\theta_2^{\mathrm{R}+a}} \frac{p_2^{\mathrm{R}}}{p_1^{\mathrm{R}}} = \mathrm{Q}_0 \left(\frac{1}{\theta_1} - \frac{1}{\theta_2}\right).$$

Now $p = bm\mathrm{VN}$, where m is the mass of a molecule, V the square root of the mean square of the velocities of all the molecules, and N the number leaving each square centimetre of the liquid surface per second and b a constant. But V^2 is proportional to θ, hence we may write $p = b'\mathrm{N}\sqrt{\theta}$, where b' is a constant. Substituting this in the above equation we get

$$\log \frac{\theta_1^{\frac{1}{2}+\frac{a}{\mathrm{R}}}\mathrm{N}_2}{\theta_2^{\frac{1}{2}+\frac{a}{\mathrm{R}}}\mathrm{N}_1} = \frac{\mathrm{Q}_0}{\mathrm{R}}\left\{\frac{1}{\theta_1} - \frac{1}{\theta_2}\right\}.$$

In the case of hot platinum in an atmosphere of its own ions, if x is the current per unit area due to ions leaving the platinum surface, then $x = \mathrm{N}e$, where e is the charge carried by one ion. Hence we get, putting $\mathrm{R} = 2$, which is its value in small calories for one gramme molecular weight of any gas,

$$\log \frac{\theta_1^{\frac{1}{2}(1+a)}x_2}{\theta_2^{\frac{1}{2}(1+a)}x_1} = \frac{\mathrm{Q}_0}{2}\left\{\frac{1}{\theta_1} - \frac{1}{\theta_2}\right\}.$$

The following table gives the values of Q calculated by means of this equation from the observed currents and taking $a = 0$. The numbers in brackets indicate which pair of experimental numbers taken from the last table given above was used.

	Mean temperature.	Q.
	° C.	
(1, 2)	1392	138,500
(2, 3)	1425	132,000
(3, 4)	1459	124,400
(4, 5)	1493	133,500
(5, 6)	1528	126,300
(6, 7)	1563	132,000
	Mean . . .	131,100

The variations in Q are not greater than can be ascribed to experimental errors. The value of Q obtained corresponds to a fall of the ionic charge through 5·74 volts. **Richardson**'s result for this quantity was 4·1 volts, but since the leaks which he obtained are about 1000 times greater than those given above, it was to be expected that his value of Q would be smaller than that which my experiments lead to.

The value of the constant A in the formula $x = \mathrm{A}\theta^{\frac{1}{2}}\epsilon^{-\mathrm{Q}/2\theta}$, calculated from the value of the current per square centimetre at 1580° C., is $6·9 \times 10^7$, so that the equation becomes

$$x = 6·9 \times 10^7\theta^{\frac{1}{2}}\epsilon^{-131,100/2\theta}.$$

The following table contains a comparison of the currents calculated by means of this formula and those found experimentally :—

Temperature.	Current per square centimetre found.	Current calculated.
°C.		
1375	$1\cdot57 \times 10^{-8}$	$1\cdot49 \times 10^{-8}$
1408·5	$3\cdot43 \times 10^{-8}$	$3\cdot33 \times 10^{-8}$
1442	$7\cdot46 \times 10^{-8}$	$7\cdot18 \times 10^{-8}$
1476	$15\cdot2 \times 10^{-8}$	$15\cdot3 \times 10^{-8}$
1510·5	$32\cdot3 \times 10^{-8}$	$31\cdot8 \times 10^{-8}$
1545	$63\cdot8 \times 10^{-8}$	$64\cdot5 \times 10^{-8}$
1580	128×10^{-8}	$128\cdot5 \times 10^{-8}$

The calculated and observed currents agree very well, so that we may conclude that a in the formula $x = A\theta^{\frac{1}{2}(1+a)}\epsilon^{-Q_0/2\theta}$ is really zero or nearly so. It is easy to show that the value of a cannot be greater than unity in order for the observed and calculated results to agree as well as they do. Consequently, since $Q_0 = 131{,}100$, Q does not vary as much as 1 part in 100,000 per degree centigrade.

The value found for Q is slightly more than double that found previously ('Phil. Trans.,' A, vol. 197, p. 430) for the work required to ionize a gramme molecular weight of air in contact with hot platinum.

All that it is necessary to assume to deduce the equation used to calculate Q either for the positive leak in air at atmospheric pressure, or for the negative leak in a vacuum, is that ions are produced in some way at the surface of the hot platinum. The results just described cannot, therefore, be regarded as any additional evidence in favour of the view that the negative leak from hot platinum is due to negative corpuscles coming out of the metal; they are, however, consistent with this view.

The positive leak in air at atmospheric pressure can be represented by the formula

$$x = A'\theta^{\frac{1}{2}}\epsilon^{-60{,}000/2\theta}.$$

The value of A′ may be obtained from the observation that the positive leak at 1550° C. is double the negative leak. This gives $A' = 0\cdot47$. The temperature at which the two leaks with the particular wire used were equal is, therefore, given by by the formula

$$6\cdot9 \times 10^{7}\theta^{\frac{1}{2}}\epsilon^{-131{,}100/2\theta} = 0\cdot47\theta^{\frac{1}{2}}\epsilon^{-60{,}000/2\theta},$$

which gives $\theta = 1895$ or 1622° C. Above 1622° C. the negative leak with this wire was greater than the positive leak, and below this temperature less.

At low pressures the positive leak is smaller. If we assume that it varies as the pressure, then it will be given at any pressure by the formula

$$x = \frac{0\cdot47p}{760}\theta^{\frac{1}{2}}\epsilon^{-60{,}000/2\theta}.$$

At 1 millim. pressure this gives $x = 6\cdot2 \times 10^{-4}\theta^{\frac{1}{2}}\epsilon^{-60{,}000/2\theta}$, and the temperature at which the positive and negative leaks are equal comes out 1127° C. These results afford an explanation of ELSTER and GEITEL'S observation that an insulated conductor near a hot wire becomes positively charged in air at atmospheric pressure, but negatively charged at low pressures.

The results described above show that the negative leak from a platinum wire is very little affected by the presence of air, nitrogen, or water vapour. It was found that putting some mercury into the tube containing the hot wire, so that it was filled with mercury vapour, increased the leak considerably at very high temperatures. The whole tube, of course, gets hot, so that the pressure of the mercury vapour must have been very considerable in this experiment. The following table gives the results obtained :—

Temperature.	Negative leak before introducing mercury.	Negative leak after introducing mercury.
° C.	divisions.	divisions.
1728	120	400
1645	37	78
1566	12	13

Thus above 1600° C. the presence of mercury in large quantities appears to increase the negative leak, but below this temperature it is without effect. The very small amount of mercury vapour ordinarily present can, therefore, safely be assumed to have no effect below 1600° C.

With different pieces of pure platinum wire cut from the same sample and treated in the same way with nitric acid fairly concordant results were obtained. Nevertheless, long continued heating of the wire diminishes the negative leak, provided the air is frequently changed. If the wire is simply left standing in air at a low pressure for a long time the leak is often greater than before on again heating the wire. The process of cleaning the wire with nitric acid and frequently changing the air in the apparatus diminishes the negative leak something like a thousand times usually. Thus the leaks given above are about one thousand times smaller than those given by RICHARDSON at the same temperatures.

These facts naturally suggest the question whether more thorough cleaning of the wire and purification of the air would not still further diminish the negative leak. To test this a wire was mounted as before and boiled in HNO_3 for about an hour. It was then left in the HNO_3 for 24 hours and a current passed from the wire to the cylinder through the HNO_3, so that the NO_3 ions were set free on the wire. The tube was then washed out and the leak measured in pure air at a low pressure, as before. The following table gives the results obtained :—

Temperature.	Negative leak per square centimetre of platinum.
° C.	ampères.
1686	4×10^{-8}
1651	2×10^{-8}
1616	1×10^{-8}

Thus the more thorough treatment of the wire with HNO_3 reduced the negative leak to about $\frac{1}{250}$th of that previously obtained, but the rate of variation of the leak with the temperature remained almost unchanged. These numbers give $Q = 155{,}000$ and $A = 6 \times 10^6$.

If $A = 6 \times 10^6$, then, on RICHARDSON's theory, the number of corpuscles (n) in a cubic centimetre of the platinum would be 8×10^{19}. PATTERSON (*loc. cit.*) obtained $n = 10^{22}$ by experiments on the variation of the resistance of platinum in a magnetic field. It appears, therefore, that n cannot really be deduced from the constant A.

On one occasion some phosphorus pentoxide accidentally got into the tube containing the hot wire, and the negative leak was increased enormously by its presence. The current at 1490° C. was about 4×10^{-4} ampère, or 10^{-3} ampère per square centimetre. The negative leak was therefore increased about one million times by the presence of the phosphorus pentoxide. Now ordinary phosphorus pentoxide usually contains phosphorus acid and other impurities, and may give off some vapours when kept in a vacuum. If any such vapours were present in the tube containing the hot wire, this result shows that they would produce a leak of negative electricity from it.

It is clear, therefore, that minute traces of various substances such as hydrogen, phosphorus pentoxide, and alkali salts produce a large increase in the negative leak from hot platinum, and that the more thorough the precautions taken to remove traces of such substances the smaller the leak becomes. I have not succeeded in reducing the leak to less than 1 part in 250,000 of that observed by RICHARDSON, but I have little doubt that, if all traces of impurities could be got rid of, the negative leak in air would be reduced to a still smaller value.

There is considerable evidence in favour of the view that the negative leak in air is due to the presence of traces of hydrogen in the platinum.* It will be shown in the next section that the negative leak in hydrogen is enormous compared with that in air, and that at low pressures it is proportional to the pressure of the hydrogen. When the pressure of the hydrogen is very small, the value of Q in the formula $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$ is nearly equal to its value in air, which makes it very probable that the small negative leak in air or a vacuum is due to the presence of traces of

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* This view was suggested long ago by BERLINER, 'Wied. Ann.,' vol. 33, p. 289 (1888).

hydrogen. It is well known that it is almost impossible to entirely get rid of the last traces of hydrogen from a vacuum tube.

This view is confirmed by the effect of nitric acid on the negative leak, for nitric acid oxidises hydrogen. It is also in agreement with the fact that the negative leak in air at low pressures falls off during long-continued heating of the wire. The rate at which the leak falls off diminishes as the leak gets smaller, so that with wires well cleaned with nitric acid the rate of fall is not very great.

Platinum wires not specially cleaned evolve gas when heated in a vacuum, and since hydrogen is the only gas which platinum is known to occlude in any quantity, this gas is no doubt hydrogen. It is practically impossible to get rid of this evolution of gas merely by long continued heating and pumping out. Thus WIEN (*loc. cit.*) states that his wires continued to evolve gas after weeks of heating in an extremely good vacuum. My wires, which had been treated with nitric acid and heated in air which was repeatedly changed, did not evolve anything like as much gas as those not so treated.

(4.) *The Leak in Hydrogen.*

In the experiments in hydrogen at low pressures the hydrogen was obtained sufficiently pure by allowing it to diffuse through platinum. A spiral of fine platinum tubing, 0·5 millim. external and 0·25 millim. internal diameter, was sealed on the apparatus at one end and the other end fused up. On heating this spiral in the flame of a spirit lamp, the hydrogen present in the flame diffused through into the apparatus. In this way the pressure could be increased several tenths of a millimetre in one minute when the total capacity of the apparatus was about 300 cub. centims.

The spectrum of a discharge in hydrogen let in in this way was examined, and appeared to consist almost entirely of the hydrogen lines. It was thought that faint traces of the CO spectrum could sometimes be seen, but it was not certain that any CO entered through the platinum spiral. For experiments at pressures above 10 millims. the hydrogen was obtained from pure zinc and hydrochloric acid, and passed into the apparatus through tubes containing soda-lime.

In some experiments the hydrogen was further purified by means of sodium let into the apparatus by electrolysis through hot glass, in the manner described by E. WARBURG.[*] This method was found to work very well, and a deposit of metallic sodium could easily be obtained. The sodium, of course, absorbed some hydrogen as well as the oxygen and other impurities possibly present.

The apparatus for this experiment is shown in fig. 6. A is the tube containing the hot wire, B a tube tightly packed with gold leaf, and C the sodium tube. This latter consisted of a thin glass tube about 15 centims. long and 1·5 centim. in diameter, with an aluminium wire electrode along its axis, as shown. It was immersed in

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[*] 'Wied. Ann.,' vol. 40, p. 1 (1890).

sodium amalgam contained in a test-tube. The test-tube was supported on asbestos wool in a thick brass tube DE, the lower end of which was closed by iron wire gauze. The gauze was heated by a small Bunsen flame and the temperature of the amalgam kept at about 280° C. At pressures above about 1 millim. a current from about 400 cells could then be passed from the amalgam to the aluminium electrode, and sodium deposited, forming a metallic mirror in the upper parts of the tube C. The discharge in C was a brilliant yellow colour, giving the D line. If oxygen was present, sodium oxide was formed, and the brilliant yellow light did not appear so strongly at first. This process did not appear to have any particular effect on the amount of leak obtained from the hot wire in hydrogen at any pressure, so that we may conclude that the increase of the leak due to letting in hydrogen is not due to the presence of impurities in the gas.

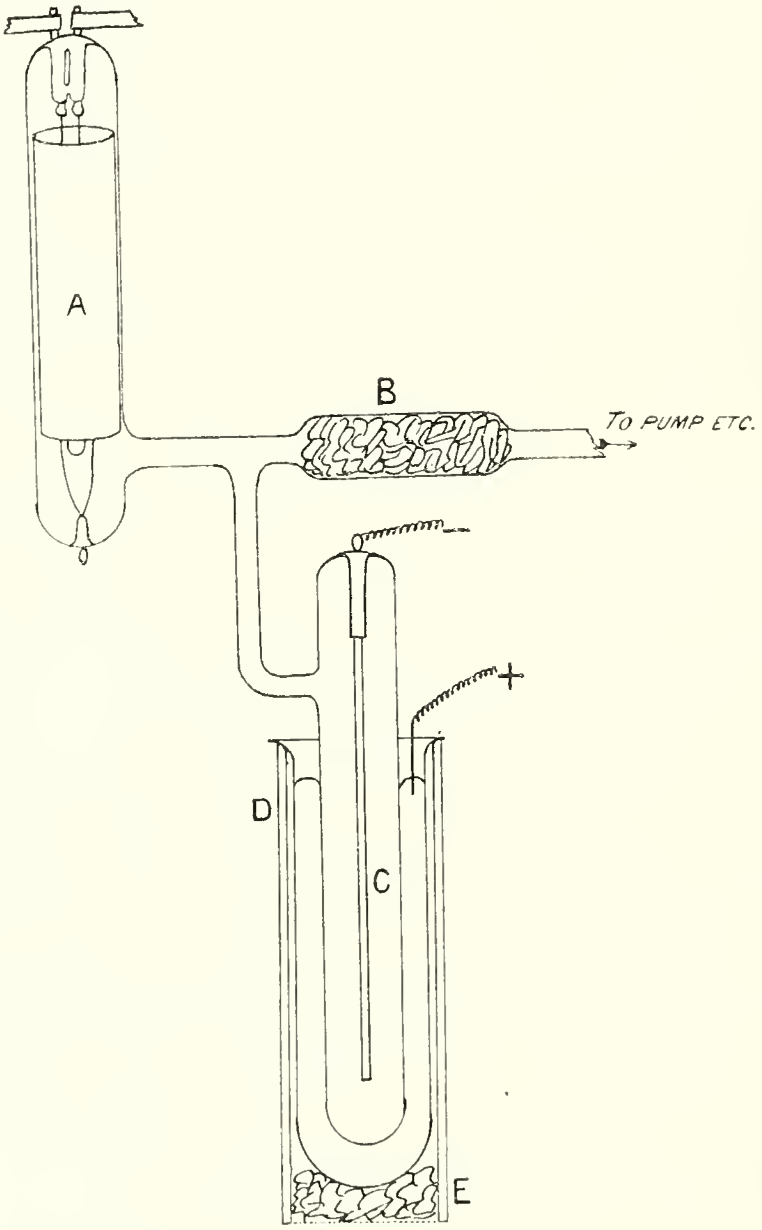

Fig. 6.

The following table gives some numbers showing the effect on the negative leak at a constant temperature of about 1350° C., due to letting in hydrogen :—

Pressure in millims. of mercury.	Current with 120 volts.
	divisions.
0·0006	10
0·0015	20
0·0033	40
0·0053	50
0·0080	75
0·014	110

This increase of the leak with the pressure cannot be ascribed to ionization by collisions, for at the highest pressure used, one negative ion can only produce 0·2 fresh negative ion in going 1 centim. The leak in air at 1350° C. from a clean wire would have given about $\frac{1}{250}$th division in the above experiment. Thus the leak in hydrogen at 0·014 millim. in this experiment was more than 25,000 times the leak from a very well cleaned wire at the same temperature in air.

In the experiment just described, the hydrogen was let in at intervals through the platinum spiral, so that the pressure increased during the experiment. Another way is to let in hydrogen to the highest pressure desired and then pump out during the experiment. It was found that the results were not the same in the two cases. On pumping down, the leak falls, but not so quickly as it rises on letting in the gas. It was soon discovered that the leak is not always a single-valued function of the pressure, but depends also on the previous treatment of the wire. The results can be explained on the hypotheses—

(1.) That the wire absorbs an amount of hydrogen depending on the pressure and temperature, and that when these are changed it takes a considerable time for equilibrium between the gas in the wire and that outside to be established ; and

(2.) That the leak at any temperature depends on the amount of hydrogen in the wire, and not directly on the pressure outside.

Consequently, if the equilibrium is established at a particular temperature and pressure, then if the temperature is raised or the pressure lowered the leak should not be steady at first under the new conditions, but should gradually fall off, in consequence of gas leaving the wire, until equilibrium is again established. On the other hand, if the temperature is lowered or the pressure increased, the leak should gradually rise until equilibrium is again established. Experiments showed that these effects occurred exactly in the way expected.

The following tables give the results of some measurements of the negative leak in hydrogen, showing the effects of suddenly changing the temperature or pressure :—

Time.	Balancing resistance ($p = 0 \cdot 10$ millim.).	Current.
minutes.		
12	3500	110
15	3500	100
16	3500	102
18	3500	102
19	3400	28
22	3400	30
23	3300	11
25	3300	15
28	3300	19
30	3300	22
33	3300	22

The above numbers show the effect of lowering the temperature at constant pressure. The current drops and then gradually rises, ultimately becoming steady when equilibrium has been established. Of course it is necessary to be sure that equilibrium has been reached at the higher temperature before changing to the lower temperature, in order to observe this effect, and to get equilibrium at the higher temperature may take a long time in some cases.

Time.	Balancing resistance ($p = 0 \cdot 34$ millim.).	Current.
minutes.		
6	3200	16
8	3200	15
11	3600	1800
16	3600	1200
23	3600	900

These numbers show the effect of suddenly raising the temperature at constant pressure in hydrogen.

Time.	Pressure (Balancing resistance = 3700).	Current.
minutes.		
30	0·071	1100
60	0·071	1100
98	0·071	1200
114	0·012	1200
116	0·012	1000
118	0·012	720
157	0·012	280

The above numbers show the effect of lowering the pressure at constant temperature.

Time.	Pressure (Balancing resistance 3800).	Current.
minutes.		
47	0·0006	540
49	0·032	600
51	0·032	1740
59	0·032	1860
60	0·032	1980

The above numbers show the effect of raising the pressure at constant temperature. The effect of raising the temperature of the wire is most marked when a wire which has been standing at the ordinary temperature in hydrogen is suddenly heated to a high temperature. In this case an enormous current is obtained for a short time. Thus a wire at a certain temperature in hydrogen at 0·045 millim. pressure gave a current of $1·6 \times 10^{-6}$ ampère when equilibrium had been established. It was then allowed to stand cold for 20 hours when, on raising the temperature to the same value, the leak was at first more than 10^{-2} ampère, and only fell to its original value after long continued heating.

Some experiments were tried in which the temperature of the wire was raised by equal steps through a series of values and then lowered again through the same series of values, several times. The following are the results obtained in an experiment of this kind at a pressure of 0·112 millim. The numbers in brackets are the times in minutes at which the currents were measured.

Temperature.	Current.				
° C.					
1520	↓	550 (50) 770 (46)	↘	500 (90) 630 (87)	↘
1459	460 (12) 400 (15)	300 (45) 410 (40)	200 (51) 210 (55)	190 (85) 220 (81)	
1400	150 (20)	150 (40) 270 (35)	67 (57) 75 (60)	65 (80) 66 (76)	65 (95)
1341	42 (25)	42 (35)	24 (61) 25 (66)	24 (75) 25 (72)	
1284	12 (30)	↗	8 (67) 9 (70)	↗	

It will be noticed that when the temperature has just been raised the leak falls on waiting, whereas when it has just been lowered the leak rises on waiting. In spite of this, however, the numbers at each temperature keep fairly concordant towards the end of the experiment, which shows that they must approximately represent the variation of the leak with the temperature for a constant state of the wire with regard to the hydrogen. This means that the time between the observations was so short that very little change in the amount of hydrogen in the wire occurred during the latter measurements, in spite of the changes made in the temperature. This may be due to the amount of hydrogen absorbed by the wire varying very slowly with the temperature at the temperatures used in this experiment. It is stated in ROSCOE and SCHORLEMMER'S 'Chemistry' (vol. 1, p. 139) that platinum at a red-heat absorbs 3·8 times its volume of hydrogen, and at 100° C. only 0·76 times its volume. If the volume absorbed were proportional to the absolute temperature, then platinum in equilibrium with hydrogen at any particular temperature would be in equilibrium at any other temperature. According to ROSCOE and SCHORLEMMER, the volume absorbed increases more rapidly than the absolute temperature up to a red heat, but on the other hand platinum certainly loses some of its hydrogen when heated to near its melting-point; consequently there must be a region of temperature between a red heat and the melting-point where the actual amount of hydrogen absorbed is nearly independent of the temperature at constant pressure. The very small variations with time in the latter of the above experiments seem to show that the range of temperature used in this experiment lies in this region. The latter numbers in the above experiment have been reduced to ampères per square centim. The results are given in the following table. The pressure in this experiment was 0·112 millim.

Temperature.	Current per square centimetre.
° C.	ampères.
1520	$7·55 \times 10^{-5}$
1459	$3·02 \times 10^{-5}$
1400	$1·15 \times 10^{-5}$
1341	$0·442 \times 10^{-5}$
1284	$0·145 \times 10^{-5}$

The formula $\frac{Q}{2}\left\{\frac{1}{\theta_1} - \frac{1}{\theta_2}\right\} = \log \frac{x_2\theta_1^{\frac{1}{2}}}{x_1\theta_2^{\frac{1}{2}}}$, when these numbers are substituted in it, gives $Q = 85,900$. A similar series of experiments done at a pressure of 0·0013 millim. of hydrogen gave the following results :—

Temperature.	Current per square centimetre.
° C.	ampères.
1516	127×10^{-8}
1457	70×10^{-8}
1400	$20 \cdot 4 \times 10^{-8}$
1343	$5 \cdot 0 \times 10^{-8}$
1287	$1 \cdot 6 \times 10^{-8}$

These numbers give Q = 120,000.

The variation of the negative leak with the temperature, using 40 volts, was also measured at a pressure of 133 millims. The following table gives the results :—

Temperature.	Current per square centimetre.
° C.	ampères.
1310	192×10^{-6}
1187	$33 \cdot 4 \times 10^{-6}$
1069	$5 \cdot 66 \times 10^{-6}$
961	$1 \cdot 04 \times 10^{-6}$

These numbers give Q = 36,000. The leak in air or in a vacuum, using a wire well cleaned with HNO_3, at 1310° C. is only about 2×10^{-11} ampère per square centimetre.

The following table gives the values of Q found at the different pressures, and also the approximate values of the constant A in the formula $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$:—

Pressure of hydrogen.	Q.	A.
millims.		
0 (wire cleaned with HNO_3 for 24 hours)	155,000	6×10^{6}
0 (wire cleaned with HNO_3 for one hour)	131,100	$6 \cdot 9 \times 10^{7}$
0·0013	120,000	10^{7}
0·112	85,900	$5 \cdot 3 \times 10^{4}$
133·0	36,000	0·1

Thus the presence of hydrogen diminishes the amount of energy required in the production of the negative ions and consequently greatly increases the leak. It seems very probable from the above results that the action of the hydrogen depends on its absorption by the platinum, for the leak obtained depends apparently on the amount of gas absorbed by the wire and only indirectly on the gas pressure in the apparatus. The leak, when there is equilibrium between the wire and gas, is nearly proportional to the pressure at low pressures, but increases less quickly than the pressure at higher pressures up to a few millimetres. The leaks in the two sets of observations given above at 0·0013 millim., and at 0·112 millim., are nearly in the ratio of the pressures. If a large P.D. is used ionization by collisions comes in at higher pressures just as with air, and the current rises with the pressure, at pressures of a few millimetres, more quickly with large P.D.'s than with small. The following table shows the variation of the leak at a constant temperature of 1340° C. with the pressure up to 760 millims., using a P.D. of 40 volts, which is too small to produce ionization by collisions :—

Pressure.	Current.
millims.	ampères.
766	3000×10^{-6}
450	1500×10^{-6}
156	222×10^{-6}
14	60×10^{-6}

At high pressures the leak is again nearly proportional to the pressure.

Fig. 7 shows the variation of the negative leak in hydrogen with the P.D. at pressures of 133 and 766 millims. The current at 133 millims. is nearly saturated with about 200 volts, but then begins to rise rapidly owing to ionization by collisions coming in. The upper part of the curve can be represented approximately by the formula obtained in the section on the leak in air.

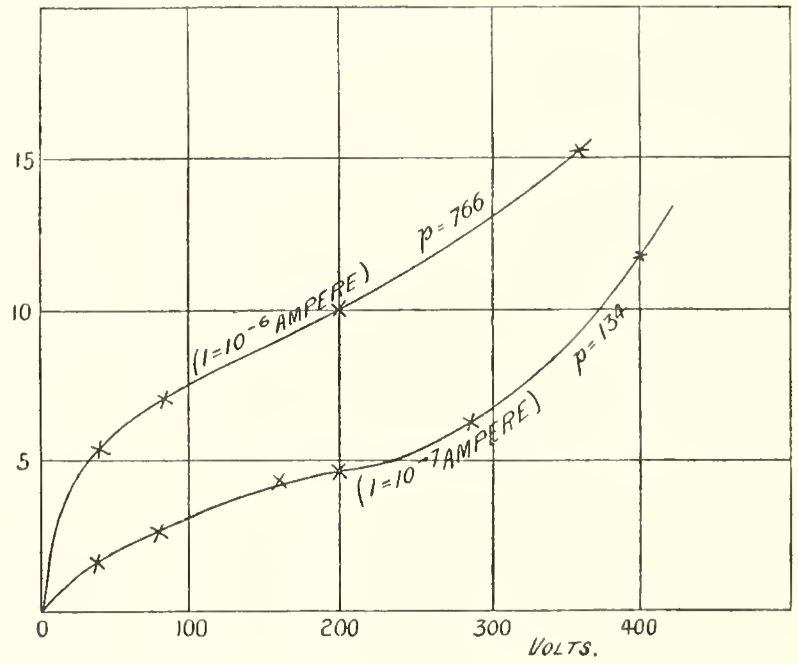

Fig. 7.

The positive leak, like the negative leak, is much increased by the presence of hydrogen. With clean wires it is, nevertheless, inappreciable on a galvanometer, except at pressures of several millimetres. The following values of the positive leak were obtained at 1300° C., using 160 volts :—

Pressure.	Positive leak.
millims.	ampères.
766	40×10^{-9}
156	24×10^{-9}
9	4×10^{-9}

The following table gives the values of the negative leak at a temperature of 1400° C. in hydrogen at several pressures :—

Pressure.	Current per square centimetre.
millims.	ampères.
133	1×10^{-3}
0·112	$1 \cdot 2 \times 10^{-5}$
0·0013	2×10^{-7}
0	$1 \cdot 2 \times 10^{-10}$

The last number is the leak from a very well cleaned wire in air at a low pressure. The leak obtained by Mr. Richardson at 1400° C. was about 3×10^{-5} ampère per square centimetre, with a gas pressure of about 0·1 millim.

(5.) *The Leak from Palladium in Hydrogen.*

Some measurements were made of the leak from a palladium wire 0·2 millim. in diameter and 13 centims. long. The wire was left about 20 hours in hydrogen at a few millimetres pressure ; after mounting it and before it was heated the pressure was reduced to 0·0003 millim. The balancing resistance (R) of the wire was 320 ohms at 18° C. On heating to R = 1100, the negative leak with 200 volts was 3 scale divisions (1 division = 3×10^{-8} ampère) and the positive leak 750 divisions. After five minutes the leaks fell to 0·5 and 130 divisions respectively, while the pressure rose to 0·022 millim. The positive leak continued to fall with the time, and ultimately, after several hours' heating, became only 6 divisions with R = 1550 ohms. It was found that the positive leak was quite independent of the pressure of the hydrogen, while the negative leak increased nearly proportionally to the pressure at small pressures. Fig. 8 shows the variation of the leaks (P.D. = 200 volts) with the pressure, the resistance R being 1400 ohms.

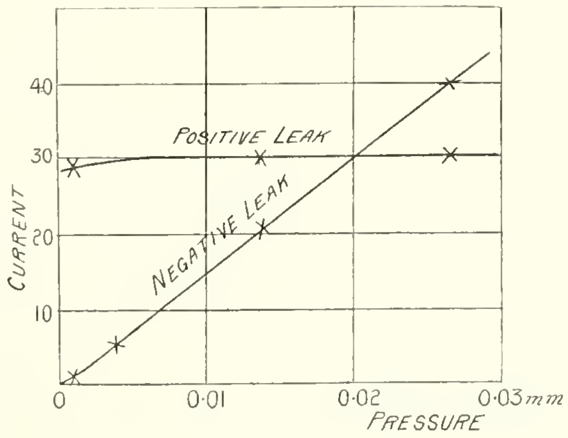

Fig. 8.

The palladium was found to "splutter" very much when hot, so that its resistance rose rapidly. The very large value of the positive leak from it when first heated is no doubt analogous to the positive leak from platinum not specially cleaned when it is first heated.

(6.) *Summary of Principal Results.*

(1.) The negative leak from a hot platinum wire in air, nitrogen, or water vapour is independent of the gas pressure, unless ionization by collisions occurs, and is the same as the negative leak from the same wire in a good vacuum.

(2.) The variation of the negative leak in air with the P.D. and pressure at constant temperature can be explained on the hypothesis that the negative ions produce ionization by collisions with the air molecules.

(3.) The number of collisions made by a negative ion probably varies inversely as the absolute temperature at constant pressure.

(4.) The variation of the negative leak per square centimetre with the temperature can be expressed by the equation $x = \mathrm{A}\theta^{\frac{1}{2}}\epsilon^{-\mathrm{Q}/2\theta}$, where x is the current in ampères, θ the absolute temperature, and Q and A are constants. For a wire very well cleaned with HNO_3, Q is 155,000 and A is about 6×10^6.

(5.) The negative leak in hydrogen is much larger than that in air or in a vacuum. At low pressures it is nearly proportional to the pressure of the hydrogen.

(6.) The presence of the hydrogen changes the value of the constants Q and A, the following being the values obtained at different pressures:—

Pressure.	Q.	A.
0	155,000*	6×10^6
0·0013	120,000	1×10^7
0·112	85,900	$5{\cdot}3 \times 10^4$
133·0	36,000	0·1

(7.) It is extremely probable that the negative leak in air or in a vacuum is due to traces of hydrogen or other substances in the wire. The leak can be reduced to $\frac{1}{250,000}$th part of its ordinary value by taking precautions to remove such traces.

(8.) On first heating a positively charged palladium wire in a vacuum it can discharge positive electricity. The rate of discharge falls off rapidly with time and ultimately becomes inappreciable. A similar effect sometimes occurs with platinum, but the amount of the leak is very small and it disappears in a few seconds. The

[* Of the three values of Q obtained at low pressures (viz. 155,000, 131,000 and 120,000) the value 131,100 is probably nearest the truth. The value 155,000 depends on measurements of very small currents and is probably too large. See Appendix.]

negative leak in hydrogen is proportional to the pressure at low pressures with palladium as with platinum.

(9.) In air and hydrogen, at pressures above several millimetres, there is a permanent positive leak from hot platinum which increases with the pressure. This leak is larger in hydrogen than in air at the same temperature.

(7.) *Conclusion.*

The question of most interest in connection with the leak of electricity from hot platinum is the method of production of the ions. RICHARDSON (*loc. cit.*) has proposed the theory that the negative leak is due to the escape of the corpuscles which, on the ionic theory of metallic conduction, metals contain. These corpuscles are supposed to move about freely inside the metal and to have a distribution of velocities the same as the molecules of an ordinary gas. All corpuscles entering the surface layers of the metal with a velocity component perpendicular to the surface greater than a definite value are supposed to escape; and from these assumptions a formula of the type $x = A\theta^{\frac{1}{2}}\epsilon^{-Q\ 2\theta}$ can be deduced, as RICHARDSON has shown. According to this theory the number of corpuscles in a cubic centimetre of the metal can be calculated from the value of the constant A, and according to this view the leak depends only on the state of the platinum and not on the surrounding gas.

The experiments described in this paper show that the phenomena cannot be explained completely by such a simple theory. There seems to be no doubt that the negative leak from hot platinum is due to the emission of negatively charged corpuscles or electrons, but the number of these emitted depends on the gases and other substances present at the surface of the platinum. With clean platinum in air at a low pressure there is, comparatively speaking, very little leak of electricity either positive or negative. In air at high pressures there is a small leak of positive electricity, while in hydrogen there is a comparatively enormous negative leak. In Mr. RICHARDSON'S experiments the gas present appears to have been that evolved by the hot metal, and so probably contained hydrogen.* This is, no doubt, the explanation of the comparatively very large currents which he obtained.

When occluded hydrogen molecules are present on the surface of the platinum, we may suppose that each molecule or atom of hydrogen has a corpuscle associated with it, and that these corpuscles have an energy distribution similar to the energy distribution of the molecules of a gas. If those corpuscles, having more than a certain amount of energy, are able to escape from the surface, these suppositions account for the existence of a negative leak in hydrogen.†

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* In RICHARDSON'S experiments the gas pressure rose considerably when the temperature of the wire was raised, showing that gases were being evolved by the wire.

† When a molecule of hydrogen has lost its corpuscle it may be supposed to combine with one of the corpuscles present in the platinum, so that on this view the hydrogen molecule serves as a sort of stepping stone to enable the corpuscles to escape from the platinum. [See Appendix.]

We may suppose also that the energy necessary to enable a corpuscle to escape from a hydrogen atom at the surface falls off as the concentration of the hydrogen atoms on the surface increases. In this way the diminution of Q by the presence of hydrogen can be explained. According to this view the number of corpuscles in a cubic centimetre of the metal cannot be deduced from the constant A.

It seems probable that the temporary positive leak from platinum and palladium, when they are first heated, is due to the presence of a small amount of some decomposable compound or volatile impurity. This view is supported by the fact that platinum wires, well cleaned with nitric acid, do not give this effect to an extent appreciable on the galvanometer.

The positive leak in gases at high pressures is no doubt due to ionization of the gas molecules at the surface of the platinum.

In conclusion, I wish to say that my best thanks are due to Professor J. J. THOMSON for advice and kindly interest in these experiments while they were being carried out at the Cavendish Laboratory.

APPENDIX.

Added October 3, 1903.—Some interesting conclusions can be drawn from the way in which the negative leak from hot platinum or palladium in hydrogen varies with the pressure of the hydrogen. We have seen that when the pressure of the hydrogen is less than about 0·02 millim. the leak is nearly proportional to the pressure. Consider two temperatures θ_1 and θ_2. Let the leak at the temperature θ_1 be represented by the equation $x_1 = B_1 p$, where x_1 is the current per square centim., p the pressure, and B_1 a constant. Let the corresponding equation at θ_2 be $x_2 = B_2 p$. If these expressions for x_1 and x_2 are substituted in the equation

$$Q\left\{\frac{1}{\theta_1} - \frac{1}{\theta_2}\right\} = 2 \log \frac{\theta_1^{\frac{1}{2}} x_2}{\theta_2^{\frac{1}{2}} x_1},$$

we see that Q is independent of the pressure of the hydrogen. Consequently, when the pressure of the hydrogen is small, the energy required for the liberation of a corpuscle is independent of the pressure of the hydrogen.

Consider now the formula $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$. Since Q is independent of p and $x = Bp$, it follows that A is proportional to p. It is clear, therefore, that A cannot be regarded as proportional to the number of corpuscles in a cubic centimetre of the platinum, because this latter number must be independent, or very nearly so, of p. A is evidently proportional to the number of corpuscles which are in a position to contribute towards the leak, so that we may conclude that this latter number is proportional to the amount of hydrogen present when this amount is small. Thus we are led to the conclusion that it is only those corpuscles which are in some way associated with hydrogen molecules or atoms which are able to escape from the platinum, at the temperatures at which it is possible to make observations.

In a note to his paper on "The Electrical Conductivity Imparted to a Vacuum by Hot Conductors" ('Phil. Trans.,' A, vol. 201, pp. 497–549) Mr. Richardson suggests that the effect of hydrogen on the negative leak which I have observed can be explained on his theory by supposing that the hydrogen diminishes Q while A remains constant. But, as we have just seen, the fact that the leak is proportional to p shows that Q is constant and A proportional to p. When p is greater than about 0·02 millim. it is found that Q does diminish as p increases, but A does not remain constant.

Mr. Richardson also suggests that my process of cleaning the platinum with nitric acid may deposit a layer of negatively charged oxygen on it which would increase Q and so diminish the leak. The leak can, however, be reduced without treating the wire with nitric acid. If the wire is simply heated in a good vacuum the leak falls off with time; and if the gases evolved by the wire are removed, the leak can be reduced in this way to as small a value as can be obtained by treating the wire with nitric acid. The nitric acid process was adopted because it enabled the hydrogen to be got rid of without long continued heating which causes the wire to disintegrate.

[Although it appears from the experiments that the negative leak obtained from hot platinum at low pressures is due to the presence of hydrogen or other substances, it is, of course, possible that with perfectly pure platinum at a sufficiently high temperature some negative leak would be obtained due to the emission of corpuscles by the platinum alone. Mr. Richardson's results for carbon, which show that there is a large emission of corpuscles from hot carbon even at very low pressures, make it probable that there would be a similar emission in the case of pure platinum at sufficiently high temperatures. The author has recently made some experiments with carbon which, as far as they have gone, confirm Mr. Richardson's results for that substance.]

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THE present memoir is intended to carry out investigations, concerned with the differential invariants of ordinary space and of surfaces in that space, similar to those in a former memoir,* concerned with the differential invariants of a surface and of curves upon that surface.

The method used in the former memoir is used here in what is the obviously natural development. It is based upon the method,† which was originated by LIE and amplified by Professor ŽORAWSKI. When applied to two-dimensional invariants, it proved possible to modify and simplify the later stages of the calculations by making them dependent upon the concomitants of a system of simultaneous binary forms. When applied to three-dimensional invariants, it proves possible to effect a corresponding simplification in the later stages of the calculations; the required functions are found to be the invariants and the contravariants of a system of simultaneous ternary forms.

The expressions for an algebraically complete aggregate of invariants up to the third order inclusive have been obtained. The calculations necessary for the construction of these invariants were laborious; indeed, the calculations for the invariants of the third order are so long that in this memoir they have been suppressed, and only the results are given. It may be mentioned incidentally that, among the invariants of the third order, six (in particular) occur possessing a special property. They can be so taken in the algebraically complete aggregate as to coincide with six quantities which were proved by CAYLEY to vanish on account of the intrinsic significance of the fundamental magnitudes. These six equations are the generalisation, to surfaces not orthogonal, of LAMÉ'S six equations for triply orthogonal surfaces.

The geometric significance of practically all the differential invariants of the first order and the second order has been obtained. I have not yet attempted to identify

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* 'Phil. Trans.,' A, vol. 201 (1903), pp. 329–402.

† References are given in the memoir just quoted.

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the invariants proper to the third order; there is reason to suppose that, when they are completely identified in association with even a single surface in space, they can be used to establish two fundamental geometrical relations affecting the surface.

The Fundamental Magnitudes.

1. The independent variables of position in space are taken to be u, v, w. That position is also defined in the customary manner by rectangular Cartesian co-ordinates x, y, z; and then u, v, w may be regarded as three independent functions of x, y, z. Conversely, we shall assume that x, y, z are expressible as functions of u, v, w, which are regular in the vicinity of any assigned position, save for singular lines or points with which we are not concerned. Moreover, if

$$u = u(x, y, z), \quad v = v(x, y, z), \quad w = w(x, y, z),$$

the surfaces $u =$ constant, $v =$ constant, $w =$ constant, form a triple family; it will not be assumed that the triple family is orthogonal. The parameters u, v, w of the surfaces are sometimes called curvilinear co-ordinates.

Fundamental magnitudes for space arise in the expression of a distance-element in terms of u, v, w, du, dv, dw. Denoting this element by ds, we have

$$\begin{aligned} ds^2 &= dx^2 + dy^2 + dz^2 \\ &= a\,du^2 + 2h\,du\,dv + 2g\,du\,dw + b\,dv^2 + 2f\,dv\,dw + c\,dw^2 \\ &= (a, b, c, f, g, h \between du, dv, dw)^2, \end{aligned}$$

in the usual notation, where

$$a = \Sigma\left(\frac{\partial x}{\partial u}\right)^2, \qquad b = \Sigma\left(\frac{\partial x}{\partial v}\right)^2, \qquad c = \Sigma\left(\frac{\partial x}{\partial w}\right)^2,$$

$$f = \Sigma\frac{\partial x}{\partial v}\frac{\partial x}{\partial w}, \qquad g = \Sigma\frac{\partial x}{\partial w}\frac{\partial x}{\partial u}, \qquad h = \Sigma\frac{\partial x}{\partial u}\frac{\partial x}{\partial v},$$

the summation being taken over the three variables x, y, z in each case.

The quantities a, b, c, f, g, h may be called the fundamental magnitudes of the first kind, as involving derivatives of only the first order. Other fundamental magnitudes may exist in association with derivatives of higher orders;* they are ignored for the purposes of the present investigation.

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* Those magnitudes, which are the natural generalisation of the magnitudes L, M, N in the Gaussian theory of surfaces, are not independent quantities; they are proved by CAYLEY, 'Coll. Math. Papers,' vol. 12, p. 4, to be expressible in terms of derivatives of a, b, c, f, g, h.

It may be added that the memoir by CAYLEY, which has just been quoted, contains the establishment of the six intrinsic equations mentioned in the introductory remarks. For reasons which will appear in the course of the memoir, I have found it desirable to deviate to some extent from CAYLEY'S notation.

Property of Invariance.

2. A combination F of any number of functions of u, v, w and of the derivatives of these functions is said to be a relative invariant if, when any new independent variables u', v', w' are introduced, and the same combination F′ of the modified functions and of their derivatives is formed, the relation

$$F = \Omega^{\mu} F'$$

is satisfied, where

$$\Omega = \frac{\partial (u', v', w')}{\partial (u, v, w)}.$$

The invariants actually considered are rational, so that μ is an integer. The invariant is called absolute when $\mu = 0$.

It is a known theorem that the property of invariance is possessed in general, if it is possessed for the most general infinitesimal transformation; we shall therefore take

$$u' = u + \xi (u, v, w)\, dt,$$

$$v' = v + \eta (u, v, w)\, dt,$$

$$w' = w + \zeta (u, v, w)\, dt,$$

where ξ, η, ζ are arbitrary integral functions of u, v, w, and dt is an infinitesimal quantity of which only the first power is retained.

Derivatives with regard to u, v, w are required; we write

$$\theta_{lmn} = \frac{\partial \theta^{l+m+n}}{\partial u^l\, \partial v^m\, \partial w^n}$$

for any quantity θ and for all values of l, m, n. With this notation, we at once have the retained value of Ω in the form

$$\Omega = 1 + (\xi_{100} + \eta_{010} + \zeta_{001})\, dt.$$

Arguments of the Invariants and their Increments.

3. As regards the possible arguments of a differential invariant of space, we shall have the fundamental magnitudes of the first kind and their derivatives. It is conceivable that properties of surfaces in the space and of curves in the space will be involved; provision for the possibility will be made by the introduction of functions such as $\phi (u, v, w)$. One of these, equated to zero or to a constant, will give a surface: two such surfaces will give a curve or curves: three such surfaces will give a point or points.

It is not difficult to see that u, v, w will not occur explicitly in the expression of the invariant, nor will any function of them such as $\phi (u, v, w)$ occur explicitly; but derivatives of such a function as ϕ will occur, and the order of the derivatives will depend upon the order of the derivatives of a, b, c, f, g, h which arise in the invariant.

Clearly one invariant is provided by the determinant

$$L^2 = \begin{vmatrix} a, & h, & g \\ h, & b, & f \\ g, & f, & c \end{vmatrix};$$

for on substituting the values of the fundamental magnitudes in terms of the derivatives of x, y, z, we have

$$\begin{aligned} L &= \frac{\partial(x, y, z)}{\partial(u, v, w)} \\ &= \Omega L', \end{aligned}$$

so that L is an invariant for which the index μ is 1.

It is convenient to denote the minors of the constituents in L^2 by A, B, C, F, G, H, where

$$A = bc - f^2, \qquad B = ca - g^2, \qquad C = ab - h^2.$$

$$F = gh - af, \qquad G = hf - bg, \qquad H = fg - ch.$$

4. The laws of transformation of the various magnitudes are required in order to construct their increments which correspond to the increments of u, v, w. Writing

$$\begin{aligned} ds^2 &= (a, b, c, f, g, h \between du, dv, dw)^2 \\ &= (a', b', c', f', g', h' \between du', dv', dw')^2, \end{aligned}$$

we have

$$\begin{aligned} a &= \left(a', b', c', f', g', h' \between \frac{\partial u'}{\partial u}, \frac{\partial v'}{\partial u}, \frac{\partial w'}{\partial u}\right)^2 \\ &= a'(1 + 2\xi_{100}\, dt) + 2h'\eta_{100}\, dt + 2g'\zeta_{100}\, dt \\ &= a' + (2a\xi_{100} + 2h\eta_{100} + 2g\zeta_{100})\, dt, \end{aligned}$$

on neglecting squares and higher powers of dt. Similarly

$$\begin{aligned} b &= b' + (2h\xi_{010} + 2b\eta_{010} + 2f\zeta_{010})\, dt, \\ c &= c' + (2g\xi_{001} + 2f\eta_{001} + 2c\zeta_{001})\, dt, \\ f &= f' + \{h\xi_{001} + g\xi_{010} + b\eta_{001} + f(\eta_{010} + \zeta_{001}) + c\zeta_{010}\}\, dt, \\ g &= g' + \{a\xi_{001} + h\eta_{001} + g(\xi_{100} + \zeta_{001}) + f\eta_{100} + c\zeta_{100}\}\, dt, \\ h &= h' + \{a\xi_{010} + h(\xi_{100} + \eta_{010}) + g\zeta_{010} + b\eta_{100} + f\zeta_{100}\}\, dt. \end{aligned}$$

These six equations at once give the increments of a, b, c, f, g, h. They can also be used to construct the increments of the derivatives of fundamental magnitudes, as follows.

5. Let u, v, w become $u+i$, $v+j$, $w+k$; and let the consequent values of u', v', w' be $u'+i'$, $v'+j'$, $w'+k'$; then

$$
\begin{aligned}
i' &= i + \{\xi(u+i,\ v+j,\ w+k) - \xi(u,\ v,\ w)\}\,dt \\
&= i + \Sigma\Sigma\Sigma' \frac{i^l j^m k^n}{l!\ m!\ n!}\,\xi_{lmn}\,dt, \\
j' &= j + \Sigma\Sigma\Sigma' \frac{i^l j^m k^n}{l!\ m!\ n!}\,\eta_{lmn}\,dt, \\
k' &= k + \Sigma\Sigma\Sigma' \frac{i^l j^m k^n}{l!\ m!\ n!}\,\zeta_{lmn}\,dt,
\end{aligned}
$$

where $\Sigma\Sigma\Sigma'$ implies summation for all positive integer (including zero) values of l, m, n, save only simultaneous zero values. Hence also for all integer values of p, q, r, we have

$$
\begin{aligned}
i'^p j'^q k'^r = i^p j^q k^r &+ p i^{p-1} j^q k^r \Sigma\Sigma\Sigma' \frac{i^l j^m k^n}{l!\ m!\ n!}\,\xi_{lmn}\,dt \\
&+ q i^p j^{q-1} k^r \Sigma\Sigma\Sigma' \frac{i^l j^m k^n}{l!\ m!\ n!}\,\eta_{lmn}\,dt \\
&+ r i^p j^q k^{r-1} \Sigma\Sigma\Sigma' \frac{i^l j^m k^n}{l!\ m!\ n!}\,\zeta_{lmn}\,dt.
\end{aligned}
$$

Now

$$
\begin{aligned}
a(u+i,\ v+j,\ w+k) = a(u'+i',\ v'+j',\ w'+k') & \\
+ 2a(u+i,\ v+j,\ w+k)\,\xi_{100}(u+i,\ v+j,\ w+k)\,dt & \\
+ 2h(u+i,\ v+j,\ w+k)\,\eta_{100}(u+i,\ v+j,\ w+k)\,dt & \\
+ 2g(u+i,\ v+j,\ w+k)\,\zeta_{100}(u+i,\ v+j,\ w+k)\,dt. &
\end{aligned}
$$

Expand the first term on the right-hand side in powers of i', j', k', and substitute for all combinations such as $i'^p j'^q k'^r$ in terms of i, j, k; expand also all the other quantities in powers of i, j, k, and select the coefficient of $i^\alpha j^\beta k^\gamma$. Let

$$
\binom{s}{t} = \frac{s!}{(s-t)!\ t!},
$$

$$
a'_{\alpha\beta\gamma} = a_{\alpha\beta\gamma} + \frac{da_{\alpha\beta\gamma}}{dt}\,dt;
$$

then, neglecting powers of dt higher than the first and multiplying up by $\alpha!\ \beta!\ \gamma!$, we have

$$
\begin{aligned}
-\frac{da_{\alpha\beta\gamma}}{dt} = \Sigma\Sigma\Sigma' \binom{\alpha}{l}\binom{\beta}{m}\binom{\gamma}{n} \{a_{\alpha+1-l,\ \beta-m,\ \gamma-n}\xi_{lmn} + a_{\alpha-l,\ \beta+1-m,\ \gamma-n}\eta_{lmn} + a_{\alpha-l,\ \beta-m,\ \gamma+1-n}\zeta_{lmn}\} & \\
+ 2\Sigma\Sigma\Sigma \binom{\alpha}{l}\binom{\beta}{m}\binom{\gamma}{n} \{a_{\alpha-l,\ \beta-m,\ \gamma-n}\xi_{l+1,\ m,\ n} + h_{\alpha-l,\ \beta-m,\ \gamma-n}\eta_{l+1,\ m,\ n} + g_{\alpha-l,\ \beta-m,\ \gamma-n}\zeta_{l+1,\ m,\ n}\}, &
\end{aligned}
$$

where the summations are for all integer values of l from 0 to α, of m from 0 to β, and of n from 0 to γ, the simultaneous zero values being excluded from the triple summations $\Sigma\Sigma\Sigma'$ in the first line of the right-hand side.

Proceeding in the same way with the expression for the increment of f, we find

$$
\begin{aligned}
-\frac{df_{\alpha\beta\gamma}}{dt} = \Sigma\Sigma\Sigma'\binom{\alpha}{l}\binom{\beta}{m}\binom{\gamma}{n}&\{f_{\alpha+1-l,\,\beta-m,\,\gamma-n}\xi_{lmn} + f_{\alpha-l,\,\beta+1-m,\,\gamma-n}\eta_{lmn} + f_{\alpha-l,\,\beta-m,\,\gamma+1-n}\zeta_{lmn}\} \\
+ \Sigma\Sigma\Sigma\binom{\alpha}{l}\binom{\beta}{m}\binom{\gamma}{n}&\{h_{\alpha-l,\,\beta-m,\,\gamma-n}\xi_{l,\,m,\,n+1} + g_{\alpha-l,\,\beta-m,\,\gamma-n}\xi_{l,\,m+1,\,n} \\
&+ b_{\alpha-l,\,\beta-m,\,\gamma-n}\eta_{l,\,m,\,n+1} + f_{\alpha-l,\,\beta-m,\,\gamma-n}\eta_{l,\,m+1,\,n} \\
&+ f_{\alpha-l,\,\beta-m,\,\gamma-n}\zeta_{l,\,m,\,n+1} + c_{\alpha-l,\,\beta-m,\,\gamma-n}\zeta_{l,\,m+1,\,n}\},
\end{aligned}
$$

where again the summations are for all integer values of l from 0 to α, of m from 0 to β, and of n from 0 to γ, the simultaneous zero values being excluded from the triple summations $\Sigma\Sigma\Sigma'$ in the first line of the right-hand side.

Effecting in these two results all the interchanges that correspond to the interchange of the variables u and v, we obtain the values of

$$
-\frac{db_{\alpha\beta\gamma}}{dt}, \qquad -\frac{dg_{\alpha\beta\gamma}}{dt};
$$

and also effecting in them all the interchanges that correspond to the interchange of the variables u and w, we obtain the values of

$$
-\frac{dc_{\alpha\beta\gamma}}{dt}, \qquad -\frac{dh_{\alpha\beta\gamma}}{dt}.
$$

The expression for the increment of the derivatives of any function $\phi(u, v, w)$, where ϕ is unaltered in value by transformation, can be obtained in the same way as was that for the increment of the derivatives of a; it is found to be

$$
-\frac{d\phi_{\alpha\beta\gamma}}{dt} = \Sigma\Sigma\Sigma'\binom{\alpha}{l}\binom{\beta}{m}\binom{\gamma}{n}\{\phi_{\alpha+1-l,\,\beta-m,\,\gamma-n}\xi_{lmn} + \phi_{\alpha-l,\,\beta+1-m,\,\gamma-n}\eta_{lmn} + \phi_{\alpha-l,\,\beta-m,\,\gamma+1-n}\zeta_{lmn}\},
$$

with the same significance for $\Sigma\Sigma\Sigma'$ as before.

It thus appears that if the highest order of derivatives of the fundamental magnitudes that occur in a differential invariant be M, the highest order of derivatives of a function ϕ that can occur is M + 1.

6. In order to avoid encumbering the memoir with vast masses of symbols, I propose to exhibit the mode of constructing differential invariants up to the second order, that is, invariants involving derivatives of a single function ϕ up to the second order and derivatives of a, b, c, f, g, h of the first order. Then I propose to indicate what are the differential invariants up to the second order that involve more than a single function ϕ. And as the last part of the merely analytical portion of the memoir, I propose to state the results for differential invariants up to the third order but to give practically none of the contributory analysis. Some idea of the protracted

character of the calculations needed for the construction of the differential invariants of the third order may be gathered from the fact, that they require the complete solution of a Jacobian system of fifty-seven simultaneous partial differential equations of the first order and the first degree.

For such analysis as will here be given in detail, we need the following particular cases of the preceding general results :—

$$-\frac{da}{dt} = 2a\xi_{100} + 2h\eta_{100} + 2g\zeta_{100},$$

$$-\frac{db}{dt} = 2h\xi_{010} + 2b\eta_{010} + 2f\zeta_{010},$$

$$-\frac{dc}{dt} = 2g\xi_{001} + 2f\eta_{001} + 2c\zeta_{001},$$

$$-\frac{df}{dt} = g\xi_{010} + h\xi_{001} + f\eta_{010} + b\eta_{001} + c\zeta_{010} + f\zeta_{001},$$

$$-\frac{dg}{dt} = g\xi_{100} + a\xi_{001} + f\eta_{100} + h\eta_{001} + c\zeta_{100} + g\zeta_{001},$$

$$-\frac{dh}{dt} = h\xi_{100} + a\xi_{010} + b\eta_{100} + h\eta_{010} + f\zeta_{100} + g\zeta_{010};$$

$$-\frac{da_{100}}{dt} = 3a_{100}\xi_{100} + 2a\xi_{200} + (a_{010} + 2h_{100})\,\eta_{100} + 2h\eta_{200} + (a_{001} + 2g_{100})\,\zeta_{100} + 2g\zeta_{200},$$

$$\begin{aligned} -\frac{da_{010}}{dt} = 2a_{010}\xi_{100} + a_{100}\xi_{010} + 2a\xi_{110} + 2h_{010}\eta_{100} + a_{010}\eta_{010} + 2h\eta_{110} \\ + 2g_{010}\zeta_{100} + a_{001}\zeta_{010} + 2g\zeta_{110}, \end{aligned}$$

$$\begin{aligned} -\frac{da_{001}}{dt} = 2a_{001}\xi_{100} + a_{100}\xi_{001} + 2a\xi_{101} + 2h_{001}\eta_{100} + a_{010}\eta_{001} + 2h\eta_{101} \\ + 2g_{001}\zeta_{100} + a_{001}\zeta_{001} + 2g\zeta_{101}; \end{aligned}$$

$$\begin{aligned} -\frac{db_{100}}{dt} = b_{100}\xi_{100} + 2h_{100}\xi_{010} + 2h\xi_{110} + b_{010}\eta_{100} + 2b_{100}\eta_{010} + 2b\eta_{110} \\ + b_{001}\zeta_{100} + 2f_{100}\zeta_{010} + 2f\zeta_{110}, \end{aligned}$$

$$-\frac{db_{010}}{dt} = (b_{100} + 2h_{010})\,\xi_{010} + 2h\xi_{020} + 3b_{010}\eta_{010} + 2b\eta_{020} + (b_{001} + 2f_{010})\,\zeta_{010} + 2f\zeta_{020},$$

$$\begin{aligned} -\frac{db_{001}}{dt} = 2h_{001}\xi_{010} + b_{100}\xi_{001} + 2h\xi_{011} + 2b_{001}\eta_{010} + b_{010}\eta_{001} + 2b\eta_{011} \\ + 2f_{001}\zeta_{010} + b_{001}\zeta_{001} + 2f\zeta_{011}; \end{aligned}$$

$$\begin{aligned} -\frac{dc_{100}}{dt} = c_{100}\xi_{100} + 2g_{100}\xi_{001} + 2g\xi_{101} + c_{010}\eta_{100} + 2f_{100}\eta_{001} + 2f\eta_{101} \\ + c_{001}\zeta_{100} + 2c_{100}\zeta_{001} + 2c\zeta_{101}, \end{aligned}$$

$$\begin{aligned} -\frac{dc_{010}}{dt} = c_{100}\xi_{010} + 2g_{010}\xi_{001} + 2g\xi_{011} + c_{010}\eta_{010} + 2f_{010}\eta_{001} + 2f\eta_{011} \\ + c_{001}\zeta_{010} + 2c_{010}\zeta_{001} + 2c\zeta_{011}, \end{aligned}$$

$$-\frac{dc_{001}}{dt} = (c_{100} + 2g_{001})\,\xi_{001} + 2g\xi_{002} + (c_{010} + 2f_{001})\,\eta_{001} + 2f\eta_{002} + 3c_{001}\zeta_{001} + 2c\zeta_{002};$$

$$
\begin{aligned}
-\frac{df_{100}}{dt} = f_{100}\xi_{100} &+ g_{100}\xi_{010} + h_{100}\xi_{001} + g\xi_{110} + h\xi_{101} \\
&+ f_{010}\eta_{100} + f_{100}\eta_{010} + b_{100}\eta_{001} + f\eta_{110} + b\eta_{101} \\
&+ f_{001}\zeta_{100} + c_{100}\zeta_{010} + f_{100}\zeta_{001} + c\zeta_{110} + f\zeta_{101},
\end{aligned}
$$

$$
\begin{aligned}
-\frac{df_{010}}{dt} = (f_{100} + g_{010})\,\xi_{010} &+ h_{010}\xi_{001} + g\xi_{020} + h\xi_{011} \\
&+ 2f_{010}\eta_{010} + b_{010}\eta_{001} + f\eta_{020} + b\eta_{011} \\
&+ (f_{001} + c_{010})\,\zeta_{010} + f_{010}\zeta_{001} + c\zeta_{020} + f\zeta_{011},
\end{aligned}
$$

$$
\begin{aligned}
-\frac{df_{001}}{dt} = g_{001}\xi_{010} &+ (f_{100} + h_{001})\,\xi_{001} + g\xi_{011} + h\xi_{002} \\
&+ f_{001}\eta_{010}\,(f_{010} + b_{001})\,\eta_{001} + f\eta_{011} + b\eta_{002} \\
&+ c_{001}\zeta_{010} + 2f_{001}\zeta_{001} + c\zeta_{011} + f\zeta_{002}\,;
\end{aligned}
$$

$$
\begin{aligned}
-\frac{dg_{100}}{dt} = 2g_{100}\xi_{100} &+ a_{100}\xi_{001} + g\xi_{200} + a\xi_{101} \\
&+ (g_{010} + f_{100})\,\eta_{100} + h_{100}\eta_{001} + f\eta_{200} + h\eta_{101} \\
&+ (g_{001} + c_{100})\,\zeta_{100} + g_{100}\zeta_{001} + c\zeta_{200} + g\zeta_{101},
\end{aligned}
$$

$$
\begin{aligned}
-\frac{dg_{010}}{dt} = g_{010}\xi_{100} &+ g_{100}\xi_{010} + a_{010}\xi_{001} + g\xi_{110} + a\xi_{011} \\
&+ f_{010}\eta_{100} + g_{010}\eta_{010} + h_{010}\eta_{001} + f\eta_{110} + h\eta_{011} \\
&+ c_{010}\zeta_{100} + g_{001}\zeta_{010} + g_{010}\zeta_{001} + c\zeta_{110} + g\zeta_{011},
\end{aligned}
$$

$$
\begin{aligned}
-\frac{dg_{001}}{dt} = g_{001}\xi_{100} &+ (a_{001} + g_{100})\,\xi_{001} + g\xi_{101} + a\xi_{002} \\
&+ f_{001}\eta_{100} + (h_{001} + g_{010})\,\eta_{001} + f\eta_{101} + h_{002} \\
&+ c_{001}\zeta_{100} + 2g_{001}\zeta_{001} + c\zeta_{101} + g\zeta_{002}\,;
\end{aligned}
$$

$$
\begin{aligned}
-\frac{dh_{100}}{dt} = 2h_{100}\xi_{100} &+ a_{100}\xi_{010} + h\xi_{200} + a\xi_{110} \\
&+ (h_{010} + b_{100})\,\eta_{100} + h_{100}\eta_{010} + b\eta_{200} + h\eta_{110} \\
&+ (h_{001} + f_{100})\,\zeta_{100} + g_{100}\zeta_{010} + f\zeta_{200} + g\zeta_{110},
\end{aligned}
$$

$$
\begin{aligned}
-\frac{dh_{010}}{dt} = h_{010}\xi_{100} &+ (a_{010} + h_{100})\,\xi_{010} + h\xi_{110} + a\xi_{020} \\
&+ b_{010}\eta_{100} + 2h_{010}\eta_{010} + b\eta_{110} + h\eta_{020} \\
&+ f_{010}\zeta_{100} + (g_{010} + h_{001})\,\zeta_{010} + f\zeta_{110} + g\zeta_{020},
\end{aligned}
$$

$$
\begin{aligned}
-\frac{dh_{001}}{dt} = h_{001}\xi_{100} &+ a_{001}\xi_{010} + h_{100}\xi_{001} + h\xi_{101} + a\xi_{011} \\
&+ b_{001}\eta_{100} + h_{001}\eta_{010} + h_{010}\eta_{001} + b\eta_{101} + h\eta_{011} \\
&+ f_{001}\zeta_{100} + g_{001}\zeta_{010} + h_{001}\zeta_{001} + f\zeta_{101} + g\zeta_{011}\,;
\end{aligned}
$$

$$-\frac{d\phi_{100}}{dt} = \phi_{100}\xi_{100} + \phi_{010}\eta_{100} + \phi_{001}\zeta_{100},$$

$$-\frac{d\phi_{010}}{dt} = \phi_{100}\xi_{010} + \phi_{010}\eta_{010} + \phi_{001}\zeta_{010}.$$

$$-\frac{d\phi_{001}}{dt} = \phi_{100}\xi_{001} + \phi_{010}\eta_{001} + \phi_{001}\zeta_{001};$$

$$-\frac{d\phi_{200}}{dt} = 2\phi_{200}\xi_{100} + \phi_{100}\xi_{200} + 2\phi_{110}\eta_{100} + \phi_{010}\eta_{200} + 2\phi_{101}\zeta_{100} + \phi_{001}\zeta_{200},$$

$$-\frac{d\phi_{020}}{dt} = 2\phi_{110}\xi_{010} + \phi_{100}\xi_{020} + 2\phi_{020}\eta_{010} + \phi_{010}\eta_{020} + 2\phi_{011}\zeta_{010} + \phi_{001}\zeta_{020},$$

$$-\frac{d\phi_{002}}{dt} = 2\phi_{101}\xi_{001} + \phi_{100}\xi_{002} + 2\phi_{011}\eta_{001} + \phi_{010}\eta_{002} + 2\phi_{002}\zeta_{001} + \phi_{001}\zeta_{002},$$

$$-\frac{d\phi_{110}}{dt} = \phi_{110}\xi_{100} + \phi_{200}\xi_{010} + \phi_{100}\xi_{110} + \phi_{020}\eta_{100} + \phi_{110}\eta_{010} + \phi_{010}\eta_{110} + \phi_{011}\zeta_{100} + \phi_{101}\zeta_{010} + \phi_{001}\zeta_{110},$$

$$-\frac{d\phi_{101}}{dt} = \phi_{101}\xi_{100} + \phi_{200}\xi_{001} + \phi_{100}\xi_{101} + \phi_{011}\eta_{100} + \phi_{110}\eta_{001} + \phi_{010}\eta_{101} + \phi_{002}\zeta_{100} + \phi_{101}\zeta_{001} + \phi_{001}\zeta_{101}.$$

$$-\frac{d\phi_{011}}{dt} = \phi_{101}\xi_{010} + \phi_{110}\xi_{001} + \phi_{100}\xi_{011} + \phi_{011}\eta_{010} + \phi_{020}\eta_{001} + \phi_{010}\eta_{011} + \phi_{002}\zeta_{010} + \phi_{011}\zeta_{001} + \phi_{001}\zeta_{011}.$$

The Differential Equations characteristic of the Invariance.

7. Let σ denote any differential invariant involving at least some of the quantities whose increments due to an infinitesimal variation have just been given. The differential equations characteristic of the invariance can be deduced from the equation

$$\sigma = \Omega^{\mu}\sigma'$$

in the usual manner: we substitute for each argument θ' in σ' its value

$$\theta + \frac{d\theta}{dt}\,dt,$$

and equate to zero the composite coefficient of dt on the right-hand side. The quantities ξ, η, ζ are arbitrary and independent; the coefficients of the various derivatives in the last equation must therefore vanish. These relations are the partial differential equations which, up to the order of differentiation retained, are characteristic of the invariants; they are as follows:

There are the three equations

$$\left.\begin{aligned}
2a\frac{\partial\sigma}{\partial a_{100}} + h\frac{\partial\sigma}{\partial h_{100}} + g\frac{\partial\sigma}{\partial g_{100}} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{200}} &= 0\\
2h\frac{\partial\sigma}{\partial a_{100}} + b\frac{\partial\sigma}{\partial h_{100}} + f\frac{\partial\sigma}{\partial g_{100}} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{200}} &= 0\\
2g\frac{\partial\sigma}{\partial a_{100}} + f\frac{\partial\sigma}{\partial h_{100}} + c\frac{\partial\sigma}{\partial g_{100}} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{200}} &= 0
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{II}_1),$$

from the coefficients of ξ_{200}, η_{200}, ζ_{200} respectively; the three equations

$$\left.\begin{aligned}
a\left(2\frac{\partial\sigma}{\partial a_{010}} + \frac{\partial\sigma}{\partial h_{100}}\right) + h\left(2\frac{\partial\sigma}{\partial b_{100}} + \frac{\partial\sigma}{\partial h_{010}}\right) + g\left(\frac{\partial\sigma}{\partial f_{100}} + \frac{\partial\sigma}{\partial g_{010}}\right) + \phi_{100}\frac{\partial\sigma}{\partial\phi_{110}} &= 0\\
h\left(2\frac{\partial\sigma}{\partial a_{010}} + \frac{\partial\sigma}{\partial h_{100}}\right) + b\left(2\frac{\partial\sigma}{\partial b_{100}} + \frac{\partial\sigma}{\partial h_{010}}\right) + f\left(\frac{\partial\sigma}{\partial f_{100}} + \frac{\partial\sigma}{\partial g_{010}}\right) + \phi_{010}\frac{\partial\sigma}{\partial\phi_{110}} &= 0\\
g\left(2\frac{\partial\sigma}{\partial a_{010}} + \frac{\partial\sigma}{\partial h_{100}}\right) + f\left(2\frac{\partial\sigma}{\partial b_{100}} + \frac{\partial\sigma}{\partial h_{010}}\right) + c\left(\frac{\partial\sigma}{\partial f_{100}} + \frac{\partial\sigma}{\partial g_{010}}\right) + \phi_{001}\frac{\partial\sigma}{\partial\phi_{110}} &= 0
\end{aligned}\right\} \quad . \quad (\mathrm{II}_2),$$

from the coefficients of ξ_{110}, η_{110}, ζ_{110} respectively; the three equations

$$\left.\begin{aligned}
a\left(2\frac{\partial\sigma}{\partial a_{001}} + \frac{\partial\sigma}{\partial g_{100}}\right) + h\left(\frac{\partial\sigma}{\partial f_{100}} + \frac{\partial\sigma}{\partial h_{001}}\right) + g\left(\frac{\partial\sigma}{\partial g_{001}} + 2\frac{\partial\sigma}{\partial c_{100}}\right) + \phi_{100}\frac{\partial\sigma}{\partial\phi_{101}} &= 0\\
h\left(2\frac{\partial\sigma}{\partial a_{001}} + \frac{\partial\sigma}{\partial g_{100}}\right) + b\left(\frac{\partial\sigma}{\partial f_{100}} + \frac{\partial\sigma}{\partial h_{001}}\right) + f\left(\frac{\partial\sigma}{\partial g_{001}} + 2\frac{\partial\sigma}{\partial c_{100}}\right) + \phi_{010}\frac{\partial\sigma}{\partial\phi_{101}} &= 0\\
g\left(2\frac{\partial\sigma}{\partial a_{001}} + \frac{\partial\sigma}{\partial g_{100}}\right) + f\left(\frac{\partial\sigma}{\partial f_{100}} + \frac{\partial\sigma}{\partial h_{001}}\right) + c\left(\frac{\partial\sigma}{\partial g_{001}} + 2\frac{\partial\sigma}{\partial c_{100}}\right) + \phi_{001}\frac{\partial\sigma}{\partial\phi_{101}} &= 0
\end{aligned}\right\} \quad . \quad (\mathrm{II}_3),$$

from the coefficients of ξ_{101}, η_{101}, ζ_{101} respectively; the three equations

$$\left.\begin{aligned}
a\frac{\partial\sigma}{\partial h_{010}} + 2h\frac{\partial\sigma}{\partial b_{010}} + g\frac{\partial\sigma}{\partial f_{010}} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{020}} &= 0\\
h\frac{\partial\sigma}{\partial h_{010}} + 2b\frac{\partial\sigma}{\partial b_{010}} + f\frac{\partial\sigma}{\partial f_{010}} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{020}} &= 0\\
g\frac{\partial\sigma}{\partial h_{010}} + 2f\frac{\partial\sigma}{\partial b_{010}} + c\frac{\partial\sigma}{\partial f_{010}} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{020}} &= 0
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{II}_4),$$

from the coefficients of ξ_{020}, η_{020}, ζ_{020} respectively; the three equations

$$\left.\begin{aligned}
a\left(\frac{\partial\sigma}{\partial h_{001}} + \frac{\partial\sigma}{\partial g_{010}}\right) + h\left(2\frac{\partial\sigma}{\partial b_{001}} + \frac{\partial\sigma}{\partial f_{010}}\right) + g\left(\frac{\partial\sigma}{\partial f_{001}} + 2\frac{\partial\sigma}{\partial c_{010}}\right) + \phi_{100}\frac{\partial\sigma}{\partial\phi_{011}} &= 0\\
h\left(\frac{\partial\sigma}{\partial h_{001}} + \frac{\partial\sigma}{\partial g_{010}}\right) + b\left(2\frac{\partial\sigma}{\partial b_{001}} + \frac{\partial\sigma}{\partial f_{010}}\right) + f\left(\frac{\partial\sigma}{\partial f_{001}} + 2\frac{\partial\sigma}{\partial c_{010}}\right) + \phi_{010}\frac{\partial\sigma}{\partial\phi_{011}} &= 0\\
g\left(\frac{\partial\sigma}{\partial h_{001}} + \frac{\partial\sigma}{\partial g_{010}}\right) + f\left(2\frac{\partial\sigma}{\partial b_{001}} + \frac{\partial\sigma}{\partial f_{010}}\right) + c\left(\frac{\partial\sigma}{\partial f_{001}} + 2\frac{\partial\sigma}{\partial c_{010}}\right) + \phi_{001}\frac{\partial\sigma}{\partial\phi_{011}} &= 0
\end{aligned}\right\} \quad . \quad (\mathrm{II}_5),$$

from the coefficients of ξ_{011}, η_{011}, ζ_{011} respectively; the three equations

$$\left.\begin{aligned} a\frac{\partial\sigma}{\partial g_{001}} + h\frac{\partial\sigma}{\partial f_{001}} + 2g\frac{\partial\sigma}{\partial c_{001}} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{002}} &= 0 \\ h\frac{\partial\sigma}{\partial g_{001}} + b\frac{\partial\sigma}{\partial f_{001}} + 2f\frac{\partial\sigma}{\partial c_{001}} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{002}} &= 0 \\ g\frac{\partial\sigma}{\partial g_{001}} + f\frac{\partial\sigma}{\partial f_{001}} + 2c\frac{\partial\sigma}{\partial c_{001}} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{002}} &= 0 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{II}_6),$$

from the coefficients of ξ_{002}, η_{002}, ζ_{002} respectively; the six equations

$$\begin{aligned} \Delta_1(\sigma) = 2h\frac{\partial\sigma}{\partial a} + b\frac{\partial\sigma}{\partial h} + f\frac{\partial\sigma}{\partial g} + 2\phi_{110}\frac{\partial\sigma}{\partial\phi_{200}} + \phi_{020}\frac{\partial\sigma}{\partial\phi_{110}} + \phi_{011}\frac{\partial\sigma}{\partial\phi_{101}} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{100}} \\ + (a_{010} + 2h_{100})\frac{\partial\sigma}{\partial a_{100}} + 2h_{010}\frac{\partial\sigma}{\partial a_{010}} + 2h_{001}\frac{\partial\sigma}{\partial a_{001}} + b_{010}\frac{\partial\sigma}{\partial b_{100}} + c_{010}\frac{\partial\sigma}{\partial c_{100}} \\ + f_{010}\frac{\partial\sigma}{\partial f_{100}} + (g_{010} + f_{100})\frac{\partial\sigma}{\partial g_{100}} + f_{010}\frac{\partial\sigma}{\partial g_{010}} + f_{001}\frac{\partial\sigma}{\partial g_{001}} \\ + (h_{010} + b_{100})\frac{\partial\sigma}{\partial h_{100}} + b_{010}\frac{\partial\sigma}{\partial h_{010}} + b_{001}\frac{\partial\sigma}{\partial h_{001}} = 0, \end{aligned}$$

$$\begin{aligned} \Delta_2(\sigma) = 2g\frac{\partial\sigma}{\partial a} + f\frac{\partial\sigma}{\partial h} + c\frac{\partial\sigma}{\partial g} + 2\phi_{101}\frac{\partial\sigma}{\partial\phi_{200}} + \phi_{011}\frac{\partial\sigma}{\partial\phi_{110}} + \phi_{002}\frac{\partial\sigma}{\partial\phi_{101}} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{100}} \\ + (a_{001} + 2g_{100})\frac{\partial\sigma}{\partial a_{100}} + 2g_{010}\frac{\partial\sigma}{\partial a_{010}} + 2g_{001}\frac{\partial\sigma}{\partial a_{001}} + b_{001}\frac{\partial\sigma}{\partial b_{100}} + c_{001}\frac{\partial\sigma}{\partial c_{100}} \\ + f_{001}\frac{\partial\sigma}{\partial f_{100}} + (g_{001} + c_{100})\frac{\partial\sigma}{\partial g_{100}} + c_{010}\frac{\partial\sigma}{\partial g_{010}} + c_{001}\frac{\partial\sigma}{\partial g_{001}} \\ + (h_{001} + f_{100})\frac{\partial\sigma}{\partial h_{100}} + f_{010}\frac{\partial\sigma}{\partial h_{010}} + f_{001}\frac{\partial\sigma}{\partial h_{001}} = 0, \end{aligned}$$

$$\begin{aligned} \Delta_3(\sigma) = a\frac{\partial\sigma}{\partial h} + 2h\frac{\partial\sigma}{\partial b} + g\frac{\partial\sigma}{\partial f} + 2\phi_{110}\frac{\partial\sigma}{\partial\phi_{020}} + \phi_{200}\frac{\partial\sigma}{\partial\phi_{110}} + \phi_{101}\frac{\partial\sigma}{\partial\phi_{011}} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{010}} \\ + a_{100}\frac{\partial\sigma}{\partial a_{010}} + 2h_{100}\frac{\partial\sigma}{\partial b_{100}} + (b_{100} + 2h_{010})\frac{\partial\sigma}{\partial b_{010}} + 2h_{001}\frac{\partial\sigma}{\partial b_{001}} + c_{100}\frac{\partial\sigma}{\partial c_{010}} \\ + g_{100}\frac{\partial\sigma}{\partial f_{100}} + (f_{100} + g_{010})\frac{\partial\sigma}{\partial f_{010}} + g_{001}\frac{\partial\sigma}{\partial f_{001}} + g_{100}\frac{\partial\sigma}{\partial g_{010}} \\ + a_{100}\frac{\partial\sigma}{\partial h_{100}} + (a_{010} + h_{100})\frac{\partial\sigma}{\partial h_{010}} + a_{001}\frac{\partial\sigma}{\partial h_{001}} = 0, \end{aligned}$$

$$\begin{aligned} \Delta_4(\sigma) = g\frac{\partial\sigma}{\partial h} + 2f\frac{\partial\sigma}{\partial b} + c\frac{\partial\sigma}{\partial f} + 2\phi_{011}\frac{\partial\sigma}{\partial\phi_{020}} + \phi_{101}\frac{\partial\sigma}{\partial\phi_{110}} + \phi_{002}\frac{\partial\sigma}{\partial\phi_{011}} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{010}} \\ + a_{001}\frac{\partial\sigma}{\partial a_{010}} + 2f_{100}\frac{\partial\sigma}{\partial b_{100}} + (b_{001} + 2f_{010})\frac{\partial\sigma}{\partial b_{010}} + 2f_{001}\frac{\partial\sigma}{\partial b_{001}} + c_{001}\frac{\partial\sigma}{\partial c_{010}} \\ + c_{100}\frac{\partial\sigma}{\partial f_{100}} + (f_{001} + c_{010})\frac{\partial\sigma}{\partial f_{010}} + c_{001}\frac{\partial\sigma}{\partial f_{001}} + g_{001}\frac{\partial\sigma}{\partial g_{010}} \\ + g_{100}\frac{\partial\sigma}{\partial h_{100}} + (g_{010} + h_{001})\frac{\partial\sigma}{\partial h_{010}} + g_{001}\frac{\partial\sigma}{\partial h_{001}} = 0, \end{aligned}$$

$$\begin{aligned}\Delta_5(\sigma) = a\frac{\partial\sigma}{\partial g} + h\frac{\partial\sigma}{\partial f} + 2g\frac{\partial\sigma}{\partial c} + 2\phi_{101}\frac{\partial\sigma}{\partial\phi_{002}} + \phi_{200}\frac{\partial\sigma}{\partial\phi_{101}} + \phi_{110}\frac{\partial\sigma}{\partial\phi_{011}} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{001}}\\ + a_{100}\frac{\partial\sigma}{\partial a_{001}} + b_{100}\frac{\partial\sigma}{\partial b_{001}} + 2g_{100}\frac{\partial\sigma}{\partial c_{100}} + 2g_{010}\frac{\partial\sigma}{\partial c_{010}} + (c_{100} + 2g_{001})\frac{\partial\sigma}{\partial c_{100}}\\ + h_{100}\frac{\partial\sigma}{\partial f_{100}} + h_{010}\frac{\partial\sigma}{\partial f_{010}} + (f_{100} + h_{001})\frac{\partial\sigma}{\partial f_{001}} + a_{100}\frac{\partial\sigma}{\partial g_{100}}\\ + a_{010}\frac{\partial\sigma}{\partial g_{010}} + (a_{001} + g_{100})\frac{\partial\sigma}{\partial g_{001}} + h_{100}\frac{\partial\sigma}{\partial h_{001}} = 0.\end{aligned}$$

$$\begin{aligned}\Delta_6(\sigma) = h\frac{\partial\sigma}{\partial g} + b\frac{\partial\sigma}{\partial f} + 2f\frac{\partial\sigma}{\partial c} + 2\phi_{011}\frac{\partial\sigma}{\partial\phi_{002}} + \phi_{110}\frac{\partial\sigma}{\partial\phi_{101}} + \phi_{020}\frac{\partial\sigma}{\partial\phi_{011}} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{001}}\\ + a_{010}\frac{\partial\sigma}{\partial a_{001}} + b_{010}\frac{\partial\sigma}{\partial b_{001}} + 2f_{100}\frac{\partial\sigma}{\partial c_{100}} + 2f_{010}\frac{\partial\sigma}{\partial c_{010}} + (c_{010} + 2f_{001})\frac{\partial\sigma}{\partial c_{100}}\\ + b_{100}\frac{\partial\sigma}{\partial f_{100}} + b_{010}\frac{\partial\sigma}{\partial f_{010}} + (b_{001} + f_{010})\frac{\partial\sigma}{\partial f_{001}} + h_{100}\frac{\partial\sigma}{\partial g_{100}}\\ + h_{010}\frac{\partial\sigma}{\partial g_{010}} + (h_{001} + g_{010})\frac{\partial\sigma}{\partial g_{001}} + h_{010}\frac{\partial\sigma}{\partial h_{001}} = 0.\end{aligned}$$

from the coefficients of η_{100}, ζ_{100}, ξ_{010}, ζ_{010}, ξ_{001}, η_{001} respectively: and the three equations

$$\begin{aligned}\Delta_7(\sigma) = 2a\frac{\partial\sigma}{\partial a} + h\frac{\partial\sigma}{\partial h} + g\frac{\partial\sigma}{\partial g} + 2\phi_{200}\frac{\partial\sigma}{\partial\phi_{200}} + \phi_{110}\frac{\partial\sigma}{\partial\phi_{110}} + \phi_{101}\frac{\partial\sigma}{\partial\phi_{101}} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{100}}\\ + 3a_{100}\frac{\partial\sigma}{\partial a_{100}} + 2a_{010}\frac{\partial\sigma}{\partial a_{010}} + 2a_{001}\frac{\partial\sigma}{\partial a_{001}} + b_{100}\frac{\partial\sigma}{\partial b_{100}} + c_{100}\frac{\partial\sigma}{\partial c_{100}}\\ + f_{100}\frac{\partial\sigma}{\partial f_{100}} + 2g_{100}\frac{\partial\sigma}{\partial g_{100}} + g_{010}\frac{\partial\sigma}{\partial g_{010}} + g_{001}\frac{\partial\sigma}{\partial g_{001}} + 2h_{100}\frac{\partial\sigma}{\partial h_{100}}\\ + h_{010}\frac{\partial\sigma}{\partial h_{010}} + h_{001}\frac{\partial\sigma}{\partial h_{001}} = \mu\sigma,\end{aligned}$$

$$\begin{aligned}\Delta_8(\sigma) = h\frac{\partial\sigma}{\partial h} + 2b\frac{\partial\sigma}{\partial b} + f\frac{\partial\sigma}{\partial f} + 2\phi_{020}\frac{\partial\sigma}{\partial\phi_{020}} + \phi_{110}\frac{\partial\sigma}{\partial\phi_{110}} + \phi_{011}\frac{\partial\sigma}{\partial\phi_{011}} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{010}}\\ + a_{010}\frac{\partial\sigma}{\partial a_{010}} + 2b_{100}\frac{\partial\sigma}{\partial b_{100}} + 3b_{010}\frac{\partial\sigma}{\partial b_{010}} + 2b_{001}\frac{\partial\sigma}{\partial b_{001}} + c_{010}\frac{\partial\sigma}{\partial c_{010}}\\ + f_{100}\frac{\partial\sigma}{\partial f_{100}} + 2f_{010}\frac{\partial\sigma}{\partial f_{010}} + f_{001}\frac{\partial\sigma}{\partial f_{001}} + g_{010}\frac{\partial\sigma}{\partial g_{010}} + h_{100}\frac{\partial\sigma}{\partial h_{100}}\\ + 2h_{010}\frac{\partial\sigma}{\partial h_{010}} + h_{001}\frac{\partial\sigma}{\partial h_{001}} = \mu\sigma,\end{aligned}$$

$$\Delta_9(\sigma) = g\frac{\partial\sigma}{\partial g} + f\frac{\partial\sigma}{\partial f} + 2c\frac{\partial\sigma}{\partial c} + 2\phi_{002}\frac{\partial\sigma}{\partial\phi_{002}} + \phi_{101}\frac{\partial\sigma}{\partial\phi_{101}} + \phi_{011}\frac{\partial\sigma}{\partial\phi_{011}} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{001}}$$
$$+ a_{001}\frac{\partial\sigma}{\partial a_{001}} + b_{001}\frac{\partial\sigma}{\partial b_{001}} + 2c_{100}\frac{\partial\sigma}{\partial c_{100}} + 2c_{010}\frac{\partial\sigma}{\partial c_{010}} + 3c_{001}\frac{\partial\sigma}{\partial c_{001}}$$
$$+ f_{100}\frac{\partial\sigma}{\partial f_{100}} + f_{010}\frac{\partial\sigma}{\partial f_{010}} + 2f_{001}\frac{\partial\sigma}{\partial f_{001}} + g_{100}\frac{\partial\sigma}{\partial g_{100}} + g_{010}\frac{\partial\sigma}{\partial g_{010}}$$
$$+ 2g_{001}\frac{\partial\sigma}{\partial g_{001}} + h_{001}\frac{\partial\sigma}{\partial h_{001}} = \mu\sigma,$$

from the coefficients of ξ_{100}, η_{010}, ζ_{001} respectively.

The simplest of the Invariants.

8. The only differential invariant, which involves a, b, c, f, g, h, without any of their derivatives and without any of the derivatives of ϕ, is L^2.

The equations (II_1), . . . , (II_6), as well as all equations arising from the higher derivatives of ξ, η, ζ are evanescent when no derivatives of a, b, c, f, g, h, ϕ occur. The six equations $\Delta_1(\sigma)$, . . . , $\Delta_6(\sigma)$ are satisfied uniquely by

$$\frac{2}{A}\frac{\partial\sigma}{\partial a} = \frac{2}{B}\frac{\partial\sigma}{\partial b} = \frac{2}{C}\frac{\partial\sigma}{\partial c} = \frac{1}{F}\frac{\partial\sigma}{\partial f} = \frac{1}{G}\frac{\partial\sigma}{\partial g} = \frac{1}{H}\frac{\partial\sigma}{\partial h}$$
$$= \rho,$$

say; and the three equations $\Delta_7(\sigma)$, $\Delta_8(\sigma)$, $\Delta_9(\sigma)$ are then satisfied uniquely by

$$\rho = \mu\frac{\sigma}{L^2}.$$

By effecting quadratures in the relation

$$d\sigma = \frac{\partial\sigma}{\partial a}da + \ldots \qquad + \frac{\partial\sigma}{\partial h}dh,$$

we find that σ is a constant multiple of L^μ. The lowest power of L, which is rational in a, b, c, f, g, h, is L^2; we therefore take L^2 as the one differential invariant of the specified character.

9. There is no proper differential invariant of the first order in the quantities a, b, c, f, g, h alone, that is, there is no invariant (other than L^2) involving these quantities and their first derivatives but no other variable magnitudes.

Let any such invariant, if it exists, be denoted by σ. The equations which arise through derivatives of ξ, η, ζ of order higher than the second are evanescent. From the equations (II_1), (II_4), $II_6)$, we have

$$\frac{\partial\sigma}{\partial a_{100}} = \frac{\partial\sigma}{\partial h_{100}} = \frac{\partial\sigma}{\partial g_{100}} = 0,$$
$$\frac{\partial\sigma}{\partial h_{010}} = \frac{\partial\sigma}{\partial b_{010}} = \frac{\partial\sigma}{\partial f_{010}} = 0,$$
$$\frac{\partial\sigma}{\partial g_{001}} = \frac{\partial\sigma}{\partial f_{001}} = \frac{\partial\sigma}{\partial c_{001}} = 0;$$

and from the equations (II_2), (II_3), (II_5), we have

$$2\frac{\partial\sigma}{\partial a_{010}} + \frac{\partial\sigma}{\partial h_{100}} = 0 = 2\frac{\partial\sigma}{\partial b_{100}} + \frac{\partial\sigma}{\partial h_{010}} = \frac{\partial\sigma}{\partial f_{100}} + \frac{\partial\sigma}{\partial g_{010}},$$

$$2\frac{\partial\sigma}{\partial a_{001}} + \frac{\partial\sigma}{\partial g_{100}} = 0 = 2\frac{\partial\sigma}{\partial c_{100}} + \frac{\partial\sigma}{\partial g_{001}} = \frac{\partial\sigma}{\partial f_{100}} + \frac{\partial\sigma}{\partial h_{001}},$$

$$2\frac{\partial\sigma}{\partial b_{001}} + \frac{\partial\sigma}{\partial f_{010}} = 0 = 2\frac{\partial\sigma}{\partial c_{010}} + \frac{\partial\sigma}{\partial f_{001}} = \frac{\partial\sigma}{\partial g_{010}} + \frac{\partial\sigma}{\partial h_{001}}.$$

These equations show that no one of the first derivatives of a, b, c, f, g, h occur in the hypothetical invariant; that is, there is no proper differential invariant of the first order in the quantities a, b, c, f, g, h alone.

10. Next, are there any differential invariants, which involve a, b, c, f, g, h but no derivatives of these quantities and which also involve derivatives of a single function ϕ of the first order but none of higher orders?

The nine characteristic equations are

$$2h\frac{\partial\sigma}{\partial a} + b\frac{\partial\sigma}{\partial h} + f\frac{\partial\sigma}{\partial g} + \phi_{010}\frac{\partial}{\partial\phi_{100}} = 0,$$

$$2g\frac{\partial\sigma}{\partial a} + f\frac{\partial\sigma}{\partial h} + c\frac{\partial\sigma}{\partial g} + \phi_{001}\frac{\partial}{\partial\phi_{100}} = 0,$$

$$a\frac{\partial\sigma}{\partial h} + 2h\frac{\partial\sigma}{\partial b} + g\frac{\partial\sigma}{\partial f} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{010}} = 0,$$

$$g\frac{\partial\sigma}{\partial h} + 2f\frac{\partial\sigma}{\partial b} + c\frac{\partial\sigma}{\partial f} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{010}} = 0,$$

$$a\frac{\partial\sigma}{\partial g} + h\frac{\partial\sigma}{\partial f} + 2g\frac{\partial\sigma}{\partial c} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{001}} = 0,$$

$$h\frac{\partial\sigma}{\partial g} + b\frac{\partial\sigma}{\partial f} + 2f\frac{\partial\sigma}{\partial c} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{001}} = 0,$$

$$2a\frac{\partial\sigma}{\partial a} + g\frac{\partial\sigma}{\partial g} - f\frac{\partial\sigma}{\partial f} - 2b\frac{\partial\sigma}{\partial b} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{100}} - \phi_{010}\frac{\partial\sigma}{\partial\phi_{010}} = 0,$$

$$2a\frac{\partial\sigma}{\partial a} + h\frac{\partial\sigma}{\partial h} - f\frac{\partial\sigma}{\partial f} - 2c\frac{\partial\sigma}{\partial c} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{100}} - \phi_{001}\frac{\partial\sigma}{\partial\phi_{001}} = 0,$$

$$\begin{aligned}2\left(a\frac{\partial\sigma}{\partial a} + b\frac{\partial\sigma}{\partial c} + c\frac{\partial\sigma}{\partial c} + f\frac{\partial\sigma}{\partial f} + g\frac{\partial\sigma}{\partial g} + h\frac{\partial\sigma}{\partial h}\right)&\\ + \phi_{100}\frac{\partial\sigma}{\partial\phi_{100}} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{010}} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{001}} &= 3\mu\sigma.\end{aligned}$$

The last three equations replace $\Delta_7(\sigma) = \mu\sigma$, $\Delta_8(\sigma) = \mu\sigma$, $\Delta_9(\sigma) = \mu\sigma$, being $\Delta_7(\sigma) - \Delta_8(\sigma) = 0$, $\Delta_7(\sigma) - \Delta_9(\sigma) = 0$, $\Delta_7(\sigma) + \Delta_8(\sigma) + \Delta_9(\sigma) = 3\mu\sigma$.

Inspection of the first eight equations shows that they are the differential equations of the invariants and the contravariants of the ternary quadratic

$$(a, b, c, f, g, h \between X, Y, Z)^2,$$

the contragradient variables being ϕ_{100}, ϕ_{010}, ϕ_{001}. Let t be such an invariant or the leading coefficient of such a contravariant, that is, the coefficient of the highest power of ϕ_{100}; in the latter case, the contravariant is uniquely determinate when t is known. Now t satisfies the five equations

$$2h\frac{\partial t}{\partial a} + b\frac{\partial t}{\partial h} + f\frac{\partial t}{\partial g} = 0\,,$$

$$2g\frac{\partial t}{\partial a} + f\frac{\partial t}{\partial h} + c\frac{\partial t}{\partial g} = 0\,,$$

$$g\frac{\partial t}{\partial h} + 2f\frac{\partial t}{\partial b} + c\frac{\partial t}{\partial f} = 0\,,$$

$$h\frac{\partial t}{\partial g} + b\frac{\partial t}{\partial f} + 2f\frac{\partial t}{\partial c} = 0\,,$$

$$2b\frac{\partial t}{\partial b} - 2c\frac{\partial t}{\partial c} + h\frac{\partial t}{\partial h} - g\frac{\partial t}{\partial g} = 0\,.$$

This is a complete Jacobian system. It apparently contains five members: but the fifth equation is a linear combination of the first four, and therefore the system really consists of four equations. It involves six variables, viz., a, b, c, f, g, h; and therefore it possesses two independent solutions. One of these is L^2; the other is easily seen to be $bc - f^2, = A$.

Returning now to the system of nine equations, and bearing in mind the fact that the first eight possess two solutions, one being L^2 and the other being a contravariant of the ternary quadratic which has A for its leading coefficient, we have the contravariant in the well-known form

$$\Theta = (A, B, C, F, G, H \between \phi_{100}, \phi_{010}, \phi_{001})^2.$$

The ninth equation is satisfied for any solution which is homogeneous in a, b, c, f, g, h of degree m and is also homogeneous in ϕ_{100}, ϕ_{010}, ϕ_{001} of degree n, provided

$$2m + n = 3\mu.$$

Hence the value of μ for Θ is 2.

There is thus a single absolute differential invariant of the type specified; its value is

$$\Theta L^{-2}.$$

11. Proceeding as in § 9, we can similarly prove that there is no proper differential invariant of the first order in the quantities a, b, c, f, g, h, which involves the first derivatives of ϕ, that is, that L^2 and Θ are the only invariants which involve the first derivatives of ϕ, the quantities a, b, c, f, g, h, and their derivatives of the first order.

Invariants of the Second Order.

12. We now proceed to consider the aggregate of algebraically independent differential invariants, which involve a, b, c, f, g, h and their first derivatives, and which also involve derivatives of ϕ up to the second order inclusive. It has been proved that when no derivative of ϕ occurs, there is only a single such invariant, viz., L^2; and that there is one such invariant involving the first derivatives of ϕ, viz., Θ.

The equations characteristic to the invariants are the set given in § 7; their number is $18 + 6 + 3 = 27$. Taking the last three in the equivalent form

$$\begin{gathered}\Delta_7(\sigma) - \Delta_8(\sigma) = 0,\\ \Delta_7(\sigma) - \Delta_9(\sigma) = 0,\\ \Delta_7(\sigma) + \Delta_8(\sigma) + \Delta_9(\sigma) = 3\mu\sigma,\end{gathered}$$

and associating the first two of these with the earlier $18 + 6$, we have 26 equations in all. They are linearly independent of one another; and they form a complete Jacobian system. The number of variables that occur is

$$\begin{array}{rl} & 6, \text{ for the quantities } a, b, c, f, g, h,\\ + & 18, \text{ for their first derivatives},\\ + & 3, \text{ for the first derivatives of } \phi,\\ + & 6, \quad . \quad . \quad \text{second} \quad . \quad . \quad . \quad \phi,\end{array}$$

being 33 in all. There are therefore 7 solutions common to the 26 equations; two of them are already known, being L^2 and Θ; and therefore other five are required. It is manifest, from the manner in which these five have been selected, that each of them must involve second derivatives of ϕ.

The remaining equation will be found to be satisfied for each of the five solutions by the appropriate determination of the index μ in each case: the actual determination is made in a simple manner, owing to properties of homogeneity possessed by the solution.

13. The mode of manipulating the equations, so as to obtain an algebraically complete aggregate of integrals, is similar to the mode in the corresponding investigation of the differential invariants of surfaces.

We begin by obtaining the proper number of independent integrals which belong to the set of eighteen equations (II_1), . . . , (II_6). This set is, in itself, a complete

Jacobian set; as it involves 33 variable magnitudes, it possesses 15 independent integrals. Of these 15, nine are easily seen to be

$$a,\ b,\ c,\ f,\ g,\ h,$$

$$\phi_{100},\ \phi_{010},\ \phi_{001}.$$

Other six are found to be

$$\left.\begin{array}{l}
\mathfrak{a} = 2L^2\phi_{200} - Pa_{100} - Q\,(2h_{100} - a_{010}) - R\,(2g_{100} - a_{001}) \\
\mathfrak{b} = 2L^2\phi_{020} - P\,(2h_{010} - b_{100}) - Qb_{010} - R\,(2f_{010} - b_{001}) \\
\mathfrak{c} = 2L^2\phi_{002} - P\,(2g_{001} - c_{100}) - Q\,(2f_{001} - c_{010}) - Rc_{001} \\
\mathfrak{f} = 2L^2\phi_{011} - P\,(-f_{100} + g_{010} + h_{001}) - Qb_{001} - Rc_{010} \\
\mathfrak{g} = 2L^2\phi_{101} - Pa_{001} - Q\,(f_{100} - g_{010} + h_{001}) - Rc_{100} \\
\mathfrak{h} = 2L^2\phi_{110} - Pa_{010} - Qb_{100} - R\,(f_{100} + g_{010} - h_{001})
\end{array}\right\},$$

where

$$P = \begin{vmatrix} \phi_{100}, & h, & g \\ \phi_{010}, & b, & f \\ \phi_{001}, & f, & c \end{vmatrix} = A\phi_{100} + H\phi_{010} + G\phi_{001},$$

$$Q = \begin{vmatrix} \phi_{100}, & g, & a \\ \phi_{010}, & f, & h \\ \phi_{001}, & c, & g \end{vmatrix} = H\phi_{100} + B\phi_{010} + F\phi_{001},$$

$$R = \begin{vmatrix} \phi_{100}, & a, & h \\ \phi_{010}, & h, & b \\ \phi_{001}, & g, & f \end{vmatrix} = G\phi_{100} + F\phi_{010} + C\phi_{001}.$$

14. A way of constructing these six solutions will be sufficiently illustrated by giving an outline of the process for any one of them, say the first. The form of the differential equations suggests that they possess solutions, which are linear in the first derivatives of a, b, c, f, g, h and in the second derivatives of ϕ; we therefore postulate a solution in the form

$$\begin{aligned}
2L^2\phi_{200} &- \alpha a_{100} - \beta h_{100} - \gamma g_{100} - \kappa b_{100} - \lambda f_{100} - \mu c_{100} \\
&- \delta a_{010} - \zeta h_{010} - \theta g_{010} - \nu b_{010} - \rho f_{010} - \tau c_{010} \\
&- \epsilon a_{001} - \eta h_{001} - \iota g_{001} - \pi b_{001} - \chi f_{001} - \upsilon c_{001},
\end{aligned}$$

where the coefficients $\alpha, \ldots, \upsilon$ do not involve first derivatives of a, b, c, f, g, h or second derivatives of ϕ. In order that this expression may satisfy the three equations (II_1), we must have

$$2a\alpha + h\beta + g\gamma = 2L^2\phi_{100},$$

$$2h\alpha + b\beta + f\gamma = 2L^2\phi_{010},$$

$$2g\alpha + f\beta + c\gamma = 2L^2\phi_{001},$$

and therefore

$$\alpha = \mathrm{P}, \quad \beta = 2\mathrm{Q}, \quad \gamma = 2\mathrm{R}.$$

In order that the three equations (II_2) may be satisfied, we must have

$$a(2\delta + \beta) + h(2\kappa + \zeta) + g(\lambda + \theta) = 0,$$

$$h(2\delta + \beta) + b(2\kappa + \zeta) + f(\lambda + \theta) = 0.$$

$$g(2\delta + \beta) + f(2\kappa + \zeta) + c(\lambda + \theta) = 0.$$

and therefore

$$2\delta + \beta = 0, \quad 2\kappa + \zeta = 0, \quad \lambda + \theta = 0.$$

The three equations (II_3) similarly give

$$2\epsilon + \gamma = 0, \quad 2\mu + \iota = 0, \quad \lambda + \eta = 0\,;$$

the three equations (II_4) give

$$\nu = 0, \quad \rho = 0, \quad \zeta = 0\,;$$

the three equations (II_5) give

$$2\pi + \rho = 0, \quad 2\tau + \chi = 0, \quad \theta + \eta = 0\,;$$

and the three equations (II_6) give

$$\upsilon = 0, \quad \chi = 0, \quad \iota = 0.$$

When these equations are solved, it appears that the only coefficients (other than α, β, γ) which do not vanish are δ and ϵ; their values are

$$\delta = -\mathrm{Q}, \quad \epsilon = -\mathrm{R}.$$

Inserting these values, we obtain the quantity which has been denoted by a. The other five solutions can be constructed in the same way.

15. It may be remarked that there exists a certain symmetry in the quantities already obtained (and in corresponding quantities of higher orders) which may be used for comparative verification of results obtained or for avoidance of long stretches of algebra by deducing new results from results obtained. The symmetry arises through the effects caused by interchanging u and v, v and w, u and w, as follows:—

	a	b	c	f	g	h	a	b	c	f	g	h	P	Q	R
u and v	b	a	c	g	f	h	b	a	c	g	f	h	Q	P	R
v and w	a	c	b	f	h	g	a	c	b	f	h	g	P	R	Q
u and w	c	b	a	h	g	f	c	b	a	h	g	f	R	Q	P

Thus R is unaltered when u and v are interchanged; it is changed to Q, when v and w are interchanged, and to P, when u and w are interchanged. The interchanges of **a**, **b**, **c** among one another, and likewise those of **f**, **g**, **h** among one another, caused by interchanges of the variables u, v, w, are indicated in the table; they could be used to deduce **b** and **c** when **a** is known, and to deduce **g** and **h** when **f** is known.

16. We have now to obtain five functional combinations (other than L^2 and Θ) of the fifteen quantities a, b, c, f, g, h, ϕ_{100}, ϕ_{010}, ϕ_{001}, **a**, **b**, **c**, **f**, **g**, **h**, which satisfy the nine equations

$$\Delta_1(\sigma) = 0, \ldots, \quad \Delta_6(\sigma) = 0,$$

$$\Delta_7(\sigma) - \Delta_8(\sigma) = 0, \quad \Delta_7(\sigma) - \Delta_9(\sigma) = 0, \quad \Delta_7(\sigma) + \Delta_8(\sigma) + \Delta_9(\sigma) = 3\mu\sigma;$$

and the functional combinations which are required must contain some of the quantities **a**, **b**, **c**, **f**, **g**, **h**.

It is easy to verify the results in the following table :—

	a	**b**	**c**	**f**	**g**	**h**
Δ_1	2**h**	0	0	0	**f**	**b**
Δ_2	2**g**	0	0	0	**c**	**f**
Δ_3	0	2**h**	0	**g**	0	**a**
Δ_4	0	2**f**	0	**c**	0	**g**
Δ_5	0	0	2**g**	**h**	**a**	0
Δ_6	0	0	2**f**	**b**		0
Δ_7	4**a**	2**b**	2**c**	2**f**	3**g**	3**h**
Δ_8	2**a**	4**b**	2**c**	3**f**	2**g**	3**h**
Δ_9	2**a**	2**b**	4**c**	3**f**	3**g**	2**h**

which should be read $\Delta_1(\mathbf{a}) = 2\mathbf{h}$, $\Delta_1(\mathbf{b}) = 0$, and so on. Hence now denoting by σ any one of the five functional combinations of the fifteen arguments, the first eight of the equations take the form

$$2h\frac{\partial\sigma}{\partial a} + b\frac{\partial\sigma}{\partial h} + f\frac{\partial\sigma}{\partial g} + 2\mathbf{h}\frac{\partial\sigma}{\partial\mathbf{a}} + \mathbf{b}\frac{\partial\sigma}{\partial\mathbf{h}} + \mathbf{f}\frac{\partial\sigma}{\partial\mathbf{g}} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{100}} = 0,$$

$$2g\frac{\partial\sigma}{\partial a} + f\frac{\partial\sigma}{\partial h} + c\frac{\partial\sigma}{\partial g} + 2\mathbf{g}\frac{\partial\sigma}{\partial\mathbf{a}} + \mathbf{f}\frac{\partial\sigma}{\partial\mathbf{h}} + \mathbf{c}\frac{\partial\sigma}{\partial\mathbf{g}} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{100}} = 0,$$

$$a\frac{\partial\sigma}{\partial h} + 2h\frac{\partial\sigma}{\partial b} + g\frac{\partial\sigma}{\partial f} + \mathbf{a}\frac{\partial\sigma}{\partial\mathbf{h}} + 2\mathbf{h}\frac{\partial\sigma}{\partial\mathbf{b}} + \mathbf{g}\frac{\partial\sigma}{\partial\mathbf{f}} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{010}} = 0.$$

$$g\frac{\partial\sigma}{\partial h} + 2f\frac{\partial\sigma}{\partial b} + \mathbf{c}\frac{\partial\sigma}{\partial f} + \mathbf{g}\frac{\partial\sigma}{\partial\mathbf{h}} + 2\mathbf{f}\frac{\partial\sigma}{\partial\mathbf{b}} + \mathbf{c}\frac{\partial\sigma}{\partial\mathbf{f}} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{010}} = 0,$$

$$a\frac{\partial\sigma}{\partial g} + h\frac{\partial\sigma}{\partial f} + 2g\frac{\partial\sigma}{\partial c} + \mathbf{a}\frac{\partial\sigma}{\partial\mathbf{g}} + \mathbf{h}\frac{\partial\sigma}{\partial\mathbf{f}} + 2\mathbf{g}\frac{\partial\sigma}{\partial\mathbf{c}} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{001}} = 0,$$

$$h\frac{\partial\sigma}{\partial g} + b\frac{\partial\sigma}{\partial f} + 2f\frac{\partial\sigma}{\partial c} + \mathbf{h}\frac{\partial\sigma}{\partial\mathbf{g}} + \mathbf{b}\frac{\partial\sigma}{\partial\mathbf{f}} + 2\mathbf{f}\frac{\partial\sigma}{\partial\mathbf{c}} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{001}} = 0,$$

$$2\left(a\frac{\partial\sigma}{\partial a} - b\frac{\partial\sigma}{\partial b}\right) + g\frac{\partial\sigma}{\partial g} - f\frac{\partial\sigma}{\partial f} + 2\left(\mathbf{a}\frac{\partial\sigma}{\partial\mathbf{a}} - \mathbf{b}\frac{\partial\sigma}{\partial\mathbf{b}}\right) + \mathbf{g}\frac{\partial\sigma}{\partial\mathbf{g}} - \mathbf{f}\frac{\partial\sigma}{\partial\mathbf{f}} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{100}} - \phi_{010}\frac{\partial\sigma}{\partial\phi_{010}} = 0,$$

$$2\left(a\frac{\partial\sigma}{\partial a} - c\frac{\partial\sigma}{\partial c}\right) + h\frac{\partial\sigma}{\partial h} - f\frac{\partial\sigma}{\partial f} + 2\left(\mathbf{a}\frac{\partial\sigma}{\partial\mathbf{a}} - \mathbf{c}\frac{\partial\sigma}{\partial\mathbf{c}}\right) + \mathbf{h}\frac{\partial\sigma}{\partial\mathbf{h}} - \mathbf{f}\frac{\partial\sigma}{\partial\mathbf{f}} + \phi_{100}\frac{\partial\sigma}{\partial\phi_{100}} - \phi_{001}\frac{\partial\sigma}{\partial\phi_{001}} = 0.$$

The ninth equation takes the form

$$\begin{aligned} &2\left(a\frac{\partial\sigma}{\partial a} + b\frac{\partial\sigma}{\partial b} + c\frac{\partial\sigma}{\partial c} + f\frac{\partial\sigma}{\partial f} + g\frac{\partial\sigma}{\partial g} + h\frac{\partial\sigma}{\partial h}\right) \\ &+ 8\left(\mathbf{a}\frac{\partial\sigma}{\partial\mathbf{a}} + \mathbf{b}\frac{\partial\sigma}{\partial\mathbf{b}} + \mathbf{c}\frac{\partial\sigma}{\partial\mathbf{c}} + \mathbf{f}\frac{\partial\sigma}{\partial\mathbf{f}} + \mathbf{g}\frac{\partial\sigma}{\partial\mathbf{g}} + \mathbf{h}\frac{\partial\sigma}{\partial\mathbf{h}}\right) \\ &\qquad + \phi_{100}\frac{\partial\sigma}{\partial\phi_{100}} + \phi_{010}\frac{\partial\sigma}{\partial\phi_{010}} + \phi_{001}\frac{\partial\sigma}{\partial\phi_{001}} = 3\mu\sigma. \end{aligned}$$

Inspection of the first eight equations in this form, coupled with the limitation that some at least of the quantities **a**, **b**, **c**, **f**, **g**, **h** occur, shews that they are the differential equations of those invariants and contravariants of the simultaneous ternary quadratics

$$(a, b, c, f, g, h \between X, Y, Z)^2,$$

$$(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{f}, \mathbf{g}, \mathbf{h} \between X, Y, Z)^2,$$

which involve the coefficients of the second of these quadratics, and that the contragradient variables (when they occur) are ϕ_{100}, ϕ_{010}, ϕ_{001}. The ninth equation is satisfied when the index μ is appropriately determined as follows: let σ be homogeneous in ϕ_{100}, ϕ_{010}, ϕ_{001} of degree n, in a, b, c, f, g, h of degree m, in **a**, **b**, **c**, **f**, **g**, **h** of degree l; then

$$8l + 2m + n = 3\mu.$$

Now the complete system (being the asyzygetically complete system and not merely that which is algebraically complete) of two ternary quadratics is known;[*] it thus enables us to select the five concomitants required which, it is to be remembered, are to involve the quantities $\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{f}, \mathbf{g}, \mathbf{h}$. Let

$$\mathbf{A} = \mathbf{bc} - \mathbf{f}^2, \qquad \mathbf{B} = \mathbf{ca} - \mathbf{g}^2, \qquad \mathbf{C} = \mathbf{ab} - \mathbf{h}^2,$$
$$\mathbf{F} = \mathbf{gh} - \mathbf{af}, \qquad \mathbf{G} = \mathbf{hf} - \mathbf{bg}, \qquad \mathbf{H} = \mathbf{fg} - \mathbf{ch},$$

$$\mathfrak{A} = b\mathbf{c} + \mathbf{b}c - 2f\mathbf{f}, \qquad \mathfrak{F} = g\mathbf{h} + \mathbf{g}h - a\mathbf{f} - \mathbf{a}f,$$
$$\mathfrak{B} = c\mathbf{a} + \mathbf{c}a - 2g\mathbf{g}, \qquad \mathfrak{G} = h\mathbf{f} + \mathbf{h}f - b\mathbf{g} - \mathbf{b}g,$$
$$\mathfrak{C} = a\mathbf{b} + \mathbf{a}b - 2h\mathbf{h}, \qquad \mathfrak{H} = f\mathbf{g} + \mathbf{f}g - c\mathbf{h} - \mathbf{c}h;$$

and, in order to exhibit the relation of the concomitants to the two quadractic forms, let

$$L^2 = \Delta_1, \qquad \Theta = \Theta_1.$$

Then the five quantities required are

$$\Theta_{12} = (\mathfrak{A}, \mathfrak{B}, \mathfrak{C}, \mathfrak{F}, \mathfrak{G}, \mathfrak{H} \between \phi_{100}, \phi_{010}, \phi_{001})^2,$$

$$\Theta_2 = (\mathbf{A}, \mathbf{B}, \mathbf{C}, \mathbf{F}, \mathbf{G}, \mathbf{H} \between \phi_{100}, \phi_{010}, \phi_{001})^2,$$

$$\Delta_{12} = A\mathbf{a} + B\mathbf{b} + C\mathbf{c} + 2F\mathbf{f} + 2G\mathbf{g} + 2H\mathbf{h},$$

$$\Delta_{21} = \mathbf{A}a + \mathbf{B}b + \mathbf{C}c + 2\mathbf{F}f + 2\mathbf{G}g + 2\mathbf{H}h,$$

$$\Delta_2 = \begin{vmatrix} \mathbf{a} & \mathbf{h} & \mathbf{g} \\ \mathbf{h} & \mathbf{b} & \mathbf{f} \\ \mathbf{g} & \mathbf{f} & \mathbf{c} \end{vmatrix}.$$

The respective values of μ, as determined from the relation $8l + 2m + n = 3\mu$, are easily found: we have

Index 4, Θ_{12}, Δ_{12};
6, Θ_2, Δ_{21};
8, Δ_2.

We have already seen that the index of $\Theta_1 (= \Theta)$ is 2 and the index of $\Delta_1 (= L^2)$ is 2.

Hence *an aggregate of algebraically independent absolute invariants, which involve* a, b, c, f, g, h *and their first derivatives and which also involve derivatives of a single function* ϕ *up to the second order inclusive, is composed of*

$$\frac{\Theta_1}{\Delta_1}, \quad \frac{\Theta_{12}}{\Delta_1^{\,2}}, \quad \frac{\Delta_{12}}{\Delta_1^{\,2}}, \quad \frac{\Theta_2}{\Delta_1^{\,3}}, \quad \frac{\Delta_{21}}{\Delta_1^{\,3}}, \quad \frac{\Delta_2}{\Delta_1^{\,4}};$$

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[*] CLEBSCH, 'Vorlesungen über Geometrie,' vol. 1, p. 290: the construction of the system is due to GORDAN.

the last five involve derivatives of ϕ of the second order as well as derivatives of the first order, and the first involves derivatives of ϕ of the first order alone.

Every other differential invariant, involving derivatives of ϕ of order not higher than the second, together with the quantities a, b, c, f, g, h and their derivatives of the first order, is expressible in terms of the members of this aggregate. Such a differential invariant is provided by the discriminant of the quantity Θ_{12}, and its expression is

$$\nabla = \begin{vmatrix} \mathfrak{A}, & \mathfrak{H}, & \mathfrak{G} \\ \mathfrak{H}, & \mathfrak{B}, & \mathfrak{F} \\ \mathfrak{G}, & \mathfrak{F}, & \mathfrak{C} \end{vmatrix}.$$

It is not difficult to prove that

$$\nabla = \Delta_{12}\Delta_{21} - \Delta_1\Delta_2.$$

17. It is also convenient, in view of the expressions for the differential invariants of the third order about to be considered, to give the umbral symbolical expressions for these invariants just considered. We write

$$\phi_{100} = u_1, \quad \phi_{010} = u_2, \quad \phi_{001} = u_3,$$
$$\mathrm{X} = x_1, \quad \mathrm{Y} = x_2, \quad \mathrm{Z} = x_3.$$

In connection with the first ternary quadratic, we introduce sets of umbral symbols a_1, a_2, a_3; b_1, b_2, b_3; and so on. In connection with the second ternary quadratic, we introduce sets of umbral symbols a'_1, a'_2, a'_3; b'_1, b'_2, b'_3; and so on. Then we write

$$(a, b, c, f, g, h)(\mathrm{X}, \mathrm{Y}, \mathrm{Z})^2 = a_x^{\,2} = b_x^{\,2} = \ldots,$$
$$(\mathrm{a}, \mathrm{b}, \mathrm{c}, \mathrm{f}, \mathrm{g}, \mathrm{h})(\mathrm{X}, \mathrm{Y}, \mathrm{Z})^2 = a'^{\,2}_x = b'^{\,2}_x = \ldots;$$

and the seven relative differential invariants are

$$\begin{aligned} \Delta_1 &= \tfrac{1}{6}(abc)^2, \\ \Theta_1 &= \tfrac{1}{2}(abu)^2, \\ \Theta_{12} &= (aa'u)^2, \\ \Theta_2 &= \tfrac{1}{2}(a'b'u)^2, \\ \Delta_{12} &= \tfrac{1}{2}(a'ab)^2, \\ \Delta_{21} &= \tfrac{1}{2}(aa'b)^2, \\ \Delta_2 &= \tfrac{1}{6}(a'b'c')^2. \end{aligned}$$

It is known* that another pure contravariant is possessed by two ternary quadratics; its symbolical expression is

$$(aa'u)(ab'c')(a'bc)(bcu)(b'c'u).$$

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* CLEBSCH, 'Vorlesungen über Geometrie,' p. 291.

Denoting this by D, we ought to be able to express D algebraically in terms of the seven preceding forms; as a matter of fact, D^2 is a polynomial combination of the forms.

18. The preceding determination of the differential invariants of the specified order has been based upon a knowledge of the complete system of concomitants of two ternary quadratics. When we pass to higher orders, the last stage in the determination of the differential invariants could be completed without further calculation, if we knew the complete system of concomitants of certain simultaneous ternary quantics some of which are of order higher than two. But, in general, such knowledge is not at present possessed; in its absence, some other method of attaining the end is necessary. Such a method can be devised in connection with the differential equations; as applied to the two quadratics, it is as follows.

As has been pointed out, the equations determine the invariants and the contravariants of two simultaneous quadratics, the contragradient variables being ϕ_{100}, ϕ_{010}, ϕ_{001}. Let such an one be

$$\sigma = t\phi_{100}{}^{n} + nt_1\phi_{100}{}^{n-1}\phi_{010} + nt_2\phi_{100}{}^{n-1}\phi_{001} + \ldots,$$

where t, t_1, t_2, . . . are independent of ϕ_{100}, ϕ_{010}, ϕ_{001}; and n is a whole number, which in the case of an invariant is zero, and which, when t is known, can always be determined by inspection. Then when this value of σ is substituted in the ordinary way in the first six equations, it appears that t satisfies the four equations

$$e_1(t) = 2h\frac{\partial t}{\partial a} + b\frac{\partial t}{\partial h} + f\frac{\partial t}{\partial g} + 2\mathrm{h}\frac{\partial t}{\partial \mathrm{a}} + \mathrm{b}\frac{\partial t}{\partial \mathrm{h}} + \mathrm{f}\frac{\partial t}{\partial \mathrm{g}} = 0,$$

$$e_2(t) = 2g\frac{\partial t}{\partial a} + f\frac{\partial t}{\partial h} + c\frac{\partial t}{\partial g} + 2\mathrm{g}\frac{\partial t}{\partial \mathrm{a}} + \mathrm{f}\frac{\partial t}{\partial \mathrm{h}} + \mathrm{c}\frac{\partial t}{\partial \mathrm{g}} = 0,$$

$$e_3(t) = g\frac{\partial t}{\partial h} + 2f\frac{\partial t}{\partial b} + c\frac{\partial t}{\partial f} + \mathrm{g}\frac{\partial t}{\partial \mathrm{h}} + 2\mathrm{f}\frac{\partial t}{\partial \mathrm{b}} + \mathrm{c}\frac{\partial t}{\partial \mathrm{f}} = 0,$$

$$e_4(t) = h\frac{\partial t}{\partial g} + b\frac{\partial t}{\partial f} + 2f\frac{\partial t}{\partial c} + \mathrm{h}\frac{\partial t}{\partial \mathrm{g}} + \mathrm{b}\frac{\partial t}{\partial \mathrm{f}} + 2\mathrm{f}\frac{\partial t}{\partial \mathrm{c}} = 0.$$

The third of the former six equations gives, merely by processes of differentiation, the succession of coefficients for ascending powers of ϕ_{010}; and the fifth of them gives the succession of coefficients for ascending powers of ϕ_{001}. The third and the fifth combined give all the coefficients when t is known. When this determination is completed, the seventh and the eighth equations are satisfied identically; and the ninth is satisfied in association with the proper value of μ.

It thus is necessary to consider the above set of four equations. When we associate the equation

$$e_5(t) = 2b\frac{\partial t}{\partial b} - 2c\frac{\partial t}{\partial c} + h\frac{\partial t}{\partial h} - g\frac{\partial t}{\partial g} + 2\mathrm{b}\frac{\partial t}{\partial \mathrm{b}} - 2\mathrm{c}\frac{\partial t}{\partial \mathrm{c}} + \mathrm{h}\frac{\partial t}{\partial \mathrm{h}} - \mathrm{g}\frac{\partial t}{\partial \mathrm{g}} = 0,$$

which is a condition that $e_3(t) = 0$ and $e_4(t) = 0$ should possess solutions in common. the increased set of five equations is found to be a complete Jacobian system. It involves 12 variables, viz., a, b, c, f, g, h, $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, $\mathbf{f}$, $\mathbf{g}$, $\mathbf{h}$, and therefore it possesses 7 simultaneous independent solutions.

Two of the seven are known; they are

$$\Delta_1 = \mathrm{L}^2 = abc + 2fgh - af^2 - bg^2 - ch^2,$$

$$A = bc = f^2,$$

where A is the "leading" coefficient of the contravariant Θ_1; two others, bearing to the second quadratic the same relation as Δ_1 and A bear to the first, may be expected in the forms

$$\Delta_2 = \mathbf{abc} + 2\mathbf{fgh} - \mathbf{af}^2 - \mathbf{bg}^2 - \mathbf{ch}^2,$$

$$\mathbf{A} = \mathbf{bc} - \mathbf{f}^2.$$

The whole set of seven, including these four, may be constructed by the known processes of solving complete Jacobian systems of homogeneous linear equations.

Invariants of two Surfaces.

19. Hitherto we have considered the differential invariants which may arise in connection with a single function ϕ of the independent variables; and they may be regarded as associated with the single surface $\phi =$ constant (or with the single family of surfaces if the constant be parametric). But in ordinary space, differential invariants may arise in connection with tortuous curves or (what is the same thing analytically) with two families of surfaces such as $\phi =$ constant, $\phi' =$ constant. They may even arise in connection with three families of surfaces such as $\phi =$ constant, $\phi' =$ constant, $\phi'' =$ constant, where there is no identical functional relation between ϕ, ϕ', ϕ'' involving constants only.

The simplest of such cases occurs when those differential invariants are required which involve no derivatives of a, b, c, f, g, h and only first derivatives of two functions ϕ and ϕ'. The number of algebraically independent relative invariants is 4; and the coefficients of the highest power of ϕ_{100} which they contain are the independent solutions of the complete Jacobian system

$$2h\frac{\partial}{\partial a} + b\frac{\partial}{\partial h} + f\frac{\partial}{\partial g} + \phi'_{010}\frac{\partial}{\partial \phi'_{100}} = 0,$$

$$2g\frac{\partial}{\partial a} + c\frac{\partial}{\partial g} + f\frac{\partial}{\partial h} + \phi'_{001}\frac{\partial}{\partial \phi'_{100}} = 0,$$

$$2f\frac{\partial}{\partial b} + g\frac{\partial}{\partial h} + c\frac{\partial}{\partial f} + \phi'_{001}\frac{\partial}{\partial \phi'_{010}} = 0,$$

$$2f\frac{\partial}{\partial c} + h\frac{\partial}{\partial g} + b\frac{\partial}{\partial f} + \phi'_{010}\frac{\partial}{\partial \phi'_{001}} = 0,$$

$$2b\frac{\partial}{\partial b} - 2c\frac{\partial}{\partial c} + h\frac{\partial}{\partial h} - g\frac{\partial}{\partial g} + \phi'_{010}\frac{\partial}{\partial \phi'_{010}} - \phi'_{001}\frac{\partial}{\partial \phi'_{001}} = 0.$$

Of these 4, two are already given by Δ_1 and Θ_1. Let

$$2\mathrm{D} = \phi'_{100}\frac{\partial}{\partial\phi_{100}} + \phi'_{010}\frac{\partial}{\partial\phi_{010}} + \phi'_{001}\frac{\partial}{\partial\phi_{001}};$$

then other two are given by $\mathrm{D}\Theta_1$ and $\mathrm{D}^2\Theta_1$. The four quantities

$$\Delta_1,\quad \Theta_1,\quad \mathrm{D}\Theta_1,\quad \mathrm{D}^2\Theta_1$$

are algebraically independent of one another; and so they constitute the required aggregate of relative differential invariants.

Similarly, we can obtain an algebraically independent aggregate of differential invariants, which involve a, b, c, f, g, h but none of their derivatives, and which involve first derivatives of three quantities ϕ, ϕ', ϕ'' unconnected by any identical functional relation. Let

$$2\mathrm{D}' = \phi''_{100}\frac{\partial}{\partial\phi_{100}} + \phi''_{010}\frac{\partial}{\partial\phi_{010}} + \phi''_{001}\frac{\partial}{\partial\phi_{001}};$$

then we have, as simultaneous invariants,

$$\Delta_1,\quad \Theta_1,\quad \mathrm{D}\Theta_1,\quad \mathrm{D}^2\Theta_1,\quad \mathrm{D}'\Theta_1,\quad \mathrm{D}\mathrm{D}'\Theta_1,\quad \mathrm{D}'^2\Theta_1,$$

and

$$\mathrm{I} = \begin{vmatrix} \phi_{100}, & \phi'_{100}, & \phi''_{100} \\ \phi_{010}, & \phi'_{010}, & \phi''_{010} \\ \phi_{001}, & \phi'_{001}, & \phi''_{001} \end{vmatrix}.$$

There should be only seven invariants in the algebraically complete aggregate; it is not difficult to prove that

$$\begin{vmatrix} \Theta_1, & \mathrm{D}\Theta_1, & \mathrm{D}'\Theta_1 \\ \mathrm{D}\Theta_1, & \mathrm{D}^2\Theta_1, & \mathrm{D}\mathrm{D}'\Theta_1 \\ \mathrm{D}'\Theta_1, & \mathrm{D}\mathrm{D}'\Theta_1, & \mathrm{D}'^2\Theta_1 \end{vmatrix} = \Delta_1{}^3\mathrm{I}^2,$$

so that the above eight quantities, subject to this one relation, constitute the aggregate.

20. We proceed similarly with the determination of the invariants of higher orders associated with two surfaces: here, we shall restrict ourselves to the consideration of those invariants which involve derivatives of a, b, c, f, g, h of the first order and also involve derivatives of two quantities ϕ and ϕ' of order not higher than the second. To obtain the expressions of such differential invariants, we take six new quantities

$$\left.\begin{aligned}
\mathfrak{a}' &= 2\mathrm{L}^2\phi'_{200} - \mathrm{P}'a_{100} - \mathrm{Q}'(2h_{100} - a_{010}) - \mathrm{R}'(2g_{100} - a_{001}) \\
\mathfrak{b}' &= 2\mathrm{L}^2\phi'_{020} - \mathrm{P}'(2h_{010} - b_{100}) - \mathrm{Q}'b_{010} - \mathrm{R}'(2f_{010} - b_{001}) \\
\mathfrak{c}' &= 2\mathrm{L}^2\phi'_{002} - \mathrm{P}'(2g_{001} - c_{100}) - \mathrm{Q}'(2f_{001} - c_{010}) - \mathrm{R}'c_{001} \\
\mathfrak{f}' &= 2\mathrm{L}^2\phi'_{011} - \mathrm{P}'(-f_{100} + g_{010} + h_{001}) - \mathrm{Q}'b_{001} - \mathrm{R}'c_{010} \\
\mathfrak{g}' &= 2\mathrm{L}^2\phi'_{101} - \mathrm{P}'a_{001} - \mathrm{Q}'(f_{100} - g_{010} + h_{001}) - \mathrm{R}'c_{100} \\
\mathfrak{h}' &= 2\mathrm{L}^2\phi'_{110} - \mathrm{P}'a_{010} - \mathrm{Q}'b_{100} - \mathrm{R}'(f_{100} + g_{010} - h_{001})
\end{aligned}\right\},$$

where

$$\left.\begin{aligned} P' &= A\phi'_{100} + H\phi'_{010} + G\phi'_{001} \\ Q' &= H\phi'_{100} + B\phi'_{010} + F\phi'_{001} \\ R' &= G\phi'_{100} + F\phi'_{010} + C\phi'_{001} \end{aligned}\right\}.$$

These quantities bear to ϕ' the same relation as the quantities $\mathfrak{a}, \mathfrak{b}, \mathfrak{c}, \mathfrak{f}, \mathfrak{g}, \mathfrak{h}$ bear to ϕ.

The differential invariants up to the order specified are the simultaneous invariants and contravariants of the simultaneous ternary quantics

$$(\phi'_{100}, \phi'_{010}, \phi'_{001} \between X, Y, Z),$$
$$(a, b, c, f, g, h \between X, Y, Z)^2,$$
$$(\mathfrak{a}, \mathfrak{b}, \mathfrak{c}, \mathfrak{f}, \mathfrak{g}, \mathfrak{h} \between X, Y, Z)^2,$$
$$(\mathfrak{a}', \mathfrak{b}', \mathfrak{c}', \mathfrak{f}', \mathfrak{g}', \mathfrak{h}' \between X, Y, Z)^2,$$

the variables of the contravariants being $\phi_{100}, \phi_{010}, \phi_{001}$. The total number of algebraically independent relative differential invariants is 16, being the number of independent solutions of five equations (as in § 18) which are a complete Jacobian set and involve 21 variables. Hence the total number of algebraically independent absolute differential invariants of the specified order involving derivatives of two functions ϕ and ϕ' is 15.

As regards the indices of the respective relative invariants, they are given as before. Let the invariant be homogeneous in $\phi_{100}, \phi_{010}, \phi_{001}$ of degree n; in $\phi'_{100}, \phi'_{010}, \phi'_{001}$ of degree n'; in a, b, c, f, g, h of degree m; in $\mathfrak{a}, \mathfrak{b}, \mathfrak{c}, \mathfrak{f}, \mathfrak{g}, \mathfrak{h}$ of degree l; and in $\mathfrak{a}', \mathfrak{b}', \mathfrak{c}', \mathfrak{f}', \mathfrak{g}', \mathfrak{h}'$ of degree l'. Then its index μ is given by

$$8(l + l') + 2m + n + n' = 3\mu.$$

21. The algebraically complete aggregate of sixteen relative invariants can be expressed in various forms that are equivalent to one another. One such aggregate of invariants of the second order can be obtained as follows. We write

$$2D = \phi'_{100}\frac{\partial}{\partial\phi_{100}} + \phi'_{010}\frac{\partial}{\partial\phi_{010}} + \phi'_{001}\frac{\partial}{\partial\phi_{001}};$$

and we use the results of § 16.

If there were only one surface ϕ, the aggregate of invariants of the second order would be

$$\Delta_1, \quad \Delta_{12}, \quad \Delta_{21}, \quad \Delta_2, \quad \Theta_1, \quad \Theta_{12}, \quad \Theta_2.$$

As there is a second surface ϕ', introducing a third ternary quadratic, the aggregate of invariants of the second order must include concomitants that may be denoted by

$$\Delta_{13}, \quad \Delta_{31}, \quad \Delta_3, \quad \Theta_{13}, \quad \Theta_3$$

(or their equivalent), these concomitants having the same relation to the third quadratic as Δ_{12}, Δ_{21}, Δ_2, Θ_{12}, Θ_2 to the second quadratic. Moreover, in the case of two surfaces ϕ and ϕ', the aggregate of invariants of the first order is

$$\Delta_1, \quad \Theta_1, \quad D\Theta_1, \quad D^2\Theta_1 :$$

and these must be included in the desired aggregate. Further, as regards the concomitants, the second and the third quadratics will have invariants, standing to them in the same relations as Δ_{12} and Δ_{21} to the first and the second or as Δ_{13} and Δ_{31} to the first and the third; we therefore have Δ_{23} and Δ_{32} as invariants.

Accordingly, we take the algebraic aggregate of sixteen relative invariants as composed of the quantities

$$\begin{array}{lllll} \Delta_1, & \Theta_1, & & & \\ \Delta_{12}, & \Delta_{21}, & \Delta_2, & \Theta_{12}, & \Theta_2, \\ \Delta_{13}, & \Delta_{31}, & \Delta_3, & \Theta_{13}, & \Theta_3, \\ D\Theta_1, & D^2\Theta_1, & & & \\ \Delta_{23}, & \Delta_{32}. & & & \end{array}$$

Let $2\mathfrak{D}$ denote the operator $\phi_{100}\dfrac{\partial}{\partial\phi'_{100}} + \phi_{010}\dfrac{\partial}{\partial\phi'_{010}} + \phi_{001}\dfrac{\partial}{\partial\phi'_{001}}$; then other relative invariants are given by

$$\begin{array}{llllll} D\Theta_2, & D^2\Theta_2, & D\Theta_{12}, & D^2\Theta_{12}, & D\Theta_{13}, & D^2\Theta_{13}, \\ \mathfrak{D}\Theta_3, & \mathfrak{D}^2\Theta_3, & & & & \end{array}$$

and so on; all of these are algebraically expressible in terms of the above aggregate of sixteen.

The umbral expressions for these invariants are easily obtained. We take the notation of § 17, and we further introduce a third set of umbral symbols a''_1, a''_2, a''_3; b''_1, b''_2, b''_3; and so on, defined as

$$(\mathrm{a}', \mathrm{b}', \mathrm{c}', \mathrm{f}', \mathrm{g}', \mathrm{h}' \between \mathrm{X}, \mathrm{Y}, \mathrm{Z})^2 = a''^2_x = b''^2_x = \ldots$$

We also write

$$\phi'_{100} = u'_1, \quad \phi'_{010} = u'_2, \quad \phi'_{001} = u'_3;$$

and then we have the following expressions for the sixteen relative invariants:—

$$\begin{array}{lll} \Delta_1 = \tfrac{1}{6}(abc)^2, & \Delta_{12} = \tfrac{1}{2}(a'ab)^2, & \Delta_{13} = \tfrac{1}{2}(a''ab)^2, \\ \Delta_2 = \tfrac{1}{6}(a'b'c')^2, & \Delta_{21} = \tfrac{1}{2}(aa'b')^2, & \Delta_{23} = \tfrac{1}{2}(a''a'b')^2, \\ \Delta_3 = \tfrac{1}{6}(a''b''c'')^2, & \Delta_{31} = \tfrac{1}{2}(aa''b'')^2, & \Delta_{32} = \tfrac{1}{2}(a'a''b'')^2, \\ \Theta_1 = \tfrac{1}{2}(abu)^2, & \Theta_{12} = (aa'u)^2, & \\ \Theta_2 = \tfrac{1}{2}(a'b'u)^2, & \Theta_{13} = (aa''u')^2, & \\ \Theta_3 = \tfrac{1}{2}(a''b''u')^2, & & \end{array}$$

$$D\Theta_1 = \tfrac{1}{2}(abu)(abu'), \qquad D^2\Theta_1 = \tfrac{1}{2}(abu')^2.$$

Other invariants manifestly are given by

$$(ua'a'')^2, \quad \tfrac{1}{2}(a'b'u)(a'b'u'), \quad \tfrac{1}{2}(a'b'u')^2, \quad \tfrac{1}{2}(a''b''u)(a''b''u'), \quad \tfrac{1}{2}(a''b''u)^2.$$

and so on ; all of them are algebraically expressible in terms of the above aggregate of sixteen.

The values of the indices of the respective invariants are given by the relation

$$8(l + l') + 2m + n + n' = 3\mu$$

in each case. The results are as follows :—

Index = 2,	Δ_1,	Θ_1,	$D\Theta_1$,	$D^2\Theta_1$,
. . = 4,	Δ_{12},	Δ_{13},	Θ_{12},	Θ_{13},
. . = 6,	Δ_{21},	Δ_{31},	Θ_2,	Θ_3,
. . = 8,	Δ_2,	Δ_3,	Δ_{23},	Δ_{32}.

The expressions of the 15 absolute invariants now are obvious.

Invariants of the Third Order.

22. The calculations, involved in this mode of constructing differential invariants, are very laborious for differential invariants of the third order, being the order next in succession. They are so extensive and demand such sustained attention merely through long processes of algebra that, if invariants of higher order are required, it will (in my opinion) be necessary to devise some other method of construction.

Only the briefest outline of what has been done in the case of differential invariants of the third order will be given, so far as concerns these laborious processes ; the results will be stated.

23. The invariants in question involve derivatives of ϕ up to the third order inclusive ; they also involve the quantities a, b, c, f, g, h, as well as their derivatives up to the second order inclusive.

The differential equations characteristic of the invariants are 57 in number ; and they range themselves in three sets. The first set consists of the thirty equations, which arise from the derivatives of ξ, η, ζ of the third order in the course of the process indicated in § 7 ; the second set consists of the eighteen equations which similarly arise from the derivatives of ξ, η, ζ of the second order ; and the third set consists of the nine equations which similarly arise from the derivatives of ξ, η, ζ of the first order.

The actual formation of the differential equations is effected as in § 7. All that is needed for the purpose, in addition to the results in § 6, is the aggregate of the expressions of the increments of the second derivatives of a, b, c, f, g, h and of the third derivatives of ϕ ; and these are special instances of the formulæ in § 5.

The first set of equations, consisting of 30 members, possesses sixteen independent integrals, as well as a, b, c, f, g, h, their derivatives of the first order, and the derivatives of ϕ of the second order. The sixteen integrals are :—

$$\theta_1 = b_{002} + c_{020} - 2f_{011},$$

$$\theta_2 = c_{200} + a_{002} - 2g_{101},$$

$$\theta_3 = a_{020} + b_{200} - 2h_{110},$$

$$\theta_4 = a_{011} - g_{110} - h_{101} + f_{200},$$

$$\theta_5 = b_{101} - h_{011} - f_{110} + g_{020},$$

$$\theta_6 = c_{110} - f_{101} - g_{011} + h_{002} ;$$

$$u_1 = 2\mathrm{L}^2\phi_{300} - \mathrm{P}a_{200} - \mathrm{Q}\,(2h_{200} - a_{110}) - \mathrm{R}\,(2g_{200} - a_{101}),$$

$$u_2 = 2\mathrm{L}^2\phi_{210} - \mathrm{P}a_{110} - \mathrm{Q}b_{200} - \mathrm{R}\,(2g_{110} - a_{011}),$$

$$u_3 = 2\mathrm{L}^2\phi_{201} - \mathrm{P}a_{101} - \mathrm{Q}\,(2h_{101} - a_{011}) - \mathrm{R}c_{200},$$

$$u_4 = 2\mathrm{L}^2\phi_{120} - \mathrm{P}a_{020} - \mathrm{Q}b_{110} - \mathrm{R}\,(2f_{110} - b_{101}),$$

$$u_5 = 2\mathrm{L}^2\phi_{111} - \mathrm{P}a_{011} - \mathrm{Q}b_{101} - \mathrm{R}c_{110},$$

$$u_6 = 2\mathrm{L}^2\phi_{102} - \mathrm{P}a_{002} - \mathrm{Q}\,(2f_{101} - c_{110}) - \mathrm{R}c_{101},$$

$$u_7 = 2\mathrm{L}^2\phi_{030} - \mathrm{P}\,(2h_{020} - b_{110}) - \mathrm{Q}b_{020} - \mathrm{R}\,(2f_{020} - b_{011}),$$

$$u_8 = 2\mathrm{L}^2\phi_{021} - \mathrm{P}\,(2h_{011} - b_{101}) - \mathrm{Q}b_{011} - \mathrm{R}c_{020},$$

$$u_9 = 2\mathrm{L}^2\phi_{012} - \mathrm{P}\,(2g_{011} - c_{110}) - \mathrm{Q}b_{002} - \mathrm{R}c_{011},$$

$$u_{10} = 2\mathrm{L}^2\phi_{003} - \mathrm{P}\,(2g_{002} - c_{101}) - \mathrm{Q}\,(2f_{002} - c_{011}) - \mathrm{R}c_{002}.$$

All these quantities are integrals of the 30 equations, as also are all functional combinations of them. The integrals of the remaining equations must accordingly be some functional combinations of $\theta_1, \ldots, \theta_6$, $u_1, \ldots, u_{10}$, as well as of a, b, c, f, g, h, their derivatives of the first order, and the derivatives of ϕ of the second order.

The second set of equations, consisting of 18 members, possesses sixteen independent integrals, in addition to **a**, **b**, **c**, **f**, **g**, **h**, a, b, c, f, g, h, and the derivatives of ϕ of the first order. The sixteen integrals are :—

$$\Theta_1 = 2L^2\theta_1 + A\alpha'_1 + H\beta'_1 + G\gamma'_1 + B\delta'_1 + F\epsilon'_1 + C\zeta'_1$$

$$\Theta_2 = 2L^2\theta_2 + A\alpha'_2 + H\beta'_2 + G\gamma'_2 + B\delta'_2 + F\epsilon'_2 + C\zeta'_2,$$

$$\Theta_3 = 2L^2\theta_3 + A\alpha'_3 + H\beta'_3 + G\gamma'_3 + B\delta'_3 + F\epsilon'_3 + C\zeta'_3,$$

$$\Theta_4 = 2L^2\theta_4 + A\alpha'_4 + H\beta'_4 + G\gamma'_4 + B\delta'_4 + F\epsilon'_4 + C\zeta'_4,$$

$$\Theta_5 = 2L^2\theta_5 + A\alpha'_5 + H\beta'_5 + G\gamma'_5 + B\delta'_5 + F\epsilon'_5 + C\zeta'_5.$$

$$\Theta_6 = 2L^2\theta_6 + A\alpha'_6 + H\beta'_6 + G\gamma'_6 + B\delta'_6 + F\epsilon'_6 + C\zeta'_6;$$

$$a'' = 2L^2u_1 - \alpha_1\phi_{200} - \beta_1\phi_{110} - \gamma_1\phi_{101} - P\lambda_1 - Q\mu_1 - R\nu_1,$$

$$k'' = 2L^2u_7 - \alpha_7\phi_{020} - \beta_7\phi_{110} - \gamma_7\phi_{011} - P\lambda_7 - Q\mu_7 - R\nu_7,$$

$$n'' = 2L^2u_{10} - \alpha_{10}\phi_{002} - \beta_{10}\phi_{011} - \gamma_{10}\phi_{101} - P\lambda_{10} - Q\mu_{10} - R\nu_{10},$$

$$h'' = 2L^2u_2 - \alpha_2\phi_{200} - \beta_2\phi_{110} - \gamma_2\phi_{101} - \delta_2\phi_{020} - \epsilon_2\phi_{011} - P\lambda_2 - Q\mu_2 - R\nu_2,$$

$$g'' = 2L^2u_3 - \alpha_3\phi_{200} - \beta_3\phi_{110} - \gamma_3\phi_{101} - \epsilon_3\phi_{011} - \zeta_3\phi_{002} - P\lambda_3 - Q\mu_3 - R\nu_3,$$

$$b'' = 2L^2u_4 - \alpha_4\phi_{200} - \beta_4\phi_{110} - \gamma_4\phi_{101} - \delta_4\phi_{020} - \epsilon_4\phi_{011} - P\lambda_4 - Q\mu_4 - R\nu_4,$$

$$c'' = 2L^2u_6 - \alpha_6\phi_{200} - \beta_6\phi_{110} - \gamma_6\phi_{101} - \epsilon_6\phi_{011} - \zeta_6\phi_{002} - P\lambda_6 - Q\mu_6 - R\nu_6.$$

$$l'' = 2L^2u_8 - \beta_8\phi_{110} - \gamma_8\phi_{101} - \delta_8\phi_{020} - \epsilon_8\phi_{011} - \zeta_8\phi_{002} - P\lambda_8 - Q\mu_8 - R\nu_8,$$

$$m'' = 2L^2u_9 - \beta_9\phi_{110} - \gamma_9\phi_{101} - \delta_9\phi_{020} - \epsilon_9\phi_{011} - \zeta_9\phi_{002} - P\lambda_9 - Q\mu_9 - R\nu_9.$$

$$f'' = 2L^2u_5 - \alpha_5\phi_{200} - \beta_5\phi_{110} - \gamma_5\phi_{101} - \delta_5\phi_{020} - \epsilon_5\phi_{011} - \zeta_5\phi_{002} - P\lambda_5 - Q\mu_5 - R\nu_5.$$

The various coefficients α, β, γ, δ, ϵ, ζ, λ, μ, ν are independent of the derivatives of ϕ.

The coefficients in the six integrals Θ_1, Θ_2, Θ_3, Θ_4,Θ_5 Θ_6 are as follows :—

$$\left\{\begin{aligned}
\alpha'_1 &= b_{100}c_{100} - 2b_{100}g_{001} - 2c_{100}h_{010} + 4g_{001}h_{010} - (-f_{100} + g_{010} + h_{001})^2, \\
\beta'_1 &= b_{100}c_{010} - 2b_{100}f_{001} + 2b_{010}g_{001} - b_{010}c_{100} + 2b_{001}f_{100} - 2b_{001}g_{010} - 2b_{001}h_{001} + 4f_{001}h_{010} - 2c_{010}h_{010}, \\
\gamma'_1 &= b_{001}c_{100} - 2c_{100}f_{010} + 2c_{001}h_{010} - b_{100}c_{001} + 2c_{010}f_{100} - 2c_{010}h_{001} - 2c_{010}g_{010} + 4f_{010}g_{001} - 2b_{001}g_{001}, \\
\delta'_1 &= -b^2_{001} + 2b_{010}f_{001} - b_{010}c_{010}, \\
\epsilon'_1 &= b_{010}c_{001} - b_{001}c_{010} - 2b_{001}f_{001} - 2c_{010}f_{010} + 4f_{010}f_{001}, \\
\zeta'_1 &= -c^2_{010} + 2c_{001}f_{010} - b_{001}c_{001}\,;
\end{aligned}\right.$$

$$\left\{\begin{aligned}
\alpha'_2 &= -a^2_{001} + 2a_{100}g_{001} - a_{100}c_{100}, \\
\beta'_2 &= a_{010}c_{100} - 2a_{010}g_{001} + 2a_{100}f_{001} - a_{100}c_{010} + 2a_{001}g_{010} - 2a_{001}f_{100} - 2a_{001}h_{001} + 4g_{001}h_{100} - 2c_{100}h_{100}, \\
\gamma'_2 &= a_{100}c_{001} - a_{001}c_{100} - 2a_{001}g_{001} - 2c_{100}g_{100} + 4g_{100}g_{001}, \\
\delta'_2 &= a_{010}c_{010} - 2a_{010}f_{001} - 2c_{010}h_{100} + 4f_{001}h_{100} - (f_{100} - g_{010} + h_{001})^2, \\
\epsilon'_2 &= a_{001}c_{010} - 2c_{010}g_{100} + 2c_{001}h_{100} - a_{010}c_{001} + 2c_{100}g_{010} - 2c_{100}h_{001} - 2c_{100}f_{100} + 4f_{001}g_{100} - 2a_{001}f_{001}, \\
\zeta'_2 &= -c^2_{100} + 2c_{001}g_{100} - a_{001}c_{001}\,;
\end{aligned}\right.$$

$$\left\{\begin{aligned}
\alpha'_3 &= -a^2_{010} + 2a_{100}h_{010} - a_{100}b_{100}, \\
\beta'_3 &= a_{100}b_{010} - a_{010}b_{100} - 2b_{100}h_{100} - 2a_{010}h_{010} + 4h_{100}h_{010}, \\
\gamma'_3 &= a_{001}b_{100} - 2a_{001}h_{010} + 2a_{100}f_{010} - a_{100}b_{001} + 2a_{010}h_{001} - 2a_{010}f_{100} - 2a_{010}g_{010} + 4g_{100}h_{010} - 2b_{100}g_{100}, \\
\delta'_3 &= -b^2_{100} + 2b_{010}h_{100} - a_{010}b_{010}, \\
\epsilon'_3 &= a_{010}b_{001} - 2b_{001}h_{100} + 2b_{010}g_{100} - a_{001}b_{010} + 2b_{100}h_{001} - 2b_{100}g_{010} - 2b_{100}f_{100} + 4f_{010}h_{100} - 2a_{010}f_{010}, \\
\zeta'_3 &= a_{001}b_{001} - 2b_{001}g_{100} - 2a_{001}f_{010} + 4g_{100}f_{010} - (f_{100} + g_{010} - h_{001})^2\,;
\end{aligned}\right.$$

$$\left\{\begin{aligned}
\alpha'_4 &= -a_{100}f_{100} + a_{100}g_{010} + a_{100}h_{001} - a_{010}a_{001}, \\
\beta'_4 &= a_{100}b_{001} - 2a_{010}h_{001} - a_{001}b_{100} - 2f_{100}h_{100} + 2g_{010}h_{100} + 2h_{100}h_{001}, \\
\gamma'_4 &= a_{100}c_{010} - 2a_{001}g_{010} - a_{010}c_{100} - 2f_{100}g_{100} + 2g_{100}h_{001} + 2g_{100}g_{010}. \\
\delta'_4 &= -a_{010}b_{001} - b_{100}f_{100} + b_{100}g_{010} - b_{100}h_{001} + 2b_{001}h_{100}, \\
\epsilon'_4 &= -a_{010}c_{010} - a_{001}b_{001} - b_{100}c_{100} + 2b_{001}g_{100} + 2c_{010}h_{100} - f^2_{100} + g^2_{010} - 2g_{010}h_{001} + h^2_{001}, \\
\zeta'_4 &= -a_{001}c_{010} - c_{100}f_{100} + c_{100}h_{001} - c_{100}g_{010} + 2c_{010}g_{100} ;
\end{aligned}\right.$$

$$\left\{\begin{aligned}
\alpha'_5 &= -a_{001}b_{100} - a_{010}g_{010} + a_{010}f_{100} - a_{010}h_{001} + 2a_{001}h_{010}, \\
\beta'_5 &= a_{001}b_{010} - 2b_{100}h_{001} - a_{010}b_{001} - 2g_{010}h_{010} + 2f_{100}h_{010} + 2h_{010}h_{001}, \\
\gamma'_5 &= -b_{100}c_{100} - a_{001}b_{001} - a_{010}c_{010} + 2a_{001}f_{010} + 2c_{100}h_{010} + f^2_{100} - g^2_{010} - 2f_{100}h_{001} + h^2_{001}. \\
\delta'_5 &= -b_{010}g_{010} + b_{010}f_{100} + b_{010}h_{001} - b_{100}b_{001}, \\
\epsilon'_5 &= b_{010}c_{100} - 2b_{001}f_{100} - b_{100}c_{010} - 2f_{010}g_{010} + 2f_{010}h_{001} + 2f_{100}f_{010}, \\
\zeta'_5 &= -b_{001}c_{100} - c_{010}g_{010} + c_{010}h_{001} - c_{010}f_{100} + 2c_{100}f_{010} ;
\end{aligned}\right.$$

$$\left\{\begin{aligned}
\alpha'_6 &= -a_{010}c_{100} - a_{001}h_{001} + a_{001}f_{100} - a_{001}g_{010} + 2a_{010}g_{001}, \\
\beta'_6 &= -a_{010}c_{010} - b_{100}c_{100} - a_{001}b_{001} + 2b_{100}g_{001} + 2a_{010}f_{001} + f^2_{100} + g^2_{010} - 2f_{100}g_{010} - h^2_{001}; \\
\gamma'_6 &= a_{010}c_{001} - 2c_{100}g_{010} - a_{001}c_{010} - 2g_{001}h_{001} + 2f_{100}g_{001} + 2g_{010}g_{001}, \\
\delta'_6 &= -b_{100}c_{010} - b_{001}h_{001} + b_{001}g_{010} - b_{001}f_{100} + 2b_{100}f_{001}, \\
\epsilon'_6 &= b_{100}c_{001} - 2c_{010}f_{100} - b_{001}c_{100} - 2f_{001}h_{001} + 2f_{001}g_{010} + 2f_{100}f_{001}, \\
\zeta'_6 &= -c_{001}h_{001} + c_{001}g_{010} + c_{001}f_{100} - c_{100}c_{010}.
\end{aligned}\right.$$

The coefficients in the ten integrals a″, b″. c″, f″. g″. h″, k″, l″, m″, n″ are as follows :—

$$\alpha_1 = 6\mathrm{L}^2\,\{\mathrm{A}a_{100} + \mathrm{H}\,(2h_{100} - a_{010}) + \mathrm{G}\,(2g_{100} - a_{001})\},$$

$$\beta_1 = 6\mathrm{L}^2\,\{\mathrm{H}a_{100} + \mathrm{B}\,(2h_{100} - a_{010}) + \mathrm{F}\,(2g_{100} - a_{001})\},$$

$$\gamma_1 = 6\mathrm{L}^2\,\{\mathrm{G}a_{100} + \mathrm{F}\,(2h_{100} - a_{010}) + \mathrm{C}\,(2g_{100} - a_{001})\},$$

$$\begin{aligned}
\lambda_1 = &-4\mathrm{A}a^2_{100} + 2\mathrm{B}\,(a^2_{010} - a_{010}h_{100} - 2h^2_{100}) + 2\mathrm{C}\,(a^2_{001} - a_{001}g_{100} - 2g^2_{100}) \\
&+ 2\mathrm{F}\,(2a_{010}a_{001} - a_{010}g_{100} - a_{001}h_{100} - 4g_{100}h_{100}) \\
&+ 2\mathrm{G}\,(a_{100}a_{001} - 5a_{100}g_{100}) + 2\mathrm{H}\,(a_{100}a_{010} - 5a_{100}h_{100}),
\end{aligned}$$

$$\begin{aligned}
\mu_1 = &\ 2\mathrm{A}\,(a_{100}a_{010} - 3a_{100}h_{100}) + 2\mathrm{B}\,(2a_{010}b_{100} - 4b_{100}h_{100}) \\
&+ 2\mathrm{C}\,(2a_{001}f_{100} - a_{001}g_{010} + a_{001}h_{001} - 4f_{100}g_{100} + 2g_{010}g_{100} - 2g_{100}h_{001}) \\
&+ 2\mathrm{F}\,(2a_{010}f_{100} - a_{010}g_{010} + a_{010}h_{001} + 2a_{001}b_{100} \\
&\qquad\qquad - 4b_{100}g_{100} - 4f_{100}h_{100} + 2g_{010}h_{100} - 2h_{001}h_{100}) \\
&+ 2\mathrm{G}\,(-2a_{100}f_{100} + a_{100}g_{010} - a_{100}h_{001} + 2a_{010}g_{100} - a_{010}a_{001} + 3h_{100}a_{001} - 6g_{100}h_{100}) \\
&+ 2\mathrm{H}\,(-2a_{100}b_{100} + 5a_{010}h_{100} - a^2_{010} - 6h^2_{100}),
\end{aligned}$$

$$\begin{aligned}
\nu_1 = &\ 2\mathrm{A}\,(a_{100}a_{001} - 3a_{100}g_{100}) + 2\mathrm{C}\,(2a_{001}c_{100} - 4c_{100}g_{100}) \\
&+ 2\mathrm{B}\,(2a_{010}f_{100} - a_{010}h_{001} + a_{010}g_{010} - 4f_{100}h_{100} + 2h_{100}h_{001} - 2g_{010}h_{100}) \\
&+ 2\mathrm{F}\,(2a_{001}f_{100} - a_{001}h_{001} + a_{001}g_{010} + 2a_{010}c_{100} \\
&\qquad\qquad - 4c_{100}h_{100} - 4f_{100}g_{100} + 2g_{100}h_{001} - 2g_{100}g_{010}) \\
&+ 2\mathrm{G}\,(-2a_{100}c_{100} + 5a_{001}g_{100} - a^2_{001} - 6g^2_{100}) \\
&+ 2\mathrm{H}\,(-2a_{100}f_{100} + a_{100}h_{001} - a_{100}g_{010} + 2a_{001}h_{100} - a_{010}a_{001} + 3g_{100}a_{010} - 6g_{100}h_{100});
\end{aligned}$$

$$\alpha_2 = 4L^2 \{Aa_{010} + Hb_{100} + G(f_{100} + g_{010} - h_{001})\},$$

$$\beta_2 = 2L^2 \{Aa_{100} + H(2h_{100} + a_{010}) + G(2g_{100} - a_{001}) + 2Bb_{100} + 2F(f_{100} + g_{010} - h_{001})\},$$

$$\gamma_2 = 4L^2 \{Ga_{010} + Fb_{100} + C(f_{100} + g_{010} - h_{001})\},$$

$$\delta_2 = 2L^2 \{Ha_{100} + B(2h_{100} - a_{010}) + F(2g_{100} - a_{001})\},$$

$$\epsilon_2 = 2L^2 \{Ga_{100} + F(2h_{100} - a_{010}) + C(2g_{100} - a_{001})\},$$

$$\begin{aligned}\lambda_2 = &- 4Aa_{100}a_{010} - 2H(a_{100}b_{100} + a_{100}h_{010} + 2a_{010}h_{100}) + 2G(- a_{100}f_{100} - 2a_{100}g_{010} + a_{100}h_{001} - 2a_{010}g_{100}) \\ &+ 2B(a_{010}h_{010} - a_{010}b_{100} - 2h_{010}h_{100}) + 2F(a_{001}h_{010} - a_{001}b_{100} + a_{010}h_{001} - a_{010}f_{100} - 2g_{100}h_{010} - 2g_{010}h_{100}) \\ &+ 2C(- a_{001}f_{100} + a_{001}h_{001} - 2g_{100}g_{010}),\end{aligned}$$

$$\begin{aligned}\mu_2 = &A(a^2_{010} - 4a_{010}h_{100} - a_{100}b_{100}) + B(a_{010}b_{010} - 3b^2_{100} - 2b_{010}h_{100}) \\ &+ C(a_{001}b_{001} - 2b_{001}g_{100} - 2f_{100}g_{010} + 2f_{100}h_{001} - 2g_{010}h_{001} - 3f^2_{100} + g^2_{010} + h^2_{001}) \\ &+ F(a_{010}b_{001} + a_{001}b_{010} - 6b_{100}f_{100} - 2b_{100}g_{010} + 2b_{100}h_{001} - 2b_{010}g_{100} - 2b_{001}h_{100}) + H(- a_{100}b_{010} - a_{010}b_{100} - 6b_{100}h_{100}) \\ &+ G(- a_{100}b_{001} - 2a_{010}f_{100} + 2a_{010}g_{010} - 2a_{010}h_{001} + a_{001}b_{100} - 2b_{100}g_{100} - 4f_{100}h_{100} - 4g_{010}h_{100} + 4h_{100}h_{001}),\end{aligned}$$

$$\begin{aligned}\nu_2 = &2A(- a_{100}g_{010} - 2a_{010}g_{100} + a_{010}a_{001}) + 2B(- 2f_{010}h_{100} + a_{010}f_{010} - b_{100}f_{100} - b_{100}g_{010} + b_{100}h_{001}) \\ &+ 2C(a_{001}c_{010} - c_{100}f_{100} - c_{100}g_{010} + c_{100}h_{001} - 2c_{010}g_{100}) \\ &+ 2H(- a_{100}f_{010} - 2g_{010}h_{100} - a_{010}f_{100} + a_{010}h_{001} + a_{001}b_{100} - 2b_{100}g_{100}) \\ &+ 2F(- 2c_{010}h_{100} + a_{010}c_{010} + a_{001}f_{010} - b_{100}c_{100} - f^2_{100} - 2f_{100}g_{010} + 2f_{100}h_{001} + 2g_{010}h_{001} - g^2_{010} - h^2_{001} - 2f_{010}g_{100}) \\ &+ 2G(- a_{100}c_{010} - a_{010}c_{100} + a_{001}f_{100} + 2a_{001}g_{010} - a_{001}h_{001} - 2g_{100}f_{100} - 4g_{100}g_{010} + 2g_{100}h_{001});\end{aligned}$$

$$\alpha_3 = 4L^2\{Aa_{001} + H(f_{100} - g_{010} + h_{001}) + Gc_{100}\},$$

$$\beta_3 = 4L^2\{Ha_{001} + B(f_{100} - g_{010} + h_{001}) + Fc_{100}\},$$

$$\gamma_3 = 2L^2\{Aa_{100} + H(2h_{100} - a_{010}) + G(2g_{100} + a_{001}) + 2F(f_{100} - g_{010} + h_{001}) + 2Cc_{100}\},$$

$$\epsilon_3 = 2L^2\{Ha_{100} + B(2h_{100} - a_{010}) + F(2g_{100} - a_{001})\},$$

$$\zeta_3 = 2L^2\{Ga_{100} + F(2h_{100} - a_{010}) + C(2g_{100} - a_{001})\},$$

$$\begin{aligned}\lambda_3 = &- 4Aa_{100}a_{001} + 2B(- a_{010}f_{100} + a_{010}g_{010} - 2h_{100}h_{001}) + 2C(a_{001}g_{001} - a_{001}c_{100} - 2g_{001}g_{100})\\ &- 2G(a_{100}c_{100} + a_{100}g_{001} + 2a_{001}g_{100}) + 2F(a_{010}g_{001} - a_{010}c_{100} + a_{001}g_{010} - a_{001}f_{100} - 2g_{001}h_{100} - 2g_{100}h_{001})\\ &+ 2H(- a_{100}f_{100} - 2a_{100}h_{001} + a_{100}g_{010} - 2a_{001}h_{100}),\end{aligned}$$

$$\begin{aligned}\mu_3 = 2A&(-a_{100}h_{001} - 2a_{001}h_{100} + a_{010}a_{001}) + 2B(a_{010}b_{001} - b_{100}f_{100} - b_{100}h_{001} + b_{100}g_{010} - 2b_{001}h_{100})\\ &+ 2C(- 2f_{001}g_{100} + a_{001}f_{001} - c_{100}f_{100} - c_{100}h_{001} + c_{100}g_{010})\\ &+ 2G(- a_{100}f_{001} - 2g_{100}h_{001} - a_{001}f_{100} + a_{001}g_{010} + a_{010}c_{100} - 2c_{100}h_{100})\\ &+ 2F(- 2b_{001}g_{100} + a_{001}b_{001} + a_{010}f_{001} - b_{100}c_{100} - f^2_{100} + 2f_{100}g_{010} - 2f_{100}h_{001} - g^2_{010} + 2g_{010}h_{001} - h^2_{001} - 2f_{001}h_{100})\\ &+ 2H(- a_{100}b_{001} - a_{001}b_{100} + a_{010}f_{100} + 2a_{010}h_{001} - a_{010}g_{010} - 2f_{100}h_{100} - 4h_{100}h_{001} + 2g_{010}h_{100}),\end{aligned}$$

$$\begin{aligned}\nu_3 = A&(a^2_{001} - 4a_{001}g_{100} - a_{100}c_{100}) + C(a_{001}c_{001} - 3c^2_{100} - 2c_{001}g_{010})\\ &+ B(a_{010}c_{010} - 2c_{010}h_{100} - 2f_{100}h_{001} + 2f_{100}g_{010} - 2g_{010}h_{001} - 3f^2_{100} + g^2_{010} + h^2_{001})\\ &+ H(- a_{100}c_{010} - 2a_{001}f_{100} + 2a_{001}h_{001} - 2a_{001}g_{010} + a_{010}c_{100} - 2c_{100}h_{100} - 4f_{100}g_{100} - 4g_{100}h_{001} + 4g_{100}g_{010})\\ &+ F(a_{001}c_{010} + a_{010}c_{001} - 6c_{100}f_{100} - 2c_{100}h_{001} + 2c_{100}g_{010} - 2c_{001}h_{100} - 2c_{010}g_{100}) + G(- a_{100}c_{001} - a_{001}c_{100} - 6c_{100}g_{100});\end{aligned}$$

$$\alpha_4 = 2\mathrm{L}^2 \{\mathrm{A}(2h_{010} - b_{100}) + \mathrm{H}b_{010} + \mathrm{G}(2f_{010} - b_{001})\},$$

$$\beta_4 = 2\mathrm{L}^2 \{2\mathrm{A}a_{010} + \mathrm{H}(2h_{010} + b_{100}) + 2\mathrm{G}(f_{100} + g_{010} - h_{001}) + \mathrm{B}b_{010} + \mathrm{F}(2f_{010} - b_{001})\},$$

$$\gamma_4 = 2\mathrm{L}^2 \{\mathrm{G}(2h_{010} - b_{100}) + \mathrm{F}b_{010} + \mathrm{C}(2f_{010} - b_{001})\},$$

$$\delta_4 = 4\mathrm{L}^2 \{\mathrm{H}a_{010} + \mathrm{B}b_{100} + \mathrm{F}(f_{100} + g_{010} - h_{001})\},$$

$$\epsilon_4 = 4\mathrm{L}^2 \{\mathrm{G}a_{010} + \mathrm{F}b_{100} + \mathrm{C}(f_{100} + g_{010} - h_{001})\},$$

$$\begin{aligned}\lambda_4 = {} & \mathrm{A}(a_{100}b_{100} - 3a^2_{010} - 2a_{100}h_{010}) + \mathrm{B}(b^2_{100} - 4b_{100}h_{010} - a_{010}b_{010}) \\ & + \mathrm{C}(a_{001}b_{001} - 2a_{001}f_{010} - 2f_{100}g_{010} + 2g_{010}h_{001} - 2f_{100}h_{001} - 3g^2_{010} + f^2_{100} + h^2_{001}) \\ & + \mathrm{F}(-a_{001}b_{010} - 2b_{100}g_{010} + 2b_{100}f_{100} - 2b_{100}h_{001} + a_{010}b_{001} - 2a_{010}f_{010} - 4g_{010}h_{010} - 4f_{100}h_{010} + 4h_{010}h_{001}) \\ & + \mathrm{G}(a_{001}b_{100} + a_{100}b_{001} - 6a_{010}g_{010} - 2a_{010}f_{100} + 2a_{010}h_{001} - 2a_{100}f_{010} - 2a_{001}h_{010}) + \mathrm{H}(-a_{100}b_{010} - a_{010}b_{100} - 6a_{010}h_{010}),\end{aligned}$$

$$\begin{aligned}\mu_4 = {} & 2\mathrm{A}(b_{100}h_{100} - a_{010}b_{100} - 2h_{010}h_{100}) - 4\mathrm{B}b_{100}b_{010} + 2\mathrm{C}(-b_{001}g_{010} + b_{001}h_{001} - 2f_{100}f_{010}) - 2\mathrm{H}(a_{010}b_{010} + b_{010}h_{100} + 2b_{100}h_{010}) \\ & + 2\mathrm{F}(-b_{010}g_{010} - 2b_{010}f_{100} + b_{010}h_{001} - 2b_{100}f_{010}) + 2\mathrm{G}(b_{001}h_{100} - a_{010}b_{001} + b_{100}h_{001} - b_{100}g_{010} - 2f_{010}h_{100} - 2f_{100}h_{010}),\end{aligned}$$

$$\begin{aligned}\nu_4 = {} & 2\mathrm{A}(-2g_{100}h_{010} + b_{100}g_{100} - a_{010}g_{010} - a_{010}f_{100} + a_{010}h_{001}) + 2\mathrm{B}(-b_{010}f_{100} - 2b_{100}f_{010} + b_{100}b_{001}) \\ & + 2\mathrm{C}(b_{001}c_{100} - c_{010}g_{010} - c_{010}f_{100} + c_{010}h_{001} - 2c_{100}f_{010}) \\ & + 2\mathrm{H}(-b_{010}g_{100} - 2f_{100}h_{010} - b_{100}g_{010} + b_{100}h_{001} + b_{001}a_{010} - 2a_{010}f_{010}) \\ & + 2\mathrm{F}(-b_{010}c_{100} - b_{100}c_{010} + b_{001}g_{010} + 2b_{001}f_{100} - b_{001}h_{001} - 2f_{010}g_{010} - 4f_{100}f_{010} + 2f_{010}h_{001}) \\ & + 2\mathrm{G}(-2c_{100}h_{010} + b_{100}c_{100} + b_{001}g_{100} - a_{010}c_{010} - f^2_{100} - 2f_{100}g_{010} + 2f_{100}h_{001} + 2g_{010}h_{001} - g^2_{010} - h^2_{001} - 2f_{010}g_{100});\end{aligned}$$

$$\alpha_5 = 2\mathrm{L}^2 \{\mathrm{A}(-f_{100} + g_{010} + h_{001}) + \mathrm{H}b_{001} + \mathrm{G}c_{010}\},$$

$$\beta_5 = 2\mathrm{L}^2 \{\mathrm{A}a_{001} + \mathrm{B}b_{001} + \mathrm{G}c_{100} + \mathrm{F}c_{010} + 2\mathrm{H}h_{001}\},$$

$$\gamma_5 = 2\mathrm{L}^2 \{\mathrm{A}a_{010} + \mathrm{H}b_{100} + \mathrm{F}b_{001} + \mathrm{C}c_{010} + 2\mathrm{G}g_{010}\},$$

$$\delta_5 = 2\mathrm{L}^2 \{\mathrm{H}a_{001} + \mathrm{B}(f_{100} - g_{010} + h_{001}) + \mathrm{F}c_{100}\},$$

$$\epsilon_5 = 2\mathrm{L}^2 \{\mathrm{H}a_{010} + \mathrm{G}a_{001} + \mathrm{B}b_{100} + \mathrm{C}c_{100} + 2\mathrm{F}f_{100}\},$$

$$\zeta_5 = 2\mathrm{L}^2 \{\mathrm{G}a_{010} + \mathrm{F}b_{100} + \mathrm{C}(f_{100} + g_{010} - h_{001})\},$$

$$\begin{aligned}\lambda_5 = \mathrm{A}\,&(a_{100}f_{100} - a_{100}g_{010} - a_{100}h_{001} - 3a_{010}a_{001}) + \mathrm{H}\,(-a_{100}b_{001} - 4a_{010}h_{001} - a_{001}b_{100} - 2a_{001}h_{010})\\
&+ \mathrm{G}\,(-a_{100}c_{010} - a_{010}c_{100} - 2a_{010}g_{001} - 4a_{001}g_{010})\\
&+ \mathrm{B}\,(-a_{010}b_{001} - b_{100}h_{001} - b_{100}g_{010} + b_{100}f_{100} - 2f_{100}h_{010} + 2g_{010}h_{010} - 2h_{010}h_{001})\\
&+ \mathrm{F}\,(-a_{010}c_{010} - a_{001}b_{001} + b_{100}c_{100} - 2b_{100}g_{001} - 2c_{100}h_{010} + f^2_{100} - 2f_{100}g_{010} - 2f_{100}h_{001} + g^2_{010} - 2g_{010}h_{001} + h^2_{001})\\
&+ \mathrm{C}\,(-a_{001}c_{010} + c_{100}f_{100} - c_{100}g_{010} - c_{100}h_{001} - 2f_{100}g_{001} - 2g_{010}g_{001} + 2g_{001}h_{001}),\end{aligned}$$

$$\begin{aligned}\mu_5 = \mathrm{A}\,&(-a_{001}b_{100} - a_{010}h_{001} - a_{010}f_{100} + a_{010}g_{010} - 2g_{010}h_{100} + 2f_{100}h_{100} - 2h_{100}h_{001})\\
&+ \mathrm{H}\,(-a_{001}b_{010} - 4b_{100}h_{001} - a_{010}b_{001} - 2b_{001}h_{100}) + \mathrm{B}\,(b_{010}g_{010} - b_{010}f_{100} - b_{010}h_{001} - 3b_{100}b_{001})\\
&+ \mathrm{F}\,(-b_{010}c_{100} - b_{100}c_{010} - 2b_{100}f_{001} - 4b_{001}f_{100})\\
&+ \mathrm{G}\,(-b_{100}c_{100} - a_{001}b_{001} + a_{010}c_{010} - 2a_{010}f_{001} - 2c_{010}h_{100} + f^2_{100} - 2f_{100}g_{010} - 2f_{100}h_{001} + g^2_{010} - 2g_{010}h_{001} + h^2_{001})\\
&+ \mathrm{C}\,(-b_{001}c_{100} + c_{010}g_{010} - c_{010}f_{100} - c_{010}h_{001} - 2f_{001}g_{010} - 2f_{100}f_{001} + 2f_{001}h_{001}),\end{aligned}$$

$$\begin{aligned}\nu_5 = \mathrm{A}\,&(-a_{010}c_{100} + a_{001}h_{001} - a_{001}g_{010} - a_{001}f_{100} - 2g_{100}h_{001} - 2g_{100}g_{010} + 2f_{100}g_{100})\\
&+ \mathrm{H}\,(-a_{010}c_{010} - b_{100}c_{100} + a_{001}b_{001} - 2b_{001}g_{100} - 2a_{001}f_{010} + f^2_{100} - 2f_{100}g_{010} - 2f_{100}h_{001} + g^2_{010} - 2g_{010}h_{001} + h^2_{001})\\
&+ \mathrm{B}\,(-b_{100}c_{010} - b_{001}f_{100} - b_{001}g_{010} + b_{001}h_{001} - 2f_{010}h_{001} + 2f_{010}g_{010} - 2f_{100}f_{010})\\
&+ \mathrm{G}\,(-a_{010}c_{001} - a_{001}c_{010} - 2c_{010}a_{100} - 4c_{100}g_{010}) + \mathrm{F}\,(-b_{100}c_{001} - 4c_{010}f_{100} - b_{001}c_{100} - 2c_{100}f_{010})\\
&+ \mathrm{C}\,(c_{001}h_{001} - c_{001}g_{010} - c_{001}f_{100} - 3c_{100}c_{010});\end{aligned}$$

$$\alpha_6 = 2\mathrm{L}^2 \{\mathrm{A}(2g_{001} - c_{100}) + \mathrm{H}(2f_{001} - c_{010}) + \mathrm{G}c_{001}\},$$

$$\beta_6 = 2\mathrm{L}^2 \{\mathrm{H}(2g_{001} - c_{100}) + \mathrm{B}(2f_{001} - c_{010}) + \mathrm{F}c_{001}\},$$

$$\gamma_6 = 2\mathrm{L}^2 \{2\mathrm{A}a_{001} + 2\mathrm{H}(f_{100} - g_{010} + h_{001}) + \mathrm{G}(2g_{001} + c_{100}) + \mathrm{F}(2f_{001} - c_{010}) + \mathrm{C}c_{001}\},$$

$$\epsilon_6 = 4\mathrm{L}^2 \{\mathrm{H}a_{001} + \mathrm{B}(f_{100} - g_{010} + h_{001}) + \mathrm{F}c_{100}\},$$

$$\zeta_6 = 4\mathrm{L}^2 \{\mathrm{G}a_{001} + \mathrm{F}(f_{100} - g_{010} + h_{001}) + \mathrm{C}c_{100}\},$$

$$\begin{aligned}\lambda_6 = {} & \mathrm{A}(a_{100}c_{100} - 3a^2{}_{001} - 2a_{100}g_{001}) + \mathrm{C}(c^2{}_{100} - 4c_{100}g_{001} - a_{001}c_{001}) \\ & + \mathrm{B}(a_{010}c_{010} - 2a_{010}f_{001} - 2f_{100}h_{001} + 2g_{010}h_{001} - 2f_{100}g_{010} - 3h^2{}_{001} + f^2{}_{100} + g^2{}_{010}) \\ & + \mathrm{F}(-a_{010}c_{001} - 2c_{100}h_{001} + 2c_{100}f_{100} - 2c_{100}g_{010} + a_{001}c_{010} - 2a_{001}f_{001} - 4g_{001}h_{001} - 4f_{100}g_{001} + 4g_{010}g_{001}) \\ & + \mathrm{G}(-a_{100}c_{001} - a_{001}c_{100} - 6a_{001}g_{001}) + \mathrm{H}(a_{010}c_{100} + a_{100}c_{010} - 6a_{001}h_{001} - 2a_{001}f_{100} + 2a_{001}g_{010} - 2a_{100}f_{001} - 2a_{010}g_{001}),\end{aligned}$$

$$\begin{aligned}\mu_6 = {} & 2\mathrm{A}(-2g_{001}h_{100} + c_{100}h_{100} - a_{001}h_{001} - a_{001}f_{100} + a_{001}g_{010}) + 2\mathrm{B}(b_{100}c_{010} - b_{001}h_{001} - b_{001}f_{100} + b_{001}g_{020} - 2b_{100}f_{001}) \\ & + 2\mathrm{C}(-c_{001}f_{100} - 2c_{100}f_{001} + c_{100}c_{010}) + 2\mathrm{G}(-c_{001}h_{100} - 2f_{100}g_{001} - c_{100}h_{001} + c_{100}g_{010} + c_{010}a_{001} - 2a_{001}f_{001}) \\ & + 2\mathrm{F}(-b_{100}c_{001} - b_{001}c_{100} + c_{010}h_{001} + 2c_{010}f_{100} - c_{010}g_{010} - 2f_{001}h_{001} - 4f_{100}f_{001} + 2f_{001}g_{010}), \\ & + 2\mathrm{H}(-2b_{100}g_{001} + b_{100}c_{100} + c_{010}h_{100} - a_{001}b_{001} - f^2{}_{100} + 2f_{100}g_{010} - 2f_{100}h_{001} + 2g_{010}h_{001} - g^2{}_{010} - h^2{}_{001} - 2f_{001}h_{100})\end{aligned}$$

$$\begin{aligned}\nu_6 = {} & 2\mathrm{A}(c_{100}g_{100} - a_{001}c_{100} - 2g_{100}g_{001}) + 2\mathrm{B}(-c_{010}h_{001} + c_{010}g_{010} - 2f_{100}f_{001}) - 4\mathrm{C}c_{100}c_{001} - 2\mathrm{G}(a_{001}c_{001} + c_{001}g_{100} + 2c_{100}g_{001}) \\ & + 2\mathrm{F}(-c_{001}h_{001} - 2c_{001}f_{100} + c_{001}g_{010} - 2c_{100}f_{001}) + 2\mathrm{H}(c_{010}g_{100} - a_{001}c_{010} + c_{100}g_{010} - c_{100}h_{001} - 2f_{001}g_{100} - 2f_{100}g_{001});\end{aligned}$$

$$\alpha_7 = 6\mathrm{L}^2 \{\mathrm{H}(2h_{010} - b_{100}) + \mathrm{B}b_{010} + \mathrm{F}(2f_{010} - b_{001})\},$$

$$\beta_7 = 6\mathrm{L}^2 \{\mathrm{A}(2h_{010} - b_{100}) + \mathrm{H}b_{010} + \mathrm{G}(2f_{010} - b_{001})\},$$

$$\gamma_7 = 6\mathrm{L}^2 \{\mathrm{G}(2h_{010} - b_{100}) + \mathrm{F}b_{010} + \mathrm{C}(2f_{010} - b_{001})\}.$$

$$\begin{aligned}\lambda_7 = {} & 2\mathrm{A}(2a_{010}b_{100} - 4a_{010}h_{010}) + 2\mathrm{B}(b_{100}b_{010} - 3b_{010}h_{010}) \\ & + 2\mathrm{C}(2b_{001}g_{010} - b_{001}f_{100} + b_{001}h_{001} - 4f_{010}g_{010} + 2f_{100}f_{010} - 2f_{010}h_{001}) \\ & + 2\mathrm{F}(-2b_{010}g_{010} + b_{010}f_{100} - b_{010}h_{001} + 2b_{100}f_{010} - b_{100}b_{001} + 3h_{010}b_{001} - 6f_{010}h_{010}) \\ & + 2\mathrm{G}(2b_{100}g_{010} - b_{100}f_{100} + b_{100}h_{001} + 2a_{010}b_{001} \\ & \qquad - 4a_{010}f_{010} - 4g_{010}h_{010} + 2f_{100}h_{010} - 2h_{010}h_{001}) \\ & + 2\mathrm{H}(-2a_{010}b_{010} + 5b_{100}h_{010} - b^2_{100} - 6h^2_{010}),\end{aligned}$$

$$\begin{aligned}\mu_7 = {} & 2\mathrm{A}(b^2_{100} - b_{100}h_{010} - 2h^2_{010}) - 4\mathrm{B}b^2_{010} + 2\mathrm{C}(b^2_{001} - b_{001}f_{010} - 2f^2_{010}) \\ & + 2\mathrm{G}(2b_{100}b_{001} - b_{100}f_{010} - b_{001}h_{010} - 4f_{010}h_{010}) \\ & + 2\mathrm{F}(b_{010}b_{001} - 5b_{010}f_{010}) + 2\mathrm{H}(b_{100}b_{010} - 5b_{010}h_{010}),\end{aligned}$$

$$\begin{aligned}\nu_7 = {} & 2\mathrm{C}(2b_{001}c_{010} - 4c_{010}f_{010}) + 2\mathrm{B}(b_{010}b_{001} - 3b_{010}f_{010}) \\ & + 2\mathrm{A}(2b_{100}g_{010} - b_{100}h_{001} + b_{100}f_{100} - 4g_{010}h_{010} + 2h_{010}h_{001} - 2f_{100}h_{010}) \\ & + 2\mathrm{G}(2b_{001}g_{010} - b_{001}h_{001} + b_{001}f_{100} + 2b_{100}c_{010} \\ & \qquad - 4c_{010}h_{010} - 4f_{010}g_{010} + 2f_{010}h_{001} - 2f_{100}f_{010}) \\ & + 2\mathrm{F}(-2b_{010}c_{010} + 5b_{001}f_{010} - b^2_{001} - 6f^2_{010}) \\ & + 2\mathrm{H}(-2b_{010}g_{010} + b_{010}h_{001} - b_{010}f_{100} + 2b_{001}h_{010} - b_{100}b_{001} + 3b_{100}f_{010} - 6f_{010}h_{010});\end{aligned}$$

$$\beta_8 = 4\mathrm{L}^2 \{\mathrm{A}(-f_{100} + g_{010} + h_{001}) + \mathrm{H}b_{001} + \mathrm{G}c_{010}\},$$

$$\gamma_8 = 2\mathrm{L}^2 \{\mathrm{A}(2h_{010} - b_{100}) + \mathrm{H}b_{010} + \mathrm{G}(2f_{010} - b_{001})\},$$

$$\delta_8 = 4\mathrm{L}^2 \{\mathrm{H}(-f_{100} + g_{010} + h_{001}) + \mathrm{B}b_{001} + \mathrm{F}c_{010}\},$$

$$\epsilon_8 = 2\mathrm{L}^2 \{\mathrm{H}(2h_{010} - b_{100}) + 2\mathrm{G}(-f_{100} + g_{010} + h_{001}) + \mathrm{B}b_{010} + \mathrm{F}(2f_{010} + b_{001}) + 2\mathrm{C}c_{010}\},$$

$$\zeta_8 = 2\mathrm{L}^2 \{\mathrm{G}(2h_{010} - b_{100}) + \mathrm{F}b_{010} + \mathrm{C}(2f_{010} - b_{001})\},$$

$$\begin{aligned}\lambda_8 = {} & 2\mathrm{A}(a_{001}b_{100} - a_{010}g_{010} - a_{010}h_{001} + a_{010}f_{100} - 2a_{001}h_{010}) + 2\mathrm{B}(-b_{010}h_{001} - 2b_{001}h_{010} + b_{100}b_{001}) \\ & + 2\mathrm{C}(-2f_{010}g_{001} + b_{001}g_{001} - c_{010}g_{010} - c_{010}h_{001} + c_{010}f_{100}) \\ & + 2\mathrm{F}(-b_{010}g_{001} - 2f_{010}h_{001} - b_{001}g_{010} + b_{001}f_{100} + b_{100}c_{010} - 2c_{010}h_{010}) \\ & + 2\mathrm{G}(-2a_{001}f_{010} + a_{001}b_{001} + b_{100}g_{001} - a_{010}c_{010} - f^2_{100} + 2f_{100}g_{010} + 2f_{100}h_{001} - g^2_{010} - 2g_{010}h_{001} - h^2_{001} - 2g_{001}h_{010}) \\ & + 2\mathrm{H}(-a_{001}b_{010} - a_{010}b_{001} + b_{100}g_{010} + 2b_{100}h_{001} - b_{100}f_{100} - 2g_{010}h_{010} - 4h_{010}h_{001} + 2f_{100}h_{010}),\end{aligned}$$

$$\begin{aligned}\mu_8 = {} & 2\mathrm{A}(-b_{100}g_{010} + b_{100}f_{100} - 2h_{010}h_{001}) - 4\mathrm{B}b_{010}b_{001} + 2\mathrm{C}(b_{001}f_{001} - b_{001}c_{010} - 2f_{001}f_{010}) - 2\mathrm{F}(b_{010}c_{010} + b_{010}f_{001} + 2b_{001}f_{010}) \\ & + 2\mathrm{G}(b_{100}f_{001} - b_{100}c_{010} + b_{001}f_{100} - b_{001}g_{010} - 2f_{001}h_{010} - 2f_{010}h_{001}) + 2\mathrm{H}(-b_{010}g_{010} - 2b_{010}h_{001} + b_{010}f_{100} - 2b_{001}h_{010}),\end{aligned}$$

$$\begin{aligned}\nu_8 = {} & \mathrm{A}(b_{100}c_{100} - 2c_{100}h_{010} - 2g_{010}h_{001} + 2f_{100}g_{010} - 2f_{100}h_{001} - 3g^2_{010} + f^2_{100} + h^2_{001}) + \mathrm{B}(b^2_{001} - 4b_{001}f_{010} - b_{010}c_{010}) \\ & + \mathrm{C}(b_{001}c_{001} - 3c^2_{010} - 2c_{001}f_{010}) + \mathrm{F}(-b_{010}c_{001} - b_{001}c_{010} - 6c_{010}f_{010}) \\ & + \mathrm{H}(-b_{010}c_{100} - 2b_{001}g_{010} + 2b_{001}h_{001} - 2b_{001}f_{100} + b_{100}c_{010} - 2c_{010}h_{010} - 4f_{010}g_{010} - 4f_{010}h_{001} + 4f_{100}f_{010}) \\ & + \mathrm{G}(b_{001}c_{100} + b_{100}c_{001} - 6c_{010}g_{010} - 2c_{010}h_{001} + 2c_{010}f_{100} - 2c_{001}h_{010} - 2c_{100}f_{010});\end{aligned}$$

$$\beta_9 = 2\mathrm{L}^2 \{\mathrm{A}(2g_{001} - c_{100}) + \mathrm{H}(2f_{001} - c_{010}) + \mathrm{G}c_{001}\},$$

$$\gamma_9 = 4\mathrm{L}^2 \{\mathrm{A}(-f_{100} + g_{010} + h_{001}) + \mathrm{H}b_{001} + \mathrm{G}c_{010}\},$$

$$\delta_9 = 2\mathrm{L}^2 \{\mathrm{H}(2g_{001} - c_{100}) + \mathrm{B}(2f_{001} - c_{010}) + \mathrm{F}c_{001}\},$$

$$\epsilon_9 = 2\mathrm{L}^2 \{2\mathrm{H}(-f_{100} + g_{010} + h_{001}) + \mathrm{G}(2g_{001} - c_{100}) + 2\mathrm{B}b_{001} + \mathrm{F}(2f_{001} + c_{010}) + \mathrm{C}c_{001}\},$$

$$\zeta_9 = 4\mathrm{L}^2 \{\mathrm{G}(-f_{100} + g_{010} + h_{001}) + \mathrm{F}b_{001} + \mathrm{C}c_{010}\},$$

$$\begin{aligned}\lambda_9 = 2\mathrm{A}\,&(a_{010}c_{100} - a_{001}h_{001} - a_{001}g_{010} + a_{001}f_{100} - 2a_{010}g_{001}) + 2\mathrm{B}(-2f_{001}h_{010} + c_{010}h_{010} - b_{001}h_{001} - b_{001}g_{010} + b_{001}f_{100})\\ &+ 2\mathrm{C}(-c_{001}g_{010} - 2c_{010}g_{001} + c_{100}c_{010}) + 2\mathrm{F}(-c_{001}h_{010} - 2f_{001}g_{010} - c_{010}h_{001} + c_{010}f_{100} + c_{100}b_{001} - 2b_{001}g_{001})\\ &+ 2\mathrm{G}(-a_{010}c_{001} - a_{001}c_{010} + c_{100}h_{001} + 2c_{100}g_{010} - c_{100}f_{100} - 2g_{001}h_{001} - 4g_{010}g_{001} + 2f_{100}g_{001})\\ &+ 2\mathrm{H}(-2a_{010}f_{001} + a_{010}c_{010} + c_{100}h_{010} - a_{001}b_{001} - f^2_{100} + 2f_{100}h_{001} + 2f_{100}g_{010} - g^2_{010} - 2g_{010}h_{001} - h^2_{001} - 2g_{001}h_{010}),\end{aligned}$$

$$\begin{aligned}\mu_9 = \mathrm{A}\,&(b_{100}c_{100} - 2b_{100}g_{001} - 2g_{010}h_{001} + 2f_{100}h_{001} - 2f_{100}g_{010} - 3h^2_{001} + f^2_{100} + g^2_{010})\\ &+ \mathrm{B}(b_{010}c_{010} - 3b^2_{001} - 2b_{010}f_{001}) + \mathrm{C}(c^2_{010} - 4c_{010}f_{001} - b_{001}c_{001})\\ &+ \mathrm{F}(-b_{010}c_{001} - b_{001}c_{010} - 6b_{001}f_{001}) + \mathrm{H}(b_{100}c_{010} + b_{010}c_{100} - 6b_{001}h_{001} - 2b_{001}g_{010} + 2b_{001}f_{100} - 2b_{010}g_{001} - 2b_{100}f_{001})\\ &+ \mathrm{G}(-b_{100}c_{001} - 2c_{010}h_{001} + 2c_{010}g_{010} - 2c_{010}f_{100} + b_{001}c_{100} - 2b_{001}g_{001} - 4f_{001}h_{001} - 4f_{001}g_{010} + 4f_{100}f_{001}),\end{aligned}$$

$$\begin{aligned}\nu_9 = 2\mathrm{A}\,&(-c_{100}h_{001} + c_{100}f_{100} - 2g_{010}g_{001}) + 2\mathrm{B}(c_{010}f_{010} - b_{001}c_{010} - 2f_{010}f_{001}) - 4\mathrm{C}c_{010}c_{001} - 2\mathrm{F}(b_{001}c_{001} + c_{001}f_{010} + 2c_{010}f_{001})\\ &+ 2\mathrm{G}(-c_{001}h_{001} - 2c_{001}g_{010} + c_{001}f_{100} - 2c_{010}g_{001}) + 2\mathrm{H}(c_{100}f_{010} - b_{001}c_{100} + c_{010}f_{100} - c_{010}h_{001} - 2f_{010}g_{001} - 2f_{001}g_{010});\end{aligned}$$

$$\alpha_{10} = 6L^2 \{G(2g_{001} - c_{100}) + F(2f_{001} - c_{010}) + Cc_{001}\},$$

$$\beta_{10} = 6L^2 \{H(2g_{001} - c_{100}) + B(2f_{001} - c_{010}) + Fc_{001}\},$$

$$\gamma_{10} = 6L^2 \{A(2g_{001} - c_{100}) + H(2f_{001} - c_{010}) + Gc_{001}\},$$

$$\begin{aligned}\lambda_{10} = {} & 2B(2c_{010}h_{001} - c_{010}f_{100} + c_{010}g_{010} - 4f_{001}h_{001} + 2f_{100}f_{001} - 2f_{001}g_{010}) \\ & + 2A(2a_{001}c_{100} - 4a_{001}g_{001}) + 2C(c_{100}c_{001} - 3c_{001}g_{001}) \\ & + 2F(-2c_{001}h_{001} + c_{001}f_{100} - c_{001}g_{010} + 2c_{100}f_{001} - c_{100}c_{010} + 3g_{001}c_{010} - 6f_{001}g_{001}) \\ & + 2G(-2a_{001}c_{001} + 5c_{100}g_{001} - c^2_{100} - 6g^2_{001}) \\ & + 2H(2c_{100}h_{001} - c_{100}f_{100} + c_{100}g_{010} + 2a_{001}c_{010} \\ & \qquad - 4a_{001}f_{001} - 4g_{001}h_{001} + 2f_{100}g_{001} - 2g_{010}g_{001}),\end{aligned}$$

$$\begin{aligned}\mu_{10} = {} & 2A(2c_{100}h_{001} - c_{100}g_{010} + c_{100}f_{100} - 4g_{001}h_{001} + 2g_{010}g_{001} - 2f_{100}g_{001}) \\ & + 2B(2b_{001}c_{010} - 4b_{001}f_{001}) + 2C(c_{010}c_{001} - 3c_{001}f_{001}) \\ & + 2F(-2b_{001}c_{001} + 5c_{010}f_{001} - c^2_{010} - 6f^2_{001}) \\ & + 2G(-2c_{001}h_{001} + c_{001}g_{010} - c_{001}f_{100} + 2c_{010}g_{001} - c_{100}c_{010} + 3c_{100}f_{001} - 6f_{001}g_{001}) \\ & + 2H(2c_{010}h_{001} - c_{010}g_{010} + c_{010}f_{100} + 2b_{001}c_{100} \\ & \qquad - 4b_{001}g_{001} - 4f_{001}h_{001} + 2f_{001}g_{010} - 2f_{100}f_{001}),\end{aligned}$$

$$\begin{aligned}\nu_{10} = {} & 2A(c^2_{100} - c_{100}g_{001} - 2g^2_{001}) + 2B(c^2_{010} - c_{010}f_{001} - 2f^2_{001}) - 4Cc^2_{001} \\ & + 2F(c_{010}c_{001} - 5c_{001}f_{001}) + 2G(c_{100}c_{001} - 5c_{001}g_{001}) \\ & + 2H(2c_{100}c_{010} - c_{010}g_{001} - c_{100}f_{001} - 4f_{001}g_{001}).\end{aligned}$$

24. Before proceeding to the third set of equations, one substantial simplification is possible. The various quantities that have been obtained are algebraically independent, so far as they occur as solutions of partial differential equations. But there may be intrinsic relations among them owing to the original properties of the quantities which they involve; such intrinsic relations are known to exist among the differential invariants of a surface.

As a matter of fact, *each of the six equations* Θ_1, Θ_2, Θ_3, Θ_4, Θ_5, Θ_6 *is equal to zero*, a result established* by CAYLEY in a somewhat different form. The six equations that thus arise, in the case where the independent variables u, v, w correspond to a triply orthogonal system, are the well known six relations given† by LAMÉ.

As the six quantities Θ_1, Θ_2, Θ_3, Θ_4, Θ_5, Θ_6 are permanently zero, we may use this property to simplify the equations in the next set.

The evanescence of these quantities might have been used earlier, in order to modify some of the preceding expressions; but no substantial advantage would have

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* 'Coll. Math. Papers,' vol. xii., pp. 12, 13.

† A reference is made by CAYLEY, *loc. cit.*, p. 17.

been derived from their use and there would have been the disadvantage that modification of the formal expressions, while changing their original form without any obvious necessity or obvious benefit, removes that form in which they naturally arise.

25. The third set of equations consists of nine numbers. By modifying them in the same way as the corresponding nine equations in § 10, we obtain similar results. Thus with the old notation for the operator Δ_1 but with the extended significance due to the occurrence of derivatives of ϕ of the third order and derivatives of a, b, c, f, g, h of the second order, we find

$$\Delta_1\mathrm{a}'' = 3\mathrm{h}'' + \mathrm{Q}\Theta_3 - 2\mathrm{R}\Theta_4.$$

$$\Delta_1\mathrm{h}'' = 2\mathrm{b}'' + \mathrm{P}\Theta_3 - 2\mathrm{R}\Theta_5.$$

$$\Delta_1\mathrm{b}'' = \mathrm{k}'',$$

$$\Delta_1\mathrm{k}'' = 0,$$

$$\Delta_1\mathrm{g}'' = 2\mathrm{f}'',$$

$$\Delta_1\mathrm{f}'' = \mathrm{l}'',$$

$$\Delta_1\mathrm{l}'' = 0,$$

$$\Delta_1\mathrm{c}'' = \mathrm{m}'' - 2\mathrm{P}\Theta_6 + \mathrm{Q}\Theta_1,$$

$$\Delta_1\mathrm{m}'' = \mathrm{P}\Theta_1,$$

$$\Delta_1\mathrm{n}'' = 0\,;$$

$$\Delta_1\Theta_1 = 0,\quad \Delta_1\Theta_2 = 2\Theta_6,\quad \Delta_1\Theta_3 = 0,\quad \Delta_1\Theta_4 = -\Theta_5,\quad \Delta_1\Theta_5 = 0,\quad \Delta_1\Theta_6 = \Theta_1\,;$$

$$\Delta_1\mathrm{P} = 0,\quad \Delta_1\mathrm{Q} = -\mathrm{P},\quad \Delta_1\mathrm{R} = 0.$$

When we insert in these equations the zero values of the quantities Θ, the first ten of them become

$$\Delta_1\mathrm{a}'' = 3\mathrm{h}'',\qquad \Delta_1\mathrm{g}'' = 2\mathrm{f}'',\qquad \Delta_1\mathrm{c}'' = \mathrm{m}'',\qquad \Delta_1\mathrm{n}'' = 0\,;$$

$$\Delta_1\mathrm{h}'' = 2\mathrm{b}'',\qquad \Delta_1\mathrm{f}'' = \mathrm{l}'',\qquad \Delta_1\mathrm{m}'' = 0,$$

$${}_1\mathrm{b}'' = \mathrm{k}'',\qquad \Delta_1\mathrm{l}'' = 0.$$

$$\Delta_1\mathrm{k}'' = 0,$$

and so for the equations of the other sets.

Proceeding now exactly as in § 16, we find ultimately that the differential invariants involving the quantities a, b, c, f, g, h and their derivatives, as well as the derivatives of ϕ, up to the respective specified orders, are the invariants and contravariants of the simultaneous ternary forms

$$\begin{array}{ll} aX^2 + 2gXZ + cZ^2, & \mathrm{a}X^2 + 2\mathrm{g}XZ + \mathrm{c}Z^2, \\ + 2hXY + 2fYZ & + 2\mathrm{h}XY + 2\mathrm{f}YZ \\ + bY^2 & + \mathrm{b}Y^2 \end{array}$$

$$\begin{array}{l} \mathrm{a}''X^3 + 3\mathrm{g}''X^2Z + 3\mathrm{c}''XZ^2 + \mathrm{n}''Z^3, \\ + 3\mathrm{h}''X^2Y + 6\mathrm{f}''XYZ + 3\mathrm{m}''YZ^2 \\ + 3\mathrm{b}''XY^2 + 3\mathrm{l}''Y^2Z \\ + \mathrm{k}''Y^3 \end{array}$$

the contragradient variables being ϕ_{100}, ϕ_{010}, ϕ_{001}. Let any such differential invariant be homogeneous in ϕ_{100}, ϕ_{010}, ϕ_{001} of degree p; in a, b, c, f, g, h, of degree q; in a, b, c, f, g, h of degree r; in a'', b'', c'', f'', g'', h'', k'', l'', m'', n'' of degree s; then the index μ of the differential invariant is given by

$$3\mu = p + 2q + 8r + 15s.$$

Further, as in § 18, there are five equations out of the set which are satisfied by the differential invariant when it is an invariant of the ternary system, and by the leading coefficient when the differential invariant is a contravariant of the ternary system. These equations are

$$e_1(t) = 0, \quad e_2(t) = 0, \quad e_3(t) = 0, \quad e_4(t) = 0, \quad e_5(t) = 0,$$

where the operators e_1, e_2, e_3, e_4, e_5 are

$$\begin{aligned} e_1 = {} & 2h\frac{\partial}{\partial a} + b\frac{\partial}{\partial h} + f\frac{\partial}{\partial g} \\ & + 2\mathrm{h}\frac{\partial}{\partial \mathrm{a}} + \mathrm{b}\frac{\partial}{\partial \mathrm{h}} + \mathrm{f}\frac{\partial}{\partial \mathrm{g}} \\ & + 3\mathrm{h}''\frac{\partial}{\partial \mathrm{a}''} + 2\mathrm{b}''\frac{\partial}{\partial \mathrm{h}''} + \mathrm{k}''\frac{\partial}{\partial \mathrm{b}''} + 2\mathrm{f}''\frac{\partial}{\partial \mathrm{g}''} + \mathrm{l}''\frac{\partial}{\partial \mathrm{f}''} + \mathrm{m}''\frac{\partial}{\partial \mathrm{c}''}, \end{aligned}$$

$$\begin{aligned} e_2 = {} & 2g\frac{\partial}{\partial a} + c\frac{\partial}{\partial g} + f\frac{\partial}{\partial h} \\ & + 2\mathrm{g}\frac{\partial}{\partial \mathrm{a}} + \mathrm{c}\frac{\partial}{\partial \mathrm{g}} + \mathrm{f}\frac{\partial}{\partial \mathrm{h}} \\ & + 3\mathrm{g}''\frac{\partial}{\partial \mathrm{a}''} + 2\mathrm{c}''\frac{\partial}{\partial \mathrm{g}''} + \mathrm{n}''\frac{\partial}{\partial \mathrm{c}''} + 2\mathrm{f}''\frac{\partial}{\partial \mathrm{h}''} + \mathrm{m}''\frac{\partial}{\partial \mathrm{f}''} + \mathrm{l}''\frac{\partial}{\partial \mathrm{b}''}, \end{aligned}$$

$$\begin{aligned} e_3 = {} & 2f\frac{\partial}{\partial b} + c\frac{\partial}{\partial f} + g\frac{\partial}{\partial h} \\ & + 2\mathrm{f}\frac{\partial}{\partial \mathrm{b}} + \mathrm{c}\frac{\partial}{\partial \mathrm{f}} + \mathrm{g}\frac{\partial}{\partial \mathrm{h}} \\ & + 3\mathrm{l}''\frac{\partial}{\partial \mathrm{k}''} + 2\mathrm{m}''\frac{\partial}{\partial \mathrm{l}''} + \mathrm{n}''\frac{\partial}{\partial \mathrm{m}''} + 2\mathrm{f}''\frac{\partial}{\partial \mathrm{b}''} + \mathrm{c}''\frac{\partial}{\partial \mathrm{f}''} + \mathrm{g}''\frac{\partial}{\partial \mathrm{h}''}, \end{aligned}$$

$$
\begin{aligned}
e_4 = {} & 2f\frac{\partial}{\partial c} + b\frac{\partial}{\partial f} + h\frac{\partial}{\partial g} \\
& + 2\mathrm{f}\frac{\partial}{\partial \mathrm{c}} + \mathrm{b}\frac{\partial}{\partial \mathrm{f}} + \mathrm{h}\frac{\partial}{\partial \mathrm{g}} \\
& + 3\mathrm{m}''\frac{\partial}{\partial \mathrm{n}''} + 2\mathrm{l}''\frac{\partial}{\partial \mathrm{m}''} + \mathrm{k}''\frac{\partial}{\partial \mathrm{l}''} + 2\mathrm{f}''\frac{\partial}{\partial \mathrm{c}''} + \mathrm{b}''\frac{\partial}{\partial \mathrm{f}''} + \mathrm{h}''\frac{\partial}{\partial \mathrm{g}''},
\end{aligned}
$$

$$
\begin{aligned}
e_5 = {} & 2b\frac{\partial}{\partial b} - 2c\frac{\partial}{\partial c} + h\frac{\partial}{\partial h} - g\frac{\partial}{\partial g} \\
& + 2\mathrm{b}\frac{\partial}{\partial \mathrm{b}} - 2\mathrm{c}\frac{\partial}{\partial \mathrm{c}} + \mathrm{h}\frac{\partial}{\partial \mathrm{h}} - \mathrm{g}\frac{\partial}{\partial \mathrm{g}} \\
& + 3\mathrm{k}''\frac{\partial}{\partial \mathrm{k}''} + \mathrm{l}''\frac{\partial}{\partial \mathrm{l}''} - \mathrm{m}''\frac{\partial}{\partial \mathrm{m}''} - 3\mathrm{n}''\frac{\partial}{\partial \mathrm{n}''} + 2\mathrm{b}''\frac{\partial}{\partial \mathrm{b}''} - 2\mathrm{c}''\frac{\partial}{\partial \mathrm{c}''} + \mathrm{h}''\frac{\partial}{\partial \mathrm{h}''} - \mathrm{g}''\frac{\partial}{\partial \mathrm{g}''}.
\end{aligned}
$$

These equations involve 22 arguments; being themselves 5 in number and a complete set, they possess 17 solutions.

Aggregate of Invariants of the Third Order.

26. The asyzygetic aggregate of concomitants of two ternary quadratics and one ternary cubic has not yet been constructed, so far as I am aware; and it therefore is not possible to select from it an algebraically complete aggregate of invariants and contravariants. But the established knowledge of the asyzygetic system of two ternary quadratics* and of the asyzygetic system of the ternary cubic† is sufficient to permit the construction of this algebraically complete aggregate: it is therefore unnecessary to proceed with the formal solution of the preceding five equations.

The most compendious way of expressing the results is to use the customary symbolical notation. We use the umbral symbols adopted in § 17; and, in addition, in connection with the ternary cubic, we introduce umbral symbols $\alpha_1, \alpha_2, \alpha_3$; $\beta_1, \beta_2, \beta_3$; and so on. Then in the usual notation, we can write

$$(a, b, c, f, g, h \between X, Y, Z)^2 = a_x^2 = b_x^2 = \ldots,$$

$$(\mathrm{a}, \mathrm{b}, \mathrm{c}, \mathrm{f}, \mathrm{g}, \mathrm{h} \between X, Y, Z)^2 = a'^2_x = b'^2_x = \ldots,$$

$$(\mathrm{a}'', \mathrm{b}'', \mathrm{c}'', \mathrm{f}'', \mathrm{g}'', \mathrm{h}'', \mathrm{k}'', \mathrm{l}'', \mathrm{m}'', \mathrm{n}'' \between X, Y, Z)^3 = \alpha_x^3 = \beta_x^3 = \ldots.$$

Then an algebraically complete aggregate of invariants and contravariants of the two quadratics and the cubic is constituted by the following seventeen members:

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* See the reference in § 16.

† GORDAN, 'Math. Ann.,' vol. 1 (1869), pp. 90–128; GUNDELFINGER, 'Math. Ann.,' vol. 4 (1871), pp. 144–163; CAYLEY, 'Coll. Math. Papers,' vol. 11, pp. 342–356.

$$
\begin{aligned}
\mathrm{I}_1 &= (abc)^2,\\
\mathrm{I}_2 &= (abu)^2,\\
\mathrm{I}_3 &= (aba')^2,\\
\mathrm{I}_4 &= (aa'u)^2,\\
\mathrm{I}_5 &= (aa'b')^2,\\
\mathrm{I}_6 &= (a'b'u)^2,\\
\mathrm{I}_7 &= (a'b'c')^2,\\
\mathrm{I}_8 &= (\alpha ab)(\beta ab)(\alpha\beta u)^2,\\
\mathrm{I}_9 &= (\alpha aa')(\beta aa')(\alpha\beta u)^2,\\
\mathrm{I}_{10} &= (\alpha a'b')(\beta a'b')(\alpha\beta u)^2,\\
\mathrm{I}_{11} &= (\alpha\beta\gamma)(\alpha\beta u)(\alpha\gamma u)(\beta\gamma u),\\
\mathrm{I}_{12} &= (\alpha\beta\gamma)(\alpha\beta\delta)(\alpha\gamma\delta)(\beta\gamma\delta),\\
\mathrm{I}_{13} &= (\alpha\beta\gamma)(\alpha\beta a)(\alpha\gamma a)(\beta\gamma u),\\
\mathrm{I}_{14} &= (\alpha\beta\gamma)(\alpha\beta a')(\beta\gamma a')(\beta\gamma u),\\
\mathrm{I}_{15} &= (\alpha\beta\gamma)(\alpha\beta\delta)(\alpha\gamma\epsilon)(\beta\gamma u)(\delta\epsilon u)^2,\\
\mathrm{I}_{16} &= (\alpha\beta\gamma)(\alpha\beta\delta)(\alpha\gamma\epsilon)(\beta\gamma\zeta)(\delta\epsilon\zeta)^2,\\
\mathrm{I}_{17} &= (\alpha\beta u)^2(\gamma\delta u)^2(\beta\gamma u)(\alpha\delta u).
\end{aligned}
$$

The first seven of these are the set of seven in § 17, which belong to the system of two quadratics. The next three are obtained, by replacing u_1, u_2, u_3 by $\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \frac{\partial}{\partial x_3}$ respectively, inserting these changes in I_2, I_4, I_6 so as to turn them into operators, and then operating upon the known mixed concomitant $\alpha_x\beta_x(\alpha\beta u)^2$ belonging to the cubic. Of the remainder, I_{11}, I_{12}, I_{15}, I_{16}, I_{17} belong to the system of the cubic; I_{13} and I_{14} are obtained by operating on I_{11} with the symbolical operators

$$\left(a_1\frac{\partial}{\partial u_1} + a_2\frac{\partial}{\partial u_2} + a_3\frac{\partial}{\partial u_3}\right)^2 \quad \text{and} \quad \left(a'_1\frac{\partial}{\partial u_1} + a'_2\frac{\partial}{\partial u_2} + a'_3\frac{\partial}{\partial u_3}\right)^2$$

respectively, or, what is the same thing, by the respective operators

$$a\frac{\partial^2}{\partial u_1^2} + b\frac{\partial^2}{\partial u_2^2} + c\frac{\partial^2}{\partial u_3^2} + 2f\frac{\partial^2}{\partial u_2\,\partial u_3} + 2g\frac{\partial^2}{\partial u_3\,\partial u_1} + 2h\frac{\partial^2}{\partial u_1\,\partial u_2},$$

$$\mathrm{a}\frac{\partial^2}{\partial u_1^2} + \mathrm{b}\frac{\partial^2}{\partial u_2^2} + \mathrm{c}\frac{\partial^2}{\partial u_3^2} + 2\mathrm{f}\frac{\partial^2}{\partial u_2\,\partial u_3} + 2\mathrm{g}\frac{\partial^2}{\partial u_3\,\partial u_1} + 2\mathrm{h}\frac{\partial^2}{\partial u_1\,\partial u_2}.$$

27. All these expressions are given in umbral symbols. Considerable labour might be involved in the process of transforming them so that the changed expressions involve the real symbols; but it is possible to avoid most of this labour by remembering that all the functions are invariants and contravariants of a system of ternary forms, many of which have been calculated and are tabulated in connection with the theory of homogeneous forms. Accordingly, the outline scheme of the real expressions is as follows.

The explicit non-umbral expressions for the first seven of these differential invariants have been given in § 16. The invariant I_{11} is given in explicit form by CAYLEY, who denotes[*] it by PU. The invariant I_{15} is given in explicit form by CAYLEY, who denotes[†] it by QU. The invariant I_{17} is given in explicit form by CAYLEY, who denotes[‡] it by FU. The invariants I_{12} and I_{16} are given in explicit form by CAYLEY, who denotes[§] them by S and T respectively. The invariants I_{13} and I_{14} are obtained by operating on I_{11} with the two operators given at the end of § 26. The actual expression for I_8 is obtained by developing the umbral form: it is found to be

$$\begin{aligned}
\mathrm{I}_8 = \{&A(\mathrm{b''c''} - \mathrm{f''}^2) + B(\mathrm{k''m''} - \mathrm{l''}^2) + C(\mathrm{l''n''} - \mathrm{m''}^2) \\
&+ F(\mathrm{k''n''} - \mathrm{l''m''}) + G(\mathrm{b''n''} + \mathrm{c''l''} - 2\mathrm{f''m''}) + H(\mathrm{b''m''} + \mathrm{c''k''} - 2\mathrm{f''l''})\}u_1^2 \\
+ \{&A(\mathrm{a''c''} - \mathrm{g''}^2) + B(\mathrm{h''m''} - \mathrm{f''}^2) + C(\mathrm{g''n''} - \mathrm{c''}^2) \\
&+ F(\mathrm{h''n''} + \mathrm{g''m''} - 2\mathrm{f''c''}) + G(\mathrm{a''n''} - \mathrm{c''g''}) + H(\mathrm{c''h''} + \mathrm{a''m''} - 2\mathrm{f''g''})\}u_2^2 \\
+ \{&A(\mathrm{a''b''} - \mathrm{h''}^2) + B(\mathrm{h''k''} - \mathrm{b''}^2) + C(\mathrm{g''l''} - \mathrm{f''}^2) \\
&+ F(\mathrm{h''l''} + \mathrm{g''k''} - 2\mathrm{b''f''}) + G(\mathrm{a''l''} + \mathrm{b''g''} - 2\mathrm{f''h''}) + H(\mathrm{a''k''} - \mathrm{b''h''})\}u_3^2 \\
+ 2\{&A(\mathrm{g''h''} - \mathrm{a''f''}) + B(\mathrm{b''f''} - \mathrm{h''l''}) + C(\mathrm{c''f''} - \mathrm{g''m''}) \\
&+ F(\mathrm{f''}^2 + \mathrm{b''c''} - \mathrm{h''m''} - \mathrm{g''l''}) + G(\mathrm{c''h''} - \mathrm{a''m''}) + H(\mathrm{b''g''} - \mathrm{a''l''})\}u_2u_3 \\
+ 2\{&A(\mathrm{f''h''} - \mathrm{b''g''}) + B(\mathrm{b''l''} - \mathrm{f''k''}) + C(\mathrm{m''f''} - \mathrm{c''l''}) \\
&+ F(\mathrm{b''m''} - \mathrm{c''k''}) + G(\mathrm{f''}^2 + \mathrm{h''m''} - \mathrm{l''g''} - \mathrm{b''c''}) + H(\mathrm{l''h''} - \mathrm{g''k''})\}u_3u_1 \\
+ 2\{&A(\mathrm{f''g''} - \mathrm{c''h''}) + B(\mathrm{f''l''} - \mathrm{b''m''}) + C(\mathrm{c''m''} - \mathrm{f''n''}) \\
&+ F(\mathrm{c''l''} - \mathrm{b''n''}) + G(\mathrm{g''m''} - \mathrm{h''n''}) + H(\mathrm{f''}^2 + \mathrm{l''g''} - \mathrm{h''m''} - \mathrm{b''c''})\}u_1u_2.
\end{aligned}$$

---

[*] 'Coll. Math. Papers,' vol. 2, p. 326. It should be mentioned that the quantities $a, b, c, f, g, h, i, j, k, l$ in CAYLEY'S memoir are to be replaced by a″, k″, n″, l″, c″, h″, m″, g″, b″, f″ respectively, that the quantities ξ, η, ζ in CAYLEY'S memoir are to be replaced by u_1, u_2, u_3, and that I_{11} contains a numerical factor 6 which can be rejected.

[†] 'Coll. Math. Papers,' vol. 2, p. 327, with similar modifications and rejection of a numerical factor.

[‡] 'Coll. Math. Papers,' vol. 2, p. 328.

[§] 'Coll. Math. Papers,' vol. 2, p. 325.

The expression of I_9 is obtained by substituting $\mathfrak{A}$, $\mathfrak{B}$, $\mathfrak{C}$, $\mathfrak{F}$, $\mathfrak{G}$, $\mathfrak{H}$ for A, B, C, F, G, H in I_8 throughout; and the expression for I_{10} is obtained similarly by substituting $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$, $\mathbf{F}$, $\mathbf{G}$, $\mathbf{H}$ for A, B, C, F, G, H in I_8 throughout.*

28. All the 17 differential invariants so far given are only relative invariants; it remains to obtain the index of each of them, so as to obtain the absolute invariants. These indices are given by the formula

$$3\mu = p + 2q + 8r + 16s$$

of § 25, and are found to be as follows :—

Index 2, I_1, I_2;
. . 4, I_3, I_4;
. . 6, I_5, I_6;
. . 8, I_7;
. . 12, I_8;
. . 14, I_9;
. . 16, I_{10}, I_{11}, I_{13};
. . 18, I_{14};
. . 20, I_{12};
. . 22, I_{17};
. . 26, I_{15};
. . 30, I_{16}.

Accordingly *there are sixteen algebraically independent absolute differential invariants up to the specified order* in the derivatives of a, b, c, f, g, h and the derivatives of ϕ; and an algebraically complete aggregate of these invariants is provided by the set

$$I_2 I_1^{-1};\ I_3 I_1^{-2},\ I_4 I_1^{-2};\ I_5 I_1^{-3},\ I_6 I_1^{-3};\ I_7 I_1^{-4};\ I_8 I_1^{-6};\ I_9 I_1^{-7};$$
$$I_{10} I_1^{-8},\ I_{11} I_1^{-8},\ I_{13} I_1^{-8};\ I_{14} I_1^{-9};\ I_{12}^{-10};\ I_{17} I_1^{-11};\ I_{15} I_1^{-13};\ I_{16} I_1^{-15}.$$

Geometric Significance of the simpler Invariants.

29. We proceed now to obtain the geometric significance of some of the differential invariants which have been obtained.

The only invariant which is free from derivatives of a, b, c, f, g, h, ϕ, ϕ', ϕ'' is the quantity, denoted sometimes by L^2 and sometimes by Δ_1. We have

$$\Delta_1 = L^2 = abc + 2fgh - af^2 - bg^2 - ch^2;$$

---

* A factor 2 needs to be dropped from I_8 and I_{10} in passing from the symbolical form to the developed form.

and we have already (§ 3) seen that

$$L = \frac{\partial(x, y, z)}{\partial(u, v, w)}.$$

The invariants, which involve the magnitudes a, b, c, f, g, h but none of their derivatives, and which involve derivatives of ϕ, ϕ', ϕ'' of the first order, may be called the differential invariants of the first order.* They are the quantities denoted (§ 19) by Θ_1, $D\Theta_1$, $D^2\Theta_1$, $D'\Theta_1$, $DD'\Theta_1$, $D'^2\Theta_1$, I. In order to give the geometric significance of these invariants, it is necessary to take account of the various directions, through the point x, y, z, as determined by the three surfaces ϕ, ϕ', ϕ''.

It will be convenient (mainly for the sake of brevity) to adopt an alternative notation† for derivatives of x, y, z with regard to u, v, w. We write

$$\frac{\partial x}{\partial u} = x_1, \quad \frac{\partial^2 x}{\partial u^2} = x_{11},$$

$$\frac{\partial x}{\partial v} = x_2, \quad \frac{\partial^2 x}{\partial u\, \partial v} = x_{12}, \quad \frac{\partial^2 x}{\partial v^2} = x_{22},$$

$$\frac{\partial x}{\partial w} = x_3, \quad \frac{\partial^2 x}{\partial u\, \partial w} = x_{13}, \quad \frac{\partial^2 x}{\partial v\, \partial w} = x_{23}, \quad \frac{\partial^2 x}{\partial w^2} = x_{33},$$

and so for derivatives of y and z. Also, following CAYLEY, we take

$$\xi_1, \xi_2, \xi_3, \eta_1, \eta_2, \eta_3, \zeta_1, \zeta_2, \zeta_3,$$

to be the minors of $x_1, x_2, x_3, y_1, y_2, y_3, z_1, z_2, z_3$ respectively in

$$\begin{vmatrix} x_1, & x_2, & x_3 \\ y_1, & y_2, & y_3 \\ z_1, & z_2, & z_3 \end{vmatrix}.$$

We then have

$$\begin{aligned} a &= x_1^2 + y_1^2 + z_1^2, & f &= x_2x_3 + y_2y_3 + z_2z_3, \\ b &= x_2^2 + y_2^2 + z_2^2, & g &= x_3x_1 + y_3y_1 + z_3z_1, \\ c &= x_3^2 + y_3^2 + z_3^2, & h &= x_1x_2 + y_1y_2 + z_1z_2; \end{aligned}$$

$$\begin{aligned} A &= \xi_1^2 + \eta_1^2 + \zeta_1^2, & F &= \xi_2\xi_3 + \eta_2\eta_3 + \zeta_2\zeta_3, \\ B &= \xi_2^2 + \eta_2^2 + \zeta_2^2, & G &= \xi_3\xi_1 + \eta_3\eta_1 + \zeta_3\zeta_1, \\ C &= \xi_3^2 + \eta_3^2 + \zeta_3^2, & H &= \xi_1\xi_2 + \eta_1\eta_2 + \zeta_1\zeta_2. \end{aligned}$$

Let dn denote an element of distance through the point, in a direction normal to the surface $\phi =$ constant, and let

$$\phi(u, v, w) = \Phi(x, y, z).$$

---

* The magnitudes a, b, c, f, g, h, by their definition, involve derivatives of x, y, z of the first order.

† This is CAYLEY'S notation; see note to § 1.

Then

$$\phi_{100} = \Phi_x x_1 + \Phi_y y_1 + \Phi_z z_1,$$
$$\phi_{010} = \Phi_x x_2 + \Phi_y y_2 + \Phi_z z_2,$$
$$\phi_{001} = \Phi_x x_3 + \Phi_y y_3 + \Phi_z z_3.$$

Now

$$\begin{aligned}\Theta &= (\mathrm{A, B, C, F, G, H})(\phi_{100}, \phi_{010}, \phi_{001})^2 \\ &= (\phi_{100}\xi_1 + \phi_{010}\xi_2 + \phi_{001}\xi_3)^2 \\ &\quad + (\phi_{100}\eta_1 + \phi_{010}\eta_2 - \phi_{001}\eta_3)^2 \\ &\quad\quad + (\phi_{100}\zeta_1 + \phi_{010}\zeta_2 + \phi_{001}\zeta_3)^2,\end{aligned}$$

on substituting for A, B, C, F, G, H; when further substitution for ϕ_{100}, ϕ_{010}, ϕ_{001} from above takes place, we have

$$\Theta_1 = (\Phi_x^2 + \Phi_y^2 + \Phi_z^2)\,\mathrm{L}^2.$$

Now

$$\frac{\dfrac{dx}{dn}}{\Phi_x} = \frac{\dfrac{dy}{dn}}{\Phi_y} = \frac{\dfrac{dz}{dn}}{\Phi_z} = \frac{1}{(\Phi_x^2 + \Phi_y^2 + \Phi_z^2)^{\frac{1}{2}}},$$

so that

$$\begin{aligned}\frac{d\phi}{dn} = \frac{d\Phi}{dn} &= \Phi_x \frac{dx}{dn} + \Phi_y \frac{dy}{dn} + \Phi_z \frac{dz}{dn} \\ &= (\Phi_x^2 + \Phi_y^2 + \Phi_z^2)^{\frac{1}{2}};\end{aligned}$$

and therefore

$$\frac{\Theta_1}{\mathrm{L}^2} = \left(\frac{d\phi}{dn}\right)^2.$$

30. Let dn' denote an element of distance through the point in a direction normal to the surface $\phi' =$ constant; and similarly let dn'' denote an element of distance through the point in a direction normal to the surface $\phi'' =$ constant. Also let

$$\phi'(u, v, w) = \Phi'(x, y, z), \quad \phi''(u, v, w) = \Phi''(x, y, z).$$

Then, as

$$2\mathrm{D} = \phi'_{100}\frac{\partial}{\partial\phi_{100}} + \phi'_{010}\frac{\partial}{\partial\phi_{010}} + \phi'_{001}\frac{\partial}{\partial\phi_{001}},$$

$$2\mathrm{D}' = \phi''_{100}\frac{\partial}{\partial\phi_{100}} + \phi''_{010}\frac{\partial}{\partial\phi_{010}} + \phi''_{001}\frac{\partial}{\partial\phi_{001}},$$

we have

$$\begin{aligned}\mathrm{D}\Theta_1 &= (\phi_{100}\xi_1 + \phi_{010}\xi_2 + \phi_{001}\xi_3)(\phi'_{100}\xi_1 + \phi'_{010}\xi_2 + \phi'_{001}\xi_3) \\ &\quad + (\phi_{100}\eta_1 + \phi_{010}\eta_2 + \phi_{001}\eta_3)(\phi'_{100}\eta_1 + \phi'_{010}\eta_2 + \phi'_{001}\eta_3) \\ &\quad + (\phi_{100}\zeta_1 + \phi_{010}\zeta_2 + \phi_{001}\zeta_3)(\phi'_{100}\zeta_1 + \phi'_{010}\zeta_2 + \phi'_{001}\zeta_3) \\ &= \mathrm{L}^2(\Phi_x\Phi'_x + \Phi_y\Phi'_y + \Phi_z\Phi'_z) \\ &= \mathrm{L}^2\frac{d\phi}{dn}\frac{d\phi'}{dn'}\left(\frac{dx}{dn}\frac{dx'}{dn'} + \frac{dy}{dn}\frac{dy'}{dn'} + \frac{dz}{dn}\frac{dz'}{dn'}\right) \\ &= \mathrm{L}^2\frac{d\phi}{dn}\frac{d\phi'}{dn'}\cos\Omega'',\end{aligned}$$

where Ω'' is the angle at which the surfaces intersect at the point, that is, the angle between the normals to the surfaces. Thus

$$\frac{D\Theta_1}{L^2} = \frac{d\phi}{dn}\frac{d\phi'}{dn'}\cos\Omega''.$$

Further, let Ω be the angle at which the two surfaces $\phi' =$ constant, $\phi'' =$ constant, intersect; and let Ω' be the angle at which the two surfaces $\phi =$ constant, $\phi'' =$ constant intersect. Then we have similarly

$$\frac{D^2\Theta_1}{L^2} = \left(\frac{d\phi'}{dn'}\right)^2, \qquad \frac{D'\Theta_1}{L^2} = \frac{d\phi}{dn}\frac{d\phi''}{dn''}\cos\Omega',$$

$$\frac{DD'\Theta_1}{L^2} = \frac{d\phi'}{dn'}\frac{d\phi''}{dn''}\cos\Omega, \qquad \frac{D'^2\Theta_1}{L^2} = \left(\frac{d\phi''}{dn''}\right)^2.$$

31. Again, let ds denote an element of arc through the point along the curve of intersection of the surfaces $\phi' =$ constant, $\phi'' =$ constant; let ds' be a similar element along the intersection of $\phi =$ constant, $\phi'' =$ constant; and let ds'' be a similar element along the intersection of $\phi =$ constant, $\phi' =$ constant. Then

$$\phi'_{100}\frac{du}{ds} + \phi'_{010}\frac{dv}{ds} + \phi'_{001}\frac{dw}{ds} = 0,$$

$$\phi''_{100}\frac{du}{ds} + \phi''_{010}\frac{dv}{ds} + \phi''_{001}\frac{dw}{ds} = 0;$$

and therefore

$$\frac{1}{\theta_1}\frac{du}{ds} = \frac{1}{\theta_2}\frac{dv}{ds} = \frac{1}{\theta_3}\frac{dw}{ds} = \mu,$$

say, where

$$\theta_1, \theta_2, \theta_3 = \begin{Vmatrix} \phi'_{100}, & \phi'_{010}, & \phi'_{001} \\ \phi''_{100}, & \phi''_{010}, & \phi''_{001} \end{Vmatrix}.$$

Now

$$(a, b, c, f, g, h \between du, dv, dw)^2 = ds^2,$$

so that

$$\frac{1}{\mu^2} = (a, b, c, f, g, h \between \theta_1, \theta_2, \theta_3)^2$$

$$= w_2,$$

say. Thus

$$\frac{1}{\theta_1}\frac{du}{ds} = \frac{1}{\theta_2}\frac{dv}{ds} = \frac{1}{\theta_3}\frac{dw}{ds} = \frac{1}{\sqrt{w_2}}.$$

Again, we have

$$\begin{aligned} w_2 &= (a, b, c, f, g, h \between \theta_1, \theta_2, \theta_3)^2 \\ &= (x_1\theta_1 + x_2\theta_2 + x_3\theta_3)^2 + (y_1\theta_1 + y_2\theta_2 + y_3\theta_3)^2 + (z_1\theta_1 + z_2\theta_2 + z_3\theta_3)^2. \end{aligned}$$

But

$$x_1\theta_1+x_2\theta_2+x_3\theta_3=\begin{vmatrix} x_1, & x_2, & x_3 \\ \phi'_{100}, & \phi'_{010}, & \phi'_{001} \\ \phi''_{100}, & \phi''_{010}, & \phi''_{001} \end{vmatrix}$$

$$=\begin{vmatrix} x_1, & x_2, & x_3 \\ \Phi'_x x_1+\Phi'_y y_1+\Phi'_z z_1, & \Phi'_x x_2+\Phi'_y y_2+\Phi'_z z_2, & \Phi'_x x_3+\Phi'_y y_3+\Phi'_z z_3 \\ \Phi''_x x_1+\Phi''_y y_1+\Phi''_z z_1, & \Phi''_x x_2+\Phi''_y y_2+\Phi''_z z_2, & \Phi''_x x_3+\Phi''_y y_3+\Phi''_z z_3 \end{vmatrix}$$

$$=(\Phi'_y\Phi''_z-\Phi'_z\Phi''_y)\,\mathrm{L},$$

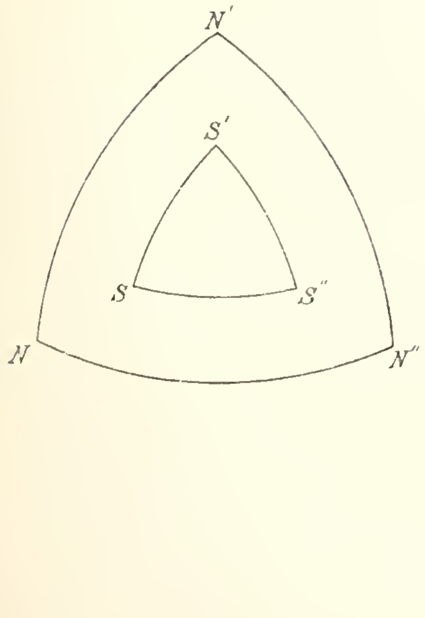
and similarly for $y_1\theta_1+y_2\theta_2+y_3\theta_3$. $z_1\theta_1+z_2\theta_2+z_3\theta_3$; hence

$$w_2=\mathrm{L}^2\{(\Phi'_y\Phi''_z-\Phi'_z\Phi''_y)^2+(\Phi'_z\Phi''_x-\Phi'_x\Phi''_z)^2+(\Phi'_x\Phi''_y-\Phi'_y\Phi''_x)^2\}$$
$$=\mathrm{L}^2\{(\Phi'^2_x+\Phi'^2_y+\Phi'^2_z)(\Phi''^2_x+\Phi''^2_y+\Phi''^2_z)-(\Phi'_x\Phi''_x+\Phi'_y\Phi''_y+\Phi'_z\Phi''_z)^2\}$$
$$=\mathrm{L}^2\left(\frac{d\phi'}{dn'}\right)^2\left(\frac{d\phi''}{dn''}\right)^2\sin^2\Omega.$$

This result is useful for the identification of the invariant I. We have

$$\mathrm{I}=\begin{vmatrix} \phi_{100}, & \phi_{010}, & \phi_{001} \\ \phi'_{100}, & \phi'_{010}, & \phi'_{001} \\ \phi''_{100}, & \phi''_{010}, & \phi''_{001} \end{vmatrix}$$
$$=\theta_1\phi_{100}+\theta_2\phi_{010}+\theta_3\phi_{001}$$
$$=\sqrt{w_2}\left(\phi_{100}\frac{du}{ds}+\phi_{010}\frac{dv}{ds}+\phi_{001}\frac{dw}{ds}\right)$$
$$=\sqrt{w_2}\,\frac{d\phi}{ds}$$
$$=\mathrm{L}\,\frac{d\phi}{ds}\,\frac{d\phi'}{dn'}\,\frac{d\phi''}{dn''}\sin\Omega.$$

This expression can be modified so as to become skew symmetric in the three surfaces. Take a sphere, having its radius unity and its centre at the point; and let the directions ds, ds', ds'', dn, dn', dn'' cut the surface at S, S′, S″, N, N′, N″. Then SS′S″ is the polar triangle of NN′N″; and N′N″ = Ω, N″N = Ω′, NN′ = Ω″. By a known property of such triangles, we have



$$\cos \mathrm{NS}\sin\Omega=\cos \mathrm{N'S'}\sin\Omega'=\cos \mathrm{N''S''}\sin\Omega''$$
$$=(1-\cos^2\Omega-\cos^2\Omega'-\cos^2\Omega''+2\cos\Omega\cos\Omega'\cos\Omega'')^{\frac{1}{2}}$$
$$=\nabla,$$

say. Now

$$dn = \cos \mathrm{SN} \,.\, ds,$$

so that

$$\frac{d\phi}{ds} = \frac{d\phi}{dn} \cos \mathrm{SN}.$$

Hence

$$\mathrm{I} = \mathrm{L} \frac{d\phi}{dn} \frac{d\phi'}{dn'} \frac{d\phi''}{dn''} \cos \mathrm{SN} \sin \Omega$$

$$= \mathrm{L}\nabla \frac{d\phi}{dn} \frac{d\phi'}{dn'} \frac{d\phi''}{dn''},$$

the skew symmetric expression required.

It is easy to verify that the values obtained for the invariants satisfy the relation in § 19.

Significance of the Invariants of the Second Order.

32. Passing now to the differential invariants of the second order associated with a single surface, we shall adopt another method of identifying them geometrically. The functions are invariantive through all changes of the independent variables and therefore possess the value given by any particular selection of variables. Now one simple transformation of the variables is that which makes x, y, z respectively equal to the independent variables, so that we take

$$x = u, \quad y = v, \quad z = w.$$

With these values, we have

$$a = 1, \quad b = 1, \quad c = 1, \quad f = 0, \quad g = 0, \quad h = 0;$$

$$\mathrm{A} = 1, \quad \mathrm{B} = 1, \quad \mathrm{C} = 1, \quad \mathrm{F} = 0, \quad \mathrm{G} = 0, \quad \mathrm{H} = 0;$$

$$\mathrm{L}^2 = 1,$$

and

$$\phi_{lmn} = \frac{\partial^{l+m+n}\phi}{\partial x^l \, \partial y^m \, \partial z^n}.$$

Also

$$\mathrm{a} = 2\phi_{200} = 2\phi_{xx}, \quad \mathrm{f} = 2\phi_{011} = 2\phi_{yz},$$

$$\mathrm{b} = 2\phi_{020} = 2\phi_{yy}, \quad \mathrm{g} = 2\phi_{101} = 2\phi_{xz},$$

$$\mathrm{c} = 2\phi_{002} = 2\phi_{zz}, \quad \mathrm{h} = 2\phi_{110} = 2\phi_{xy}.$$

Hence

$$\frac{\Theta_1}{\Delta_1} = \phi_x^2 + \phi_y^2 + \phi_z^2,$$

$$\tfrac{1}{2} \frac{\Theta_{12}}{\Delta_1^2} = (\phi_{yy} + \phi_{zz}) \phi_x^2 + (\phi_{zz} + \phi_{xx}) \phi_y^2 + (\phi_{xx} + \phi_{yy}) \phi_z^2$$
$$- 2\phi_x\phi_y\phi_{xy} - 2\phi_x\phi_z\phi_{xz} - 2\phi_y\phi_z\phi_{yz},$$

$$\tfrac{1}{2} \frac{\Delta_{12}}{\Delta_1^2} = \phi_{xx} + \phi_{yy} + \phi_{zz},$$

$$\tfrac{1}{4}\frac{\Theta_2}{\Delta_1^{\,3}} = -\begin{vmatrix} \phi_{xx}, & \phi_{xy}, & \phi_{xz}, & \phi_x \\ \phi_{xy}, & \phi_{yy}, & \phi_{zy}, & \phi_y \\ \phi_{xz}, & \phi_{yz}, & \phi_{zz}, & \phi_z \\ \phi_x, & \phi_y, & \phi_z, & 0 \end{vmatrix}$$

$$= (\phi_{yy}\phi_{zz} - \phi_{yz}^{\,2})\,\phi_x^{\,2} + \ldots$$

$$\tfrac{1}{4}\frac{\Delta_{21}}{\Delta_1^{\,3}} = \phi_{yy}\phi_{zz} - \phi_{yz}^{\,2} + \phi_{zz}\phi_{xx} - \phi_{zx}^{\,2} + \phi_{xx}\phi_{yy} - \phi_{xy}^{\,2},$$

$$\tfrac{1}{8}\frac{\Delta_2}{\Delta_1^{\,4}} = \begin{vmatrix} \phi_{xx}, & \phi_{xy}, & \phi_{xz} \\ \phi_{xy}, & \phi_{yy}, & \phi_{yz} \\ \phi_{xz}, & \phi_{yz}, & \phi_{zz} \end{vmatrix}.$$

As usual, let R_1 and R_2 be the principal radii of curvature of the surface $\phi =$ constant; and let

$$\sigma = \frac{1}{R}(\phi_x^{\,2} + \phi_y^{\,2} + \phi_z^{\,2})^{\frac{1}{2}},$$

for the radii $R_1 = R$, and $R_2 = R$. Then* the two values of σ are given by the equation

$$\begin{vmatrix} \phi_{xx} - \sigma, & \phi_{xy}, & \phi_{xz}, & \phi_x \\ \phi_{xy}, & \phi_{yy} - \sigma, & \phi_{yz}, & \phi_y \\ \phi_{xz}, & \phi_{yz}, & \phi_{zz} - \sigma, & \phi_z \\ \phi_x, & \phi_y, & \phi_z, & 0 \end{vmatrix} = 0;$$

and therefore

$$\sigma_1\sigma_2 = \frac{(\phi_{yy}\phi_{zz} - \phi_{yz}^{\,2})\,\phi_x^{\,2} + \ldots}{\phi_x^{\,2} + \phi_y^{\,2} + \phi_z^{\,2}}$$

$$\sigma_1 + \sigma_2 = \frac{(\phi_{yy} + \phi_{zz})\,\phi_x^{\,2} + \ldots - 2\phi_x\phi_y\phi_{xy} - \ldots}{\phi_x^{\,2} + \phi_y^{\,2} + \phi_z^{\,2}}.$$

Consequently

$$\frac{\Theta_2}{4\Theta_1\Delta_1^{\,2}} = \sigma_1\sigma_2 = \frac{\phi_x^{\,2} + \phi_y^{\,2} + \phi_z^{\,2}}{\rho_1\rho_2}$$

$$= \frac{\Theta_1}{\Delta_1}\,\frac{1}{R_1R_2};$$

and therefore

$$\frac{\Theta_2}{\Delta_1^{\,3}} = 4\,\frac{\Theta_1^{\,2}}{\Delta_1^{\,2}}\,\frac{1}{R_1R_2}$$

$$= \frac{4}{R_1R_2}\left(\frac{d\phi}{dn}\right)^4.$$

---

* FROST, 'Solid Geometry,' p. 293

Similarly

$$\frac{\Theta_{12}}{2\Theta_1\Delta_1} = \sigma_1 + \sigma_2$$

$$= \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\left(\frac{\Theta_1}{\Delta_1}\right)^{\frac{1}{2}};$$

and therefore

$$\frac{\Theta_{12}}{\Delta_1^{\,2}} = 2\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\left(\frac{\Theta_1}{\Delta_1}\right)^{\frac{3}{2}}$$

$$= 2\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\left(\frac{d\phi}{dn}\right)^3.$$

Again, we have

$$\frac{d}{dn} = \frac{\phi_x\dfrac{\partial}{\partial x} + \phi_y\dfrac{\partial}{\partial y} + \phi_z\dfrac{\partial}{\partial z}}{(\phi_x^{\,2} + \phi_y^{\,2} + \phi_z^{\,2})^{\frac{1}{2}}},$$

so that

$$\frac{d\phi}{dn} = (\phi_x^{\,2} + \phi_y^{\,2} + \phi_z^{\,2})^{\frac{1}{2}},$$

and therefore

$$\frac{d^2\phi}{dn^2} = \frac{\phi_{xx}\phi_x^{\,2} + 2\phi_{xy}\phi_x\phi_y + 2\phi_{xz}\phi_x\phi_z + \phi_{yy}\phi_y^{\,2} + 2\phi_{yz}\phi_y\phi_z + \phi_{zz}\phi_z^{\,2}}{\phi_x^{\,2} + \phi_y^{\,2} + \phi_z^{\,2}}.$$

Hence

$$\frac{\Theta_1}{\Delta_1}\frac{d^2\phi}{dn^2} = \tfrac{1}{2}\frac{\Delta_{12}}{\Delta_1^{\,2}}\frac{\Theta_1}{\Delta_1} - \tfrac{1}{2}\frac{\Theta_{12}}{\Delta_1^{\,2}},$$

that is,

$$\left(\frac{d\phi}{dn}\right)^2\frac{d^2\phi}{dn^2} = \tfrac{1}{2}\frac{\Delta_{12}}{\Delta_1^{\,2}}\left(\frac{d\phi}{dn}\right)^2 - \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\left(\frac{d\phi}{dn}\right)^3,$$

and therefore

$$\frac{\Delta_{12}}{\Delta_1^{\,2}} = 2\frac{d^2\phi}{dn^2} + 2\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\frac{d\phi}{dn}.$$

33. Let U, V, W denote ϕ_{100}, ϕ_{010}, ϕ_{001} respectively; then the directions of the lines of curvature, through the point x, y, z on the surface $\phi =$ constant, are given by the equations

$$\begin{vmatrix} dU, & U, & dx \\ dV, & V, & dy \\ dW, & W, & dz \end{vmatrix} = 0,$$

$$U\,dx + V\,dy + W\,dz = 0.$$

Let l, m, n denote the direction-cosines of either line; then

$$\begin{vmatrix} al + hm + gn, & U, & l \\ hl + bm + fn, & V, & m \\ gl + fm + cn, & W, & n \end{vmatrix} = 0,$$

$$Ul + Vm + Wn = 0.$$

The former of these can be replaced by the three equations

$$\left.\begin{aligned} \mathrm{a}l + \mathrm{h}m + \mathrm{g}n &= \rho \mathrm{U} + \sigma l \\ \mathrm{h}l + \mathrm{b}m + \mathrm{f}n &= \rho \mathrm{V} + \sigma m \\ \mathrm{g}l + \mathrm{f}m + \mathrm{c}n &= \rho \mathrm{W} + \sigma n \end{aligned}\right\} ;$$

and we also have

$$l^2 + m^2 + n^2 = 1.$$

Let ds be an element of arc of a line of curvature; then

$$\begin{aligned} \frac{d}{ds}\left(\frac{d\phi}{dn}\right) &= \left(l\frac{\partial}{\partial x} + m\frac{\partial}{\partial y} + n\frac{\partial}{\partial z}\right)\frac{\partial\phi}{\partial n} \\ &= \left(l\frac{\partial}{\partial x} + m\frac{\partial}{\partial y} + n\frac{\partial}{\partial z}\right)(\phi_x^2 + \phi_y^2 + \phi_z^2)^{\frac{1}{2}} \\ &= \frac{l(\mathrm{Ua} + \mathrm{Vh} + \mathrm{Wg}) + m(\mathrm{Uh} + \mathrm{Vb} + \mathrm{Wf}) + n(\mathrm{Ug} + \mathrm{Vf} + \mathrm{Wc})}{2(\mathrm{U}^2 + \mathrm{V}^2 + \mathrm{W}^2)^{\frac{1}{2}}}. \end{aligned}$$

Multiplying the foregoing three equations by U, V, W and adding, we have

$$\rho(\mathrm{U}^2 + \mathrm{V}^2 + \mathrm{W}^2) = 2(\mathrm{U}^2 + \mathrm{V}^2 + \mathrm{W}^2)^{\frac{1}{2}}\frac{d}{ds}\left(\frac{d\phi}{dn}\right),$$

that is,

$$\rho\frac{d\phi}{dn} = 2\frac{d}{ds}\left(\frac{d\phi}{dn}\right) = 2\mathrm{S},$$

say. Multiplying the same three equations by l, m, n and adding, we have

$$\begin{aligned} \sigma &= \mathrm{a}l^2 + 2\mathrm{h}lm + 2\mathrm{g}ln + \mathrm{b}m^2 + 2\mathrm{f}mn + \mathrm{c}n^2 \\ &= \frac{2}{\mathrm{R}}\frac{\partial\phi}{\partial n}, \end{aligned}$$

where R is the radius of curvature of the principal normal section at the point.* Thus ρ and σ can be regarded as known.

Again, solving the three equations for l, m, n, we obtain three results of the form

$$\begin{vmatrix} \mathrm{a} - \sigma, & \mathrm{h}\ , & \mathrm{g} \\ \mathrm{h}\ , & \mathrm{b} - \sigma, & \mathrm{f} \\ \mathrm{g}\ , & \mathrm{f}\ , & \mathrm{c} - \sigma \end{vmatrix} l = \rho \begin{vmatrix} \mathrm{U}, & \mathrm{h}\ , & \mathrm{g} \\ \mathrm{V}, & \mathrm{b} - \sigma, & \mathrm{f} \\ \mathrm{W}, & \mathrm{f}\ , & \mathrm{c} - \sigma \end{vmatrix}.$$

When these are substituted in $l^2 + m^2 + n^2 = 1$, we have

$$\begin{vmatrix} \mathrm{a} - \sigma, & \mathrm{h}\ , & \mathrm{g} \\ \mathrm{h}\ , & \mathrm{b} - \sigma, & \mathrm{f} \\ \mathrm{g}\ , & \mathrm{f}\ , & \mathrm{c} - \sigma \end{vmatrix}^2 = \rho^2\Phi,$$

---

* Frost, 'Solid Geometry,' p. 290.

where, after some reduction, Φ is found to be given by

$$\Phi = \sigma^4 \frac{\Theta_1}{\Delta_1} - 2\sigma^3 \frac{\Theta_{12}}{\Delta_1^{\,2}} + \sigma^2 \left(\frac{\Delta_{12}\Theta_{12}}{\Delta_1^{\,4}} - \frac{\Delta_{21}\Theta_1}{\Delta_1^{\,4}} + 3\,\frac{\Theta_2}{\Delta_1^{\,3}} \right)$$

$$- 2\sigma \frac{\Theta_2\Delta_{12} - \Delta_2\Theta_1}{\Delta_1^{\,5}} + \frac{\Theta_2\Delta_{21} - \Delta_2\Theta_{12}}{\Delta_1^{\,6}} .$$

Moreover

$$\begin{vmatrix} a - \sigma, & h\ , & g \\ h\ , & b - \sigma, & f \\ g\ , & f\ , & c - \sigma \end{vmatrix} = \frac{\Delta_2}{\Delta_1^{\,4}} - \frac{\Delta_{21}}{\Delta_1^{\,3}}\,\sigma + \frac{\Delta_{12}}{\Delta_1^{\,2}}\,\sigma^2 - \sigma^3 ;$$

consequently

$$\frac{1}{\rho^2}\left(\frac{\Delta_2}{\Delta_1^{\,4}} - \frac{\Delta_{21}}{\Delta_1^{\,3}}\,\sigma + \frac{\Delta_{12}}{\Delta_1^{\,2}}\,\sigma^2 - \sigma^3 \right)^2$$

$$= \sigma^4 \frac{\Theta_1}{\Delta_1} - 2\sigma^3 \frac{\Theta_{12}}{\Delta_1^{\,2}} + \frac{\sigma^2}{\Delta_1^{\,4}} (\Delta_{12}\Theta_{12} - \Delta_{21}\Theta_1 + 3\Delta_1\Theta_2)$$

$$- \frac{2\sigma}{\Delta_1^{\,5}} (\Theta_2\Delta_{12} - \Delta_2\Theta_1) + \frac{1}{\Delta_1^{\,6}} (\Theta_2\Delta_{21} - \Delta_2\Theta_{12}).$$

When $\sigma = \sigma_1$, we may take

$$\rho = \rho_1 = \frac{2S_1}{\dfrac{d\phi}{dn}} = \frac{2}{\dfrac{d\phi}{dn}} \frac{d}{ds_1} \left(\frac{d\phi}{dn} \right);$$

when $\sigma = \sigma_2$, we may take

$$\rho = \rho_2 = \frac{2S_2}{\dfrac{d\phi}{dn}} = \frac{2}{\dfrac{d\phi}{dn}} \frac{d}{ds_2} \left(\frac{d\phi}{dn} \right).$$

The two equations which thus arise by taking $\sigma = \sigma_1$, and $\sigma = \sigma_2$, when combined symmetrically and rationally, may be regarded as two equations defining Δ_{21} and Δ_2 algebraically in terms of the quantities $\dfrac{d}{ds_1}\left(\dfrac{d\phi}{dn}\right)$ and $\dfrac{d}{ds_2}\left(\dfrac{d\phi}{dn}\right)$.

34. The geometric significance of most, if not all, the differential invariants of the second order, which occur (§ 21) in the algebraic aggregate when two surfaces are given, can be obtained by noting the properties for the second surface corresponding to those discussed for the first surface; they will not be considered further in this memoir.

Nor is it my intention in this place to discuss the geometric significance of the sixteen members of the algebraic aggregate of differential invariants up to the third order inclusive which occur (§ 28) when there is only a single surface. But one remark may be made. Out of the aggregate of sixteen, six already have been identified; they are invariants of order less than three, so that there remains the identification of the ten invariants which actually involve quantities of the third order. Let H and K denote the mean curvature and the specific curvature respectively of the surface $\phi =$ constant, so that

$$\mathrm{H} = \frac{1}{\mathrm{R}_1} + \frac{1}{\mathrm{R}_2}, \qquad \mathrm{K} = \frac{1}{\mathrm{R}_1 \mathrm{R}_2}.$$

Then the geometrical magnitudes available for the identification of the invariants are

$$\begin{array}{ccc}
\dfrac{d\mathrm{H}}{dn}, & \dfrac{d\mathrm{H}}{ds_1}, & \dfrac{d\mathrm{H}}{ds_2}, \\[2ex]
\dfrac{d\mathrm{K}}{dn}, & \dfrac{d\mathrm{K}}{ds_1}, & \dfrac{d\mathrm{K}}{ds_2}, \\[2ex]
\dfrac{d^3\phi}{dn^3}, & \dfrac{d}{ds_1}\left(\dfrac{d^2\phi}{dn^2}\right); & \dfrac{d}{ds_2}\left(\dfrac{d^2\phi}{dn^2}\right), \\[2ex]
\dfrac{d^2}{ds_1^{\,2}}\left(\dfrac{d\phi}{dn}\right), & \dfrac{d^2}{ds_1\, ds_2}\left(\dfrac{d\phi}{dn}\right), & \dfrac{d^2}{ds_2^{\,2}}\left(\dfrac{d\phi}{dn}\right),
\end{array}$$

being twelve in number. Accordingly, it is to be expected that, among these quantities and the quantities already used, which are

$$\mathrm{H}, \quad \mathrm{K}, \quad \frac{d\phi}{dn}, \quad \frac{d^2\phi}{dn^2}, \quad \frac{d}{ds_1}\left(\frac{d\phi}{dn}\right), \quad \frac{d}{ds_2}\left(\frac{d\phi}{dn}\right),$$

two algebraical relations exist.

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WITH

A DISCUSSION OF CERTAIN PHENOMENA IN THE ABSOLUTE OBSERVATIONS

BY

CHARLES CHREE, Sc.D., LL.D., F.R.S.,
SUPERINTENDENT OF THE OBSERVATORY DEPARTMENT OF THE NATIONAL PHYSICAL LABORATORY.

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IX. *An Analysis of the Results from the Kew Magnetographs on "Quiet" Days during the Eleven Years* 1890 *to* 1900, *with a Discussion of Certain Phenomena in the Absolute Observations.*

By CHARLES CHREE, *Sc.D., LL.D., F.R.S., Superintendent of the Observatory Department of the National Physical Laboratory.*

(*From the National Physical Laboratory.*)

Received May 1,—Read May 28, 1903.

CONTENTS.

§ 1. IN 1889 the then Kew Committee agreed to take part in a scheme which provided that at the end of each year the Astronomer Royal should select five magnetically *quiet* days for each month with a view to the tabulation of their records. The scheme has been in continuous operation since 1890, and the results from the selected quiet days have been published annually in the 'Report' made to the Royal Society.

In 1895 I contributed to the British Association 'Report' an analysis of the declination and horizontal force records for the years 1890 to 1894, and described the previously unnoticed "non-cyclic effects" which appear to be characteristic of magnetically quiet days at Kew and elsewhere. In 1901 the development of electric traction in the West of London rendered it clear that no further records at Kew would be free from suspicion of artificial disturbances, and that it would be necessary in the near future to make arrangements for continuing the magnetic work elsewhere. Both contingencies pointed to the expediency of a complete discussion of the data obtained from 1890 to 1900, which I accordingly commenced. The delay in the execution of the scheme is largely due to the occurrence of various unforeseen difficulties, which have, however, I think been at last fairly satisfactorily surmounted. The object of the paper is not so much to put observations on record, as to make a critical use of them. The data used are mainly derived from old Kew 'Reports,' to which reference must be made for particulars.

§ 2. One of the questions dealt with is the relation between sun-spots and terrestrial magnetism. The sun-spot data made use of are from the very important table published by WOLFER in the 'Met. Zeit.'* WOLFER's table gives the mean monthly values assigned to the sun-spot frequency by WOLF and WOLFER for a very long series of years. As frequent reference has to be made to sun-spot data throughout the whole of this paper, it is convenient to reproduce at once that part of WOLFER's table which applies to the period 1890 to 1900 now under review. This will be found in Table I. In addition to WOLFER's own figures I give the mean sun-spot frequency obtained for each month of the year when we combine the 11 years 1890 to 1900.

It will be noticed that the four years 1892 to 1895 are conspicuously years of sun-spot maximum, while 1890, 1899, and 1900 are years of very few sun-spots. The mean frequency for the 12 months commencing August, 1893, and ending July, 1894, is higher than for any other 12 successive months in the 11-year period. Considering that so many as 11 years are included, the irregularity in the mean values for the several months of the year is rather surprising. March and November in particular show a remarkably low mean frequency. This is to be regretted, as it introduces a certain element of uncertainty into some of the calculations made in the latter part of the paper.

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* May, 1902, p. 193, *et seq.*

TABLE I.—Sun-Spot Frequency (after WOLFER).

	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.	Means for each month of the year.
January .	5·3	13·5	69·1	75·0	83·2	63·3	29·0	40·6	30·2	19·5	9·4	39·8
February .	0·6	22·2	75·6	73·0	84·6	67·2	57·4	29·4	36·4	9·2	13·6	42·65
March . .	5·1	10·4	49·9	65·7	52·3	61·0	52·0	29·1	38·3	18·1	8·6	35·5
April . .	1·6	20·5	69·6	88·1	81·6	76·9	43·8	31·0	14·5	14·2	16·0	41·6
May . .	4·8	41·1	79·6	84·7	101·2	67·5	27·7	20·0	25·8	7·7	15·2	43·2
June . .	1·3	48·3	76·3	88·2	98·9	71·5	49·0	11·3	22·3	20·5	12·1	45·4
July . .	11·6	58·8	76·8	88·8	106·0	47·8	45·0	27·6	9·0	13·5	8·3	44·8
August .	8·5	33·2	101·4	129·2	70·3	68·9	27·2	21·8	31·4	2·9	4·3	45·4
September	17·2	53·8	62·8	77·9	65·9	57·7	61·3	48·1	34·8	8·4	8·3	45·1
October .	11·2	51·5	70·5	79·7	75·5	67·9	28·4	14·3	34·4	13·0	12·9	41·75
November	9·6	41·9	65·4	75·1	56·6	47·2	38·0	8·4	30·9	7·8	4·5	35·0
December.	7·8	32·2	78·6	93·8	60·0	70·7	42·6	33·3	12·6	10·5	0·3	40·2
Means for individual years . .	7·1	35·6	73·0	84·9	78·0	64·0	41·8	26·2	26·7	12·1	9·5	41·72

Secular Change.

§ 3. Few people at all appreciate the difficulty of arriving at anything approaching certainty as to the true value of the secular change of magnetic elements from one year to the next. An examination of the published records of any two observatories, at such moderate distances apart as Potsdam and Parc St. Maur (Paris), or even when so close together as Kew and Greenwich, discloses irregularities which are not shared by the two stations. In the present state of our knowledge, we can only say that such irregularities *may* be absolutely faithful representations of the operations of Nature, but personally I am inclined to the belief that they often owe a good deal to instrumental or similar causes. Building operations, changes of instruments, of observers, or of methods of reduction, are all apt to influence observational results, and of late years electric trams have been wrecking observatories, or introducing uncertainties into their records, all over the world. In the present case, this last and worst cause of uncertainty may be left out of account, but some of the others had, unfortunately, to be dealt with. Whenever it appeared necessary, I have referred to the original records, and have calculated so far as possible what the results would have been if the methods and instruments employed had been the same as of late years. To explain the situation, a brief account is necessary of the present method of deducing results from the measurement of the curves. To economise space, I shall throughout the rest of the paper distinguish the several magnetic elements by letters, and employ these, when convenient, in the text and tables. The letters so employed and their meanings are as follows:—

D = declination,
I = inclination,
H = horizontal force,
V = vertical force,
N = northerly component of H.
W = westerly " "
T = total force (resultant of H and V, or of N, W and V).

§ 4. Taking first the case of D, as simplest, we have the scale value—that is the equivalent of 1 centim. of curve ordinate—dependent only on the distance between the photographic paper and the mirror carried by the declination magnet. There is no occasion to move this mirror except slightly in azimuth, as the magnet turns with secular change, and no appreciable change of scale value has occurred during the period dealt with. In this case no temperature compensation is necessary, so far as is known; and the scale value being determined once for all, there remains only to determine the value of the declination which answers to the base (or time) line, from which ordinates are measured. This is done by comparing the results of the absolute observations, taken usually three or four times a month, with the corresponding curve ordinates; each month is dealt with by itself. With the exception of a few months early in 1890, the same magnet has been used throughout for the absolute observations, and an elaborate intercomparison of it with the magnet previously accepted as the standard, before the latter was laid aside, gave mean results as nearly as possible identical. The magnetometer employed has been in use for about half a century. Certain additions were made to it in January, 1891, but were discarded after a few weeks' trial, and the results obtained with it during these weeks were rejected.

Coming next to H, the scale value here is affected by change either in the magnetograph magnet itself or in its bifilar suspension. During the whole eleven years the aim has been to keep the scale value at 1 centim. $= 50\gamma$ (where $1\gamma \equiv 1 \times 10^{-5}$ C.G.S. unit). The magnet is an old one, whose moment alters extremely slowly, and when the instrument is left to itself, the change of scale value taking place in twelve months seldom amounts to 1 per cent. As in the case of D, the value of the base line is determined by comparing absolute values of H, determined three or four times a month, with the corresponding curve ordinates, and each month is treated independently. A temperature correction is applied, which allows for the difference between the temperature of the magnetograph room at the hour considered and at the times of the absolute determinations of H in the month in question. The temperature coefficient of the H magnetograph is very small, and the correction comparatively unimportant.

The procedure in the case of V and I is less direct. Here the absolute observation gives I, while the curve gives V. The value of 1 centim. of ordinate is found as in the case of H by direct experiment, and the instrument is adjusted—usually once a year—so as to keep the sensitiveness as close as possible to 1 centim. $= 50\gamma$. Three or four absolute observations of I are made each month, usually on the days of the observations of H. The H observation is corrected to the time of the corresponding

I observation, by allowing for any change of curve ordinate and for any change of magnetograph room temperature that may have occurred meantime. Combining the observed values of I and of H, as corrected, one obtains an absolute value for V, and so can institute a comparison with the V curve and determine the value of its base line.

The hourly values of inclination are obtained by combining corresponding hourly values of H and V as given by the curves. The same inclinometer has been in use throughout the eleven years. The needles originally employed were damaged in 1899 and had to be replaced. The needles then introduced had been previously compared with the discarded pair, and no appreciable difference was detected.

§ 5. The methods of reduction just described had not been strictly adhered to in some of the earlier years. For instance, no satisfactory allowance had been made prior to 1894 for change in H between the hours of the H and I observations. This had the effect of depressing the values of V and I by something like 30γ and $1'$ respectively. Trouble also arose from an addition made to the Observatory building in 1892, introducing various discontinuities into the curves, which had not been altogether successfully dealt with at the time. Reference to the original records, however, enabled these defects to be removed fairly satisfactorily, and when this was done the more striking irregularities apparent in the secular changes of V and I between 1890 and 1894 mainly disappeared. There still remained rather a prominent discontinuity in the values for 1896. On examining into the matter, I found that in March, 1896, an old weak pair of bar magnets used for stroking the dip needles had been replaced by a much stronger pair. The secular change obtained by comparing the results for the six months immediately following the introduction of the new bar magnets with the results for the corresponding six months of the previous year amounted to only $1'$, whereas by comparing results from the six months immediately preceding the change with the results from the corresponding months of the previous year, and by comparing results from the six months immediately following the change with the results from the corresponding months of the subsequent year, one got values for the secular change which were in good agreement and averaged $2'\cdot8$. This seemed to point pretty conclusively to a sudden discontinuity amounting to about $1'\cdot8$, and simultaneous to all appearance with the introduction of the new bar magnets. For our present purpose it is immaterial whether the cause of this discontinuity was the introduction of the new bar magnets, or something else occurring approximately at the same time, so long as it is admitted that it is legitimate to apply a correction of the amount $1'\cdot8$ indicated above. One's approval of any such correction must largely depend on one's estimate of the knowledge and judgment of the person who decides to apply it. It may be added, however, as evidence in its favour that it wiped out discontinuities in the 1896 values alike of V, I, and T. The consequence of the several corrections introduced was to alter the mean annual values of the elements as published in the annual 'Reports' to the following extent :—

Year	1890.	1891.	1892.	1893.	1894.	1895.	1896.
H	-4γ	—	$+2\gamma$	—	—	—	—
V	—	$+72\gamma$	$+93\gamma$	$+96\gamma$	$+57\gamma$	$+57\gamma$	$+13\gamma$
I	—	$+2'\cdot0$	$+2'\cdot6$	$+2'\cdot7$	$+1'\cdot6$	$+1'\cdot6$	$+0'\cdot4$

So far as can be judged, no correction is necessary for personal equation in the observations. During the whole period dealt with, the magnetic work has been under the charge of the Chief Assistant, Mr. T. W. BAKER, who has himself observed on the great majority of occasions. During 1891 to 1893 Mr. R. S. WHIPPLE observed pretty frequently, and since then, during Mr. BAKER'S holidays, the horizontal force observations have been mainly taken by myself, and the declination and inclination observations by Mr. W. BOXALL. No certain difference has, however, manifested itself between the several observers.

§ 6. The mean annual values of the elements as corrected are given in Table II., and the corresponding secular changes appear in Table III. The values of N, W, and T were calculated from those of D, H, and I by the formulæ

$$N = H\cos D, \qquad W = H\sin D, \qquad T = H\sec I.$$

The action of the vertical-force magnetograph during the last two or three months of 1890 was not considered satisfactory at the time, and the corresponding results were discarded. Thus 1891 was the first year for which satisfactory mean annual values were obtainable for V and I. The mean values at the foot of Table II. are thus calculated for 10 years only in the case of V, T, and I, as against 11 years in the other cases. These mean values are wanted later, they do not possess any immediate significance in connection with secular change.

In Table III. I have added mean values of the secular changes at Parc St. Maur and Potsdam, for comparison with the mean changes at Kew. The Parc St. Maur data are from publications by MOUREAUX.* As data for 1900 were not available the means in this case are for the period 1890 to 1899 for D and H, and the period 1891 to 1899 for I and V. The Potsdam data are from a paper by ESCHENHAGEN;† they refer to exactly the same periods as the corresponding Kew data.

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* 'Ann. du Bureau Central Météorologique de France,' 1897, "Mémoires," p. B. 65.

† 'Ann. der Physik,' vol. 6, 1901, p. 424.

Table II.—Mean Annual Values.

Year.	D.	I.	H.	W.	N.	V.	T.
1890	17° 50′·6	° ′ —	·18169	·05567	·17295	—	—
1891	17 41·9	67 33·2	·18193	·05531	·17332	·44034	·47648
1892	17 36·7	67 32·0	·18204	·05508	·17351	·44012	·47636
1893	17 28·8	67 29·0	·18238	·05478	·17396	·43992	·47625
1894	17 23·0	67 27·6	·18251	·05453	·17417	·43971	·47612
1895	17 16·8	67 25·4	·18278	·05429	·17453	·43958	·47608
1896	17 10·8	67 22·7	·18309	·05408	·17492	·43937	·47600
1897	17 6·4	67 19·6	·18342	·05395	·17532	·43906	·47583
1898	17 1·4	67 17·6	·18364	·05376	·17559	·43885	·47574
1899	16 57·1	67 14·7	·18393	·05363	·17594	·43852	·47553
1900	16 52·7	67 11·8	·18428	·05350	·17634	·43831	·47548
Means . . .	17 18·8	67 23·4	·18288	·05442	·17460	·43938	·47599

Table III.—Secular Changes.

Year.	D.	I.	H.	W.	N.	V.	T.
1890–1	−8′·7	′ —	+24γ	−36γ	+37γ	—	—
1891–2	−5·2	−1·2	+11γ	−23γ	+19γ	−22γ	−12γ
1892–3	−7·9	−3·0	+34γ	−30γ	+45γ	−20γ	−11γ
1893–4	−5·8	−1·4	+13γ	−25γ	+21γ	−21γ	−13γ
1894–5	−6·2	−2·2	+27γ	−24γ	+36γ	−13γ	− 4γ
1895–6	−6·0	−2·7	+31γ	−21γ	+39γ	−21γ	− 8γ
1896–7	−4·4	−3·1	+33γ	−13γ	+40γ	−31γ	−17γ
1897–8	−5·0	−2·0	+22γ	−19γ	+27γ	−21γ	− 9γ
1898–9	−4·3	−2·9	+29γ	−13γ	+35γ	−33γ	−21γ
1899–1900	−4·4	−2·9	+35γ	−13γ	+40γ	−21γ	− 5γ
Mean annual change at—							
Kew	−5·79	−2·38	+25·9γ	−21·7γ	+33·9γ	−22·6γ	−11·1γ
Parc St. Maur . . .	−5·46	−1·60	+25·3γ	—	—	− 0·3γ	—
Potsdam.	−5·23	−1·14	+22·7γ	—	—	+13·9γ	+21·8γ

§ 7. It will be observed that the mean secular changes in D and H at Parc St. Maur and Potsdam are very similar to those at Kew. There is even, in the case of these elements, a fair resemblance in the variations from year to year. All three stations, for instance, show a decidedly slackened rate of change in D since 1896. In 1898–9 and 1899–1900, the changes in D at Potsdam were absolutely identical with those at Kew; but in 1892–3 the change at Potsdam was less by 1′ than in either 1891–2 or 1893–4, whereas at Kew it was 2′ greater in 1892–3 than in the two adjacent years.

Kew and Potsdam agree in representing the change in H during 1891–2 as particularly small, and the changes in 1893–4 and 1897–8 were also at both places decidedly below the average. Again, we have specially large changes of H at Kew and Potsdam in 1892–3, 1895–6, 1896–7, and 1899–1900. Parc St. Maur agrees with Potsdam and Kew in having a specially small change of H in 1893–4. and specially large changes in 1892–3 and 1896–7: but it differs in showing an average change in 1891–2 and a less than average change in 1895–6.

In inclination and vertical force the mean data at the three stations are widely different; Parc St. Maur shows a nearly stationary value of V, as against a distinctly rising value at Potsdam, and a still more distinctly falling value at Kew. The inclination is diminishing at all three places, but the rate of fall appears considerably less at Potsdam than at Parc St. Maur, and considerably less at Parc St. Maur than at Kew.

Speaking generally, the secular changes in I, V, and T appear to have been much more irregular at Potsdam and Parc St. Maur than at Kew. Thus, at Parc St. Maur V rose 29γ in 1891–2 and fell 40γ in 1893–4; while at Potsdam V increased by 40γ in 1891–2, 43γ in 1892–3, and 74γ in 1899–1900, and fell 16γ in each of the three years 1893–4, 1894–5, and 1898–9. There are corresponding fluctuations, of course, in T. At Kew the accuracy of the estimate of secular change in V and T is really dependent in the main on the accuracy of the determination of I. An error of 1′ in I—and such an error might arise from very slight deterioration of either circle or needles—means an error of over 30γ in both V and T. Taking this into account, I do not think much weight can be assigned to the values of the secular change for individual years. The comparative smoothness of the V and T data in Table III. is probably not more a tribute to the uniformity of Nature than to the care and skill of Mr. BAKER as an observer.

The theory has been advanced that secular changes are particularly large in years of sun-spot maximum. The data in Table III. can hardly be said to support this. The changes of D were certainly larger in 1892–6 when sun-spots were numerous, than in 1898–1900 when they were few; but the largest change in D occurred in 1890–91 near sun-spot minimum, and in 1893–4 about sun-spot maximum the secular change was about average in D and particularly small in H and I.

§ 8. To assist in the comprehension of the secular change I have drawn a curve, fig. 1, which shows the change from year to year in the direction of an imaginary magnet, freely suspended from its C.G. so as to point along the line of total force. The curve may be supposed drawn by a style attached to the dipping end of the magnet, the paper being supposed to lie on a plane tangential to a sphere, concentric with the magnet, at the point answering to the mean position of the dipping end during the period 1891 to 1900. With increasing I, the dipping end would move towards an observer who stood with his back to the south, looking at the paper. The west, *i.e.*, the direction of + D, would then be on the observer's left. The crosses mark the positions of the end of the magnet at the middle of the years specified. The magnet or style is supposed to be so long that the difference between arc and tangent may be neglected, so that equal lengths on the paper represent equal changes of direction in the magnet. The curve, it will be noticed, does not depart very far from a straight line.

§ 9. The above graphical method throws no direct light on the absolute magnitudes of the changes of the components of force. It is, however, of some interest to know the direction and amplitude of the disturbing force to which the secular change may be attributed. To find this we may proceed as follows:—

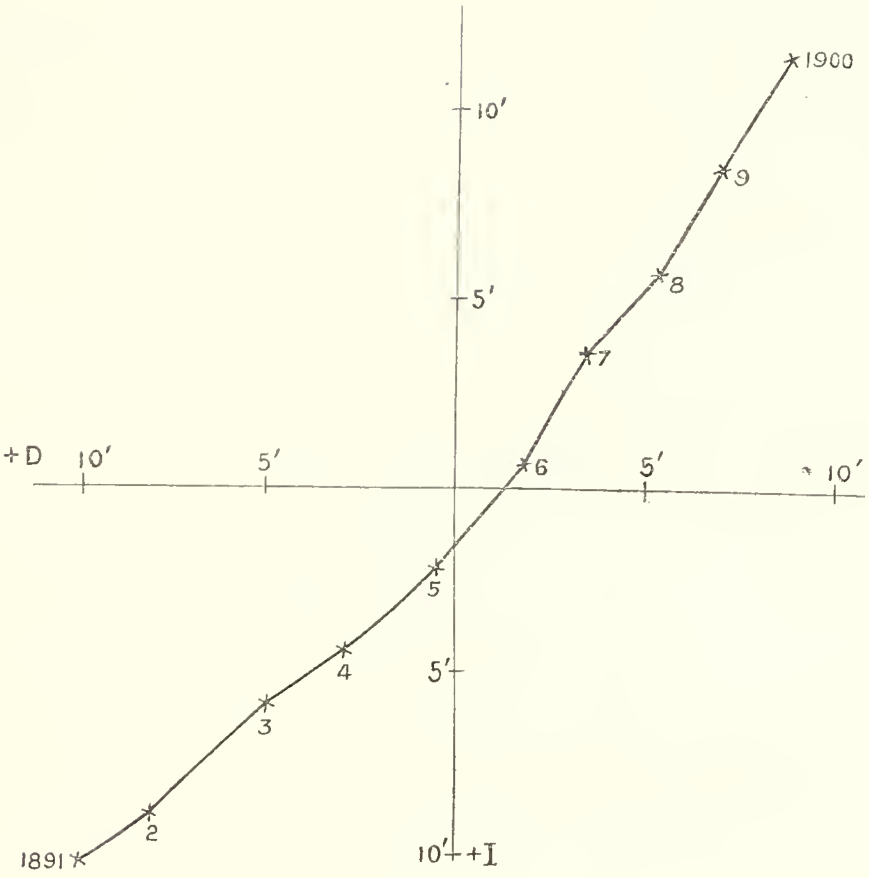

Fig. 1.

Let N, W, V represent the values of the northerly, westerly, and vertical components of force at the beginning of a period, at the end of which the values have become $N + \delta N$, $W + \delta W$, $V + \delta V$. The total force meantime has changed from T to $T + \delta T$.

δN, δW, δV represent the components of a force δR (totally different usually from δT) which may be regarded as producing the secular change. If secular change data for individual years were sufficiently reliable, one would naturally take the δR answering to a single year's change as measuring in direction and magnitude the force to which the secular change may be attributed.

In general, however, it will be best to calculate a δR for a considerable number of years interval, and to regard its line of action as indicating the general direction of the secular change force throughout the period.

In the present instance we get for the period 1891 to 1900, at Kew,

$$\delta N = +302\gamma, \quad \delta W = -181\gamma, \quad \delta V = -203\gamma.$$

Thence we find $\delta R = 406\gamma$, and its line of action makes with three rectangular axes drawn respectively to the north, the *east*, and vertically *upwards* the angles 42°·0, 63°·5, and 60°·0.

The projection of the line of action of δR on the horizontal plane is inclined to the geographical meridian at the angle 30°·9, running in a north-*easterly* direction.

Annual Inequality.

§ 10. If the secular change proceeded at a uniform rate throughout the year, the mean value E_n of any element answering to the middle of the n^{th} month of the year should be derivable from the mean value $\overline{E}$ for the whole year by the formula

$$E_n = \overline{E} + (2n - 13)\, s/24,$$

where s is the secular change for the entire year.

This neglects the differences between the lengths of months, as being for the present purpose immaterial.

Conversely, if one applies to $E_n - \overline{E}$ the correction $-(2n - 13)\, s/24$, one eliminates the effect of a regularly progressive secular change, and obtains what is known as the "Annual Inequality."

In practice, complications arise from the apparent variability in the secular change from year to year. To illustrate the consequences of such irregularity, take the simple hypothetical case where the secular change of declination proceeds uniformly from January 1 to December 31 of a year at the rate of 12′ a year, and then proceeds for the next twelve months at the uniform rate of 6′ a year. From the mean values for the two years we should deduce a secular change, not of 12′ or of 6′, but of 9′ a year, and if we corrected the two years' monthly values independently, on the assumption of a secular change of 9′ a year, we should deduce for each year a wholly fictitious annual inequality. Combining the monthly values for the two years we should in this case conclude, rightly enough, that there was no true annual inequality, but that is merely an accident of the particular hypothesis. The illustration will show how uncertain is the physical interpretation to be put on an apparent annual inequality in the case of an element whose secular change is irregular, unless we deal with mean monthly values from a large number of years.

The results in Table IV. have been obtained by combining 10 years' results for I, V, and T, and 11 years' results for the other elements. The data assigned to the "middle of the month" are the values actually obtained for the differences between the mean monthly values and the mean annual value after the application of the corrective term $-(2n-13)\,s/24$. The value assigned to s in each case was that given in Table III. as the mean for the 10 or 11-year period considered. The results under the heading "beginning of month" are each the arithmetic mean of two adjacent mid-month values; for example, the value assigned to January refers to January 1, and is the mean of the values for mid-December and mid-January. The mid-month data are the most suitable for use in a critical examination into the true nature of the phenomena; but, assuming the existence of a true annual inequality, the beginning of the month data are probably the more reliable measures of its amplitude.

In all the force components, unity represents 1γ.

TABLE IV.—Annual Inequality.

	Middle of month.				Beginning of month.						
	D.	I.	H.	V.	D.	I.	H.	W.	N.	V.	T.
January . .	+0′·08	−0′·03	−0·9	− 0·4	+0′·17	−0′·16	−0·1	+0·8	−0·4	− 4·1	−3·8
February . .	+0·48	−0·07	+1·9	+ 2·1	+0·28	−0·05	+0·5	+1·6	0·0	+ 0·8	+1·0
March . . .	+0·03	+0·53	−0·1	+14·4	+0·25	+0·23	+0·9	+1·6	+0·4	+ 8·2	+8·0
April . . .	−0·31	+0·18	−0·6	+ 5·7	−0·14	+0·35	−0·3	−0·8	−0·1	+10·0	+9·1
May . . .	−0·39	−0·15	+2·7	+ 1·5	−0·35	+0·02	+1·0	−1·5	+1·6	+ 3·6	+3·7
June . . .	−0·47	−0·35	+5·2	− 0·3	−0·43	−0·25	+4·0	−1·0	+4·5	+ 0·6	+2·1
July . . .	−0·30	−0·13	+3·8	+ 5·4	−0·38	−0·24	+4·5	−0·6	+4·9	+ 2·5	+4·0
August . .	+0·08	−0·19	+0·5	− 3·5	−0·11	−0·16	+2·2	+0·1	+2·2	+ 0·9	+1·7
September .	+0·29	+0·20	−4·4	− 6·6	+0·19	+0·01	−2·0	+0·4	−2·2	− 5·1	−5·4
October . .	+0·06	0·00	−4·4	− 7·6	+0·18	+0·10	−4·4	−0·4	−4·5	− 7·1	−8·3
November .	+0·17	+0·18	−4·4	− 2·7	+0·12	+0·09	−4·4	−0·7	−4·4	− 5·2	−6·5
December. .	+0·26	−0·29	+0·6	− 7·8	+0·22	−0·05	−1·9	+0·5	−2·1	− 5·2	−5·6

§ 11. If we take the beginning of the month data in Table IV. we have the following results:—

	D.	I.	H.	W.	N.	V.	T.
Range of annual inequality . .	0′·71	0′·60	8·9γ	3·1γ	9·4γ	17·1γ	17·4γ
Range ÷ secular change . . .	0·12	0·25	0·34	0·14	0·28	0·76	1·57

The ratio borne by the range of the annual inequality to the mean secular change is certainly largest in those elements in which the uncertainties are greatest.

In the case of D and H (or of W and N) we are dealing with elements whose secular change has been comparatively regular, and there are other grounds for regarding the annual inequalities obtained for them as the most reliable.

They show a pretty close resemblance in general character to results obtained previously* for Kew from the five years 1890–4. At the same time, the ranges now found are somewhat conspicuously less than the ranges, $1'\cdot 22$ in D and $12\cdot 9\gamma$ in H, obtained on the previous occasion.

In the case of D and H, the variation in the mid-monthly values in Table IV. seems altogether too regular to be ascribed to chance, and even in I and V something more than chance seems involved. It must be allowed, however, that in these last two elements the value for March stands out in a way one can hardly suppose to be truly representative of Nature, and in the case of V, the tendency to negative values in the latter half of the year, and the apparent jump from December to January, are somewhat suggestive of an under-estimate of the true secular change.

§ 12. One possibility to which attention should be drawn is that an annual inequality may be in no way ascribable to errors of observation, or of estimation of the secular change, and yet be absolutely fictitious so far as terrestrial magnetism is concerned. For example, if the distant mark used in absolute observations of D shifted in any way dependent on the temperature of the air, or on the temperature or moisture of the soil, an apparent annual inequality would ensue. A similar result would happen in the case of H if the law of variation with temperature in the moment of inertia of the collimator magnet were wrongly assumed. In the present case I have applied an elaborate check—whose description would take me too far afield—calculated to disclose any appreciable uncorrected effect of temperature on absolute observations of H, and the conclusion it led to was that if any such effect existed it was small compared to the range found for the annual inequality. It is also noteworthy that in all the elements the beginning of the month data indicate a large semi-annual term in the annual inequality, which is not what one would expect to find if the true cause of the phenomena were moisture or temperature.

Non-cyclic Effect.

§ 13. In virtue of the secular changes shown in Table III., the value of an element should exceed its value 24 hours earlier, on the average throughout the period now dealt with, by the following amounts :—

D.	I.	H.	W.	N.	V.	T.
$-0'\cdot 016$	$-0'\cdot 007$	$+0\cdot 07\gamma$	$-0\cdot 06\gamma$	$+0\cdot 09\gamma$	$-0\cdot 06\gamma$	$-0\cdot 03\gamma$

These quantities are all much less than can be directly measured on the magnetograms. Such as they are, however, they contribute to what I have termed the "non-cyclic effect."†

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* 'British Association Report for 1895,' p. 226.

† 'British Association Report for 1895,' p. 210.

Again, the annual inequality, when such exists, implies an increment or decrement in the course of 24 hours, varying with the time of year; and if Table IV. may be trusted, this increment at certain seasons should be considerably larger than that due to the secular change. But even the most prominent monthly change in the table, viz., from $2{\cdot}1\gamma$ to $14{\cdot}4\gamma$ in the case of V, would represent an increment of only about $0{\cdot}4\gamma$ in a day. Any increment, of course, due to annual inequality would change in sign with the season, and would cut out for the year as a whole.

There are other known causes tending to introduce a difference between the values of the magnetogram ordinates answering to the beginning and end of a day. There are the irregular movements visible in most curves, especially at times of sun-spot maximum, and imperfections in the temperature corrections applied, at least in the case of V. These two last mentioned sources would, however, only introduce irregularities into the monthly values of the non-cyclic effect, without appreciably affecting the mean for the year.

A more troublesome source of non-cyclic effect is instrumental change. In the case of D there does not seem to be any appreciable uncertainty on this head. This might be inferred from the nature of the declination magnetograph, but it is at least desirable to have observational confirmation. During the eleven years dealt with, the magnet mirror had been re-adjusted only once, viz., in 1898, when its azimuth was altered so as to increase the curve ordinate by the equivalent of about 36′ of declination. Allowing for this, the curve ordinate had diminished by the equivalent of about 53′, between the taking of absolute observations in January, 1890, and December, 1900, which showed an actual decrease of 63′ in D. This leaves only about 10′ of shift unaccounted for by true secular change. Spread over 11 years, this would represent an exceedingly small non-cyclic effect. In the case of the bifilar magnetograph also, only one slight artificial alteration had been made in the distance between the trace and the base line. Allowing for this, the curve ordinate increased by about 65γ, whilst H really increased by about 280γ. The deficiency 215γ represents presumably in the main decrease in the moment of the bifilar magnet. Spread over 11 years, this represents a mean non-cyclic effect of about $0{\cdot}05\gamma$ per day. This, as we shall see, is only about a sixtieth of the average non-cyclic effect actually observed on quiet days. If we combine the effects due to true secular change and instrumental causes, we have a mean non-cyclic effect of only about $0{\cdot}02\gamma$ per day. This is in the same direction as the non-cyclic effect actually observed in H, but is wholly insignificant.

Results confirmatory of our conclusion as to the smallness of the non-cyclic effect in H, due to secular change and instrumental causes combined, were obtained from measurements of the curve ordinates at the beginning and end of a series of individual years.

In the case of V, the magnet mirror had been altered seven or eight times in the course of 11 years, usually early in January, at the time of the scale determinations.

As the balance had usually been altered at the same time, it was difficult to arrive at direct conclusions as to the true effect on the curve ordinates. A comparison, however, of the curve ordinates after the scale determinations in January with those in the following December, on seven years when no intermediate change had been made, showed a decrease in the ordinate due to instrumental causes at the average rate of 24γ a year. The change was in the same direction each year. An annual change of -24γ gives a mean non-cyclic effect of $-0{\cdot}07\gamma$ per day. Combining instrumental causes with true secular change, we get a non-cyclic effect of about $-0{\cdot}13\gamma$ per day. This represents, as we shall see, about 15 per cent. of the average non-cyclic effect actually observed on quiet days.

§ 14. There is unavoidably some uncertainty in the estimates of artificial non-cyclic effects, and I have attempted no correction to the results as observed.

The H and V magnets would probably be more exposed to losses of magnetism during magnetic storms than on ordinary occasions, and the chances are that any estimate we should make of the contribution from instrumental causes to the observed non-cyclic effect on quiet days would be in excess, in the case at least of V. Again, as will be seen presently, we have to correct the observed readings of the curves for non-cyclic effect, and, so far as the corrections are concerned, what we have to deal with is the entire effect, whatever its sources. It is desirable to have on record the actual corrections made, so that anyone can reproduce the actual observation results who wishes to do so.

The quantities then actually recorded under the heading "non-cyclic effect" in the following tables V. to X. represent the algebraic excess of the recorded value of an element at the second midnight over that at the first midnight of a "quiet" day, irrespective of the source to which the increment is due.

In Table X., as subsequently, the year is sub-divided into three seasons—

"Winter," comprising the four months November, December, January, February;
"Equinox" ,, ,, ,, March, April, September, October;
"Summer" ,, ,, ,, May, June, July, August.

TABLE V.—Non-Cyclic Effect in D.

	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.	Monthly means.	Number of months when effect—		
													+	0	–
January . .	+0′·1	+0′·1	+0′·2	+2′·5	+0′·3	+0′·6	–0′·8	+0′·1	0′·0	+0′·1	–0′·2	+0′·27	8	1	2
February .	–0·8	+0·5	+0·2	–0·1	+2·1	+0·1	–0·6	–0·2	–0·4	–0·2	+0·2	+0·07	5	0	6
March . .	–0·1	+0·6	+0·9	–0·2	+0·1	–0·2	0·0	+0·2	+0·3	+0·2	0·0	+0·16	6	2	3
April . . .	–0·3	+0·6	+0·1	0·0	+0·5	–0·2	+0·6	–0·1	+0·2	+0·2	–0·3	+0·12	6	1	4
May . . .	–0·3	+1·0	–0·1	+0·5	+0·2	–0·9	–0·3	–0·5	–0·4	0·0	+0·2	–0·055	4	1	6
June . . .	–0·7	+0·1	+0·1	–0·2	–0·6	+0·3	+0·8	–0·4	–0·1	+0·1	+0·1	–0·045	6	0	5
July . . .	–0·5	+0·2	–0·6	+0·4	–1·7	+0·8	+0·1	0·0	0·0	+0·1	–0·2	–0·13	5	2	4
August . .	–0·4	+0·1	–0·7	0·0	–0·5	–0·3	+0·2	+0·4	+0·4	+0·1	+0·1	–0·055	6	1	4
September .	–0·2	+0·4	+0·2	–0·4	+0·8	–0·1	–0·4	+0·4	–0·3	0·0	–0·1	+0·03	4	1	6
October . .	–0·5	+0·4	+1·2	–0·4	0·0	–0·5	–0·1	–0·3	–0·1	–0·1	0·0	–0·04	2	2	7
November .	0·0	–0·7	+0·2	+1·1	+0·7	–0·2	–0·1	–0·2	+0·5	+0·2	+0·4	+0·17	6	1	4
December .	–0·6	+0·2	0·0	–0·1	–0·1	0·0	+0·5	+0·1	+0·2	–0·1	+0·1	+0·02	5	2	4
Mean for year .	–0·36	+0·29	+0·14	+0·26	+0·15	–0·05	–0·01	–0·04	+0·025	+0·05	+0·025	+0·044	—	—	—

TABLE VI.—Non-Cyclic Effect in I.

	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.	Monthly means.	Number of months when effect—		
													+	0	−
January . .	+0′·1	−0′·4	−0′·6	−1′·0	−0′·4	−0′·5	0′·0	0′·0	−0′·1	−0′·3	−0′·2	−0′·31	1	2	8
February .	−0·2	+0·1	−0·4	−0·3	−0·8	−0·5	−0·3	−0·1	−0·1	−0·3	−0·3	−0·29	1	0	10
March . .	+0·4	−0·1	−0·7	0·0	−0·1	−0·5	−0·6	−0·1	−0·7	−0·1	−0·4	−0·26	1	1	9
April . . .	−0·2	−0·3	−0·5	0·0	+0·1	−0·3	−0·8	−0·8	−0·1	−0·3	−0·3	−0·32	1	1	9
May . . .	−0·6	−0·3	−0·2	−0·8	+0·2	+0·1	−0·8	−0·5	0·0	−0·2	−0·5	−0·33	2	1	8
June . . .	+0·1	−0·2	−0·1	−0·6	0·0	−0·5	−0·3	−0·2	0·0	−0·1	+0·2	−0·155	2	2	7
July . . .	0·0	−0·1	−0·5	0·0	−0·2	−0·5	−0·2	−0·2	−0·3	−0·3	+0·2	−0·19	1	2	8
August . .	−0·2	−0·2	−0·7	−0·4	−0·1	0·0	+0·1	−0·3	−0·2	−0·4	−0·3	−0·245	1	1	9
September .	−0·1	−0·3	−0·2	−0·1	+0·1	−0·5	−0·2	−0·3	−0·6	−0·1	0·0	−0·21	1	1	9
October . .	−0·3	−0·2	−0·5	−0·3	−0·5	+0·1	0·0	−0·3	−0·2	−0·2	−0·1	−0·23	1	1	9
November .	—	−0·1	−0·5	−0·5	−0·4	−0·5	−0·1	−0·2	−0·2	−0·3	0·0	−0·28	0	1	9
December .	—	−0·1	0·0	−0·2	0·0	−0·4	0·0	−0·3	−0·2	−0·2	+0·1	−0·13	1	3	6
Mean for year .	−0·10	−0·18	−0·41	−0·35	−0·175	−0·33	−0·27	−0·275	−0·225	−0·23	−0·13	−0·245	—	—	—

TABLE VII.—Non-Cyclic Effect in H. (Unity ≡ 1γ.)

	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.	Monthly means.	Number of months when effect—		
													+	0	−
January	−2	+3	+7	+13	+4	+5	+2	+1	+3	+3	+2	+3·7	10	0	1
February	+6	0	+6	+3	+12	+7	+5	+2	+1	+4	+3	+4·5	10	1	0
March	+1	+4	+6	0	+1	+5	+6	+3	+7	+1	+5	+3·5	10	1	0
April	+5	0	+3	+2	−2	+4	+10	+10	+1	+5	+4	+3·8	9	1	1
May	+6	+6	0	+8	+2	+1	+7	+5	+2	+1	+6	+4·0	10	1	0
June	−1	+1	+2	+5	0	+6	+4	+3	−1	+1	−2	+1·6	7	1	3
July	0	0	+6	+1	+3	+6	+3	+2	+5	+5	−2	+2·6	8	2	1
August	+4	+4	+10	+3	+2	−1	+1	+3	+2	+5	+2	+3·2	10	0	1
September	+1	+4	+4	+5	+3	+6	+5	+4	+7	+1	0	+3·6	10	1	0
October	+2	+5	+9	+2	+7	+5	0	+3	+2	+3	+2	+3·6	10	1	0
November	+5	+2	+7	+5	+7	+6	0	+3	+3	+5	0	+3·9	9	2	0
December	+1	−1	+4	+1	+1	+3	+2	+5	+2	+4	−1	+1·9	9	0	2
Mean for year	+2·3	+2·3	+5·3	+4·0	+3·3	+4·4	+3·8	+3·7	+2·8	+3·2	+1·6	+3·34	—	—	—

TABLE VIII.—Non-Cyclic Effect in V. (Unity ≡ 1γ.)

	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.	Monthly means.	Number of months when effect—		
													+	0	–
January . .	– 4	– 8	– 5	– 3	– 5	– 6	+ 2	+ 1	0	– 2	– 2	– 2·9	2	1	8
February . .	+ 5	+ 3	+ 1	– 1	– 1	– 4	+ 2	– 1	0	– 2	– 2	0·0	4	1	6
March . . .	+ 18	+ 7	– 13	0	0	– 4	– 8	+ 1	– 5	– 2	– 1	– 0·6	3	2	6
April . . .	+ 8	– 10	– 8	+ 4	– 4	– 3	– 7	– 3	– 1	– 1	– 4	– 2·6	2	0	9
May . . .	– 7	+ 1	– 9	– 7	+ 10	+ 5	– 14	– 3	+ 2	– 3	– 3	– 2·5	4	0	7
June . . .	– 1	– 4	+ 1	– 7	– 2	– 4	– 3	+ 2	– 1	– 2	+ 3	– 1·6	3	0	8
July . . .	– 2	– 2	– 1	+ 2	– 2	– 3	0	0	+ 1	– 1	+ 3	– 0·5	3	2	6
August . .	+ 5	+ 1	– 2	– 8	+ 2	– 3	+ 5	– 4	– 1	– 2	– 3	– 0·9	4	0	7
September .	0	– 3	+ 1	+ 7	+ 14	– 1	+ 2	0	– 4	– 2	+ 1	+ 1·4	5	2	4
October . .	– 7	+ 3	+ 2	– 6	– 3	+ 14	+ 2	– 3	– 1	– 1	+ 1	+ 0·1	5	0	6
November .	—	+ 2	– 1	– 7	+ 4	– 4	– 2	+ 1	+ 1	+ 2	0	– 0·4	5	1	4
December .	—	– 5	+ 10	– 5	+ 2	– 5	+ 4	+ 1	+ 1	+ 2	+ 1	+ 0·6	7	0	3
Mean for year . .	+ 1·5	– 1·25	– 2·0	– 2·6	+ 1·25	– 1·5	– 1·4	– 0·7	– 0·7	– 1·2	– 0·5	– 0·84	—	—	—

TABLE IX.—Non-cyclic Effect.

Year.	Declination. Number of months.			Inclination. Number of months.			Horizontal force. Number of months.			Vertical force. Number of months.		
	+	0	−	+	0	−	+	0	−	+	0	−
1890 . . .	1	1	10	3	1	6	9	1	2	4	1	5
1891 . . .	11	0	1	1	0	11	8	3	1	6	0	6
1892 . . .	8	1	3	0	1	11	11	1	0	5	0	7
1893 . . .	4	2	6	0	3	9	11	1	0	3	1	8
1894 . . .	7	1	4	3	2	7	10	1	1	5	1	6
1895 . . .	4	1	7	2	1	9	11	0	1	2	0	10
1896 . . .	5	1	6	1	3	8	10	2	0	6	1	5
1897 . . .	5	1	6	0	1	11	12	0	0	5	2	5
1898 . . .	5	2	5	0	2	10	11	0	1	4	2	6
1899 . . .	7	2	3	0	0	12	12	0	0	2	0	10
1900 . . .	6	2	4	3	2	7	7	2	3	5	1	6
Totals. .	63	14	55	13	16	101	112	11	9	47	9	74

TABLE X.—Non-cyclic Effect, Seasonal Values (Means from 11 Years). Unit = 1γ in case of Force.

	D.	W.	H.	N.	I.	V.	T.
Winter. . . .	+0′·134	+1·72	+3·50	+3·13	−0′·252	−0·68	+0·72
Equinox . . .	+0·068	+1·44	+3·66	+3·39	−0·254	−0·46	+0·99
Summer . . .	−0·070	+0·50	+2·86	+2·84	−0·230	−1·39	−0·18
Year	+0·044	+1·22	+3·34	+3·12	−0·245	−0·84	+0·51

§ 15. The declination (see Table V.) is the element in which the non-cyclic effect is smallest and most variable in sign. The D curves are read only to the nearest 0′·1, so that apparent non-cyclic changes of this amount *on individual days* possess little, if any, significance. If we take the last six years in Table V., we see that the mean non-cyclic effect for the year in no case exceeds 0′·05, and if we combine these six years, we obtain a mean non-cyclic effect which absolutely vanishes. Again, while the mean non-cyclic effects for 1890 and 1891 are of substantial size, they are opposite in sign.

These facts are certainly calculated to rouse suspicions as to the *bonâ fide* nature of the non-cyclic effect in D. There are, however, a variety of considerations which point to its having a real physical origin.

In the first place, the contribution of the true secular change to the mean non-cyclic effect in D, viz., − 0′·016, is in the opposite direction to the resultant effect, so that the daily change which we have to account for really amounts on the average of the eleven years to 0'·044 + 0'·016 or 0'·06. Again, the annual inequality is in general such as to diminish the numerical values found for the non-cyclic effect. In fact we see from Tables IV. and V. that the non-cyclic effect is positive in March and April, the months in which the annual inequality is changing fastest from positive to negative, while it is negative in July and August, months in which the annual inequality is changing from negative to positive.

This brings us to another suggestive feature. Four of the five months in which the mean non-cyclic effect is negative are summer months, while it is positive in six successive months, November to April, including all the mid-winter months. Then, as regards differences of sign in different years, sun-spots were exceptionally few in 1890, and though fairly numerous were rapidly diminishing in 1895, 1896, and 1897, the other three years in which the mean non-cyclic effect was negative. On the other hand, 1891 to 1894, the years in which the non-cyclic effect has its largest positive values, were years in which sun-spots were either very numerous or increasing rapidly in number. Thus I think that whilst it would be unwise to dogmatise as to the cause of the apparent non-cyclic effect in D, the evidence distinctly points to the conclusion that it is a true magnetic phenomenon which varies, however, with the season of the year, and with the position of the year in the sun-spot cycle.

§ 16. In the case of I (see Table VI.), the non-cyclic effect is evidently no chance phenomenon. The means for every year of the eleven, and for every month of the twelve, alike come out negative, and the preponderance of individual months in which the effect is negative is overwhelming. The true secular change is here in the same direction as the apparent non-cyclic effect, and so tends to increase it, but only to an insignificant extent. In fact it requires only 10 average quiet days to bring about a decrease in I equal to the secular change observed in an entire year.

The absolute magnitude of the non-cyclic change in I, as we see from Table X., does not vary very conspicuously with the season of the year, but relative to the range of the diurnal inequality it is most important in winter. In January, in fact, it averaged fully 30 per cent. of the range of the proper cyclic diurnal variation.

§ 17. The non-cyclic effect in H, see Table VII., is as prominent as in I. Here also it is increased by the contribution from the secular change, but 8 average quiet days suffice to produce an increment in the force equal to the full secular change for the year. The non-cyclic effect in H is on the whole wonderfully uniform throughout the year, but it appears somewhat reduced at midsummer. Relative to the range of the diurnal inequality, it is most important in winter; in January, in fact, it averaged over 20 per cent. of the observed range.

In V, see Table VIII., the non-cyclic effect is considerably less conspicuous than in H or I, but more conspicuous than in D. There is a decided preponderance of months in which it has the negative sign, and the mean annual value is positive in only 2 out of the 11 years. According to Table X., the magnitude of the non-cyclic effect in V is considerably dependent on the season of the year, being greater in summer than in winter. We have already seen that an appreciable though small fraction of the effect in V is ascribable to secular change and instrumental causes: and if these causes are as potent in winter as in summer, the difference between the phenomena observed in summer and winter is all the more noteworthy.

In the case of W, N and T, I have confined myself to mean seasonal values (see Table X.). The equivalent in force of $1'$ in D is $5\cdot3\ \gamma$ approximately. Hence it will be seen that the mean non-cyclic effect in W, though much less than in H, is larger than in D. The non-cyclic effect in N approaches closely that in H.

In T the non-cyclic effect appears to be but little larger than in D, and it also shows the peculiarity of being positive in winter but negative in summer. The secular change and the instrumental causes described in dealing with V would tend to produce a slight (algebraic) reduction in the results obtained for T.

Solar Diurnal Inequality.

§ 18. By the diurnal inequality is meant the *periodic* change taking place in the value of an element throughout the 24 hours. In the case of a magnetic element on quiet days, there is as we have seen an appreciable non-cyclic effect, in virtue of which the value recorded at the second midnight of a day exceeds that recorded at the first midnight by a quantity, say N, which may be positive or negative. To obtain the proper *periodic* change, N must be eliminated, for unless this is done a diurnal inequality is obtained which is not periodic, which presents a discontinuity between two successive hourly values, and which is partly dependent on which hour of the 24 we select as the first hour of our day. If we assume N to result from some cause operating uniformly throughout the day, and count our day from midnight, 0 hours, to midnight, 24 hours, the necessary elimination is effected by applying to each hourly value the correction

$$N\ (12 - n)/24,$$

where n is the hour counted from midnight (0 hours).

This correction brings of course the values answering to hours 0 and 24 into harmony, and leaves unaltered the mean value M of the element for the day as given by

$$M = \tfrac{1}{24}\left\{\tfrac{1}{2}[0] + \tfrac{1}{2}[24] + [1] + \ldots + [23]\right\},$$

where $[n]$ represents the value of the element at hour n. When dealing with hourly values from a single day, or as in the present case with hourly means from 5 days a month, we really do not know how the non-cyclic effect comes in, and our method of elimination *may* introduce a factor not present in diurnal inequalities based on all days of the month.

Another source of slight uncertainty may be noticed. The magnetic elements have in all probability a lunar as well as a solar diurnal variation. The incidence of the selected 5 quiet days in the lunar month is largely a matter of accident, and consequently the way in which the lunar variation affects hourly values based on the selected 5 quiet days must vary from month to month. The lunar influence appears however to be so small that any uncertainty on this ground must be trifling, even in the case of data from a single year, and when we are dealing with data from 5 or 6 years, the uncertainty should be no greater than in the case of data derived from all days in a single month.

A further point that is more fully dealt with in § 31 need only be mentioned now. The hours to which the curve measurements refer are G.M.T., whereas a true solar diurnal variation is connected presumably with the true local solar time. The fact that noon at Kew is 1¼ minutes later than noon at Greenwich is comparatively unimportant, as the difference is small and affects all seasons of the year alike, but the considerable annual range—some 31 minutes—in the "equation of time" must be borne in mind.

§ 19. A really serious difficulty remains to be mentioned. The Kew magnetographs are placed in a room partly underground in the basement of the Observatory, where the annual variation of temperature, though much less of course than in an unprotected upstairs room, still amounts to some 20° F. At some seasons of the year this implies a somewhat troublesome change of temperature from day to day, but speaking generally there is seldom a difference of more than 1° F., and usually only a difference of a few tenths of a degree between the mean temperature on successive days. It was thus possible to allow pretty satisfactorily for the difference between the mean temperature of the room on the five quiet days a month and on the days of the absolute observations, from eye readings of a mercury thermometer placed under the glass shade containing the vertical-force magnet. Up to the end of 1896 the readings of this thermometer were the only direct source of information as to the temperature of the magnetographs. During 1896 the thermometer had been read usually thrice a day, at 10 A.M., 4 P.M., and 10 P.M. Prior to that it had been read twice a day, but in the earlier years of the period only once a day. In the end of 1896 the late Kew Committee, on my initiative, introduced a thermograph. It was so situated and protected as to give readings in close accordance with those of the mercury thermometer—still read thrice daily—and temperature corrections based on its readings have been applied from 1897 onwards to the H and V curves. In the case of the H magnetograph the temperature coefficient is little over 1γ for 1° F., and the temperature correction is very small. In the case of V the correction is distinctly appreciable. An examination however of the thermograph results obtained early in 1897—at the season, as it has turned out, when the diurnal variation of temperature is least—and a comparison of the annual and semi-annual magnetic inequalities for 1896 and 1897, led me unfortunately to the conclusion that the neglect of the diurnal variation of temperature in previous years was less serious than I had feared. Influenced by this investigation, I accepted the data for 1890 to 1896 as published in the annual 'Reports,' and all the tables of diurnal inequalities, and numerous others, were originally calculated on this basis. The results so obtained were utilised in the "Preliminary Note on the Relationships between Sun-spots and Terrestrial Magnetism," published in the 'Roy. Soc. Proc.,' vol. 71, p. 221. Subsequently I noticed that the ranges in the mean annual inequalities for V for 1898 and 1899 appeared larger relative to the ranges in earlier years than one would have anticipated from the relationships I had observed between Sun-spots and Terrestrial Magnetism, and I had little difficulty in tracing the cause to the neglect of the temperature correction in the earlier years. Owing to the smallness of the temperature coefficient in the H magnetograph, the absence of a temperature correction in the data for years prior to 1897 is of little importance. It became obvious, however, that the earlier years' data for V must be corrected or dispensed with. The correction has entailed a great amount of labour, involving the complete recalculation of all the diurnal inequalities for V and I and of the corresponding Fourier coefficients, &c. The thermograph records from 1897 to 1901 gave smooth diurnal inequalities of temperature for each month of the year. The range varied largely with the season, being much less at midwinter than at midsummer, but the hours of maximum and minimum and the general features were nearly independent of the time of year. The magnetograph room and its environment remained unchanged from 1890 to 1901, and the readings from the mercury thermometer throughout the period confirmed the view that if the mean diurnal inequalities of temperature obtained for the several months of the year since 1897 were assumed to apply to years prior to 1897, satisfactory average corrections would be obtained. This accordingly has been done, and I do not think that the results now published are affected by any serious source of uncertainty.

§ 20. Diurnal inequalities for D, I, H, V, N, W, and T appear in Tables XI. to XVII. In the case of the first four elements inequalities are given for each month of the year. The values ascribed to any one month, say January, were obtained by adding together the hourly values from each January of the period included, applying a non-cyclic correction to the sums thus formed, and then taking the arithmetic means. The annual inequality for the year was obtained by summing up the mean hourly values for the 12 months—as corrected for non-cyclic effect—and taking their means. In the case of D and H mean inequalities are given, not merely for the whole 11 years, but for two combinations of years, viz., 1890, 1899, and 1900, years of few sun-spots, and 1892 to 1895, years of great sun-spot frequency.

The inequalities for N, W, and T were derived by means of the formulæ :—

$$\delta N = \cos D\, \delta H - H \sin D\, \delta D,$$
$$\delta W = \sin D\, \delta H + H \cos D\, \delta D,$$
$$\delta T = \cos I\, \delta H + \sin I\, \delta V,$$

where δN, for instance, represents the hourly value in the diurnal inequality of N, which corresponds to the values δH and δD, answering to the same hour, in the inequalities of H and D. To the necessary degree of accuracy, we may ascribe to D, H, and I in these formulæ their mean values for the period considered, and the formulæ actually used were (see Table II.):—

$$\delta N = \cdot 955\,\delta H - 1\cdot 58\,\delta D,$$
$$\delta W = \cdot 298\,\delta H + 5\cdot 08\,\delta D,$$
$$\delta T = \cdot 385\,\delta H + \cdot 923\,\delta V.$$

Here δD is supposed to be measured in minutes of arc. In the case of N, W, and T, inequalities are given for only three months of the year, selected one from each of the three seasons; in the case of N and W mean inequalities are given for two groups of years, as well as for the whole 11 years.

In a good many cases there are two distinct maxima and two distinct minima in the inequalities. All maxima and minima whose existence seems absolutely unmistakable are indicated by heavy type, but in cases where the second maximum and minimum are missing or doubtfully represented only the extreme values for the day are so marked. In the case of D the terms "maximum" and "minimum" are applied respectively to an extreme westerly and an extreme easterly position of the magnet. This is of course purely arbitrary, and is opposed to the practice of a good many writers, who measure declination positively to the east. As a mathematician, I am perfectly alive to the weight of the arguments advanced in support of this practice, which has its conveniences when mathematical calculations are being made involving the use of Cartesian co-ordinates. At a station, however, such as Kew, where the declination is westerly, and the prominent feature is the rapid forenoon movement of the needle to the west, it is much more convenient for descriptive purposes to take the west as the + direction. If one wishes to employ co-ordinate axes, with the east as positive direction, it is a simple matter to change the sign.

§ 21. In addition to the hourly values, the tables give the *Range* of the inequality, defined as the difference between the algebraically greatest and least of the mean *hourly* values. They also give the sum of the differences of the 24 hourly values from their arithmetic mean—*i.e.*, from the mean for the day—taken numerically.

The meaning assigned to the term "range" is carefully to be borne in mind, because there are a variety of usages, some of which are technically more exact. If we suppose for simplicity that the phenomena are absolutely identical for each day of a month, then the maximum and minimum for each day will occur at fixed times, which will also be the times of occurrence of the maximum and minimum in the mean diurnal inequality for the month. And if it happen in addition that the times of occurrence of the maximum and minimum each coincides with an exact hour G.M.T., then the meaning to be assigned to the term "range" has no ambiguity. In practice, however, the maximum and minimum in any single day seldom come at exact hours, so that if we confine ourselves to hourly values we do not as a rule hit on either the absolute maximum or absolute minimum, and the difference between the greatest and least of our hourly values as a rule is less than the amplitude proper of the diurnal movement. Again, the times of occurrence of the maximum and minimum really vary from day to day, so that the range we obtain by considering mean hourly values from a series of days tends to be less than the arithmetic mean of the ranges deduced from the individual days results. This last consideration doubly requires to be taken into account in connection with inequalities for the year or for a season.

TABLE XI.—Diurnal Inequality

	Forenoon.											
Hour	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
January (1890 to 1900)	−0′·88	−0′·60	**−0′·45**	−0′·48	−0′·58	−0′·65	−0′·82	−1′·08	**−1′·12**	−0′·23	+1′·10	+2′·30
February ,, ...	−1·15	−1·02	−0·90	**−0·89**	−1·01	−1·14	−1·28	−1·43	**−1·45**	−0·51	+1·17	+2·67
March ,, ...	−0·98	**−0·93**	−1·08	−1·26	−1·29	−1·60	−2·24	**−3·33**	−3·31	−1·64	+1·33	+4·18
April ,, ...	−0·83	−0·92	−1 09	−1·40	−1·66	−2·38	−3·62	**−4·52**	−4·16	−2·06	+1·09	+4·33
May ,, ...	−0·74	−1·01	−1·22	−1·87	−3·04	−4·01	**−4·78**	−4·50	−3·21	−0·43	+2·64	+5·32
June ,, ...	−0·74	−0·98	−1·23	−2·00	−3·41	−4·60	**−5·02**	−4·79	−3·63	−1·23	+1·63	+4·42
July ,, ...	−0·80	−1·03	−1·34	−1·98	−3·29	−4·20	**−4·37**	−4·27	−3·21	−1·22	+1·49	+4·22
August ,, ...	−1·05	−1·28	−1·61	−2·02	−2·85	−3·71	**−4·37**	−4·09	−2·62	+0·07	+3·03	+5·61
September ,, ...	−1·19	−1·25	−1·53	−1·92	−2·10	−2·72	−3·45	**−3·68**	−2·46	+0·11	+3·02	+5·41
October ,, ...	−1·03	−0·94	**−0·91**	−1·00	−1·12	−1·41	−1·97	−2·83	**−2·84**	−1·15	+1·65	+3·84
November ,, ...	−0·82	−0·64	−0·51	**−0·47**	−0·66	−0·89	−1·03	−1·44	**−1·52**	−0·36	+1·44	+2·78
December ,, ...	−0·56	−0·30	−0·23	**−0·23**	−0·26	−0·46	−0·63	−0·77	**−0·80**	+0·01	+0·98	+1·83
Mean for year (1890 to 1900)	**−0·90**	−0·91	−1·01	−1·29	−1·77	−2·31	−2·80	**−3·06**	−2·53	−0·72	+1·71	+3·91
,, ,, (1890, 1899, 1900). . .	**−0·63**	−0·63	−0·76	−1·02	−1·45	−1·88	−2·32	**−2·56**	−2·05	−0·48	+1·61	+3·49
,, ,, (1892 to 1895)	**−1·12**	−1·18	−1·30	−1·60	−2·18	−2·86	−3·39	**−3·68**	−3·06	−0·98	+1·83	+4·45

TABLE XII.—Diurnal

	Forenoon.											
Hour	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
January (1891 to 1900)	−0′·03	−0′·08	−0′·13	−0′·27	−0′·37	−0′·41	**−0′·43**	−0′·27	+0′·12	+0′·39	**+0′·55**	+0′·42
February ,, ...	−0·12	−0·14	−0·12	−0·17	−0·28	**−0·36**	−0·36	−0·24	+0·19	+0·49	**+0·65**	+0·51
March ,, ...	−0·28	−0·28	−0·28	−0·27	**−0·39**	−0·38	−0·24	+0·15	+0·71	**+0·99**	+0·98	+0·66
April ,, ...	−0·37	−0·36	−0·34	−0·32	−0·29	−0·27	−0·05	+0·40	+0·92	**+1·36**	**+1·36**	+0·93
May ,, ...	−0·36	−0·26	−0·21	−0·13	−0·01	+0·26	+0·70	+1·10	**+1·32**	+1·23	+0·93	+0·44
June ,, ...	−0·29	−0·24	−0·21	−0·17	−0·04	+0·26	+0·68	+1·03	**+1·27**	+1·26	+0·95	+0·51
July ,, ...	−0·34	−0·29	−0·29	−0·21	−0·08	+0·22	+0·56	+0·86	+1·20	**+1·38**	+1·06	+0·65
August ,, ...	−0·45	−0·37	−0·31	−0·27	−0·07	+0·17	+0·61	+1·13	**+1·45**	+1·43	+1·07	+0·46
September ,, ...	−0·44	−0·40	−0·31	−0·28	−0·19	+0·01	+0·42	+0·94	+1·34	**+1·43**	+1·04	+0·38
October ,, ...	−0·34	−0·29	−0·33	−0·34	**−0·44**	−0·41	−0·21	+0·24	+0·80	**+1·13**	+1·11	+0·78
November ,, ...	−0·14	−0·16	−0·21	−0·32	−0·43	**−0·50**	−0·38	−0·08	+0·42	+0·75	**+0·77**	+0·63
December ,, ...	+0·08	+0·06	−0·04	−0·15	−0·22	−0·27	**−0·30**	−0·20	−0·07	+0·16	**+0·33**	+0·28
Mean for year (1891 to 1900)	−0·26	−0·23	−0·23	−0·24	−0·23	−0·14	+0·08	+0·42	+0·81	**+1·00**	+0·90	+0·55

of Declination. (+ to West.)

Afternoon.												Range.	Sum of 24 differences from mean.	
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.			
+2′·89	+2′·21	+1′·37	+1′·05	+0′·67	+0′·24	−0′·14	−0′·54	−0′·93	−1′·07	−1′·18	−1′·11	4′·07	23′·69	January (1890 to 1900).
+3·31	+3·27	+2·46	+1·19	+0·75	+0·44	+0·11	−0·33	−0·78	−0·98	−1·22	−1·31	4·76	30·77	February ,,
+5·49	+5·23	+3·64	+1·72	+0·45	+0·03	−0·35	−0·50	−0·68	−0·87	−0·95	−1·04	8·82	44·12	March ,,
+6·05	+5·72	+4·12	+2·46	+1·04	+0·14	−0·25	−0·22	−0·18	−0·33	−0·55	−0·85	10·57	49·97	April ,,
+6·14	+5·55	+3·96	+2·12	+0·84	+0·04	−0·18	−0·27	−0·22	−0·21	−0·37	−0·66	10·92	53·33	May ,,
+5·60	+5·50	+4·49	+3·20	+1·83	+1·00	+0·38	+0·17	+0·06	+0·14	−0·28	−0·55	10·62	56·88	June ,,
+5·76	+5·81	+4·61	+2·77	+1·24	+0·39	+0·17	+0·10	+0·07	+0·02	−0·27	−0·62	10·18	53·25	July ,,
+6·64	+5·78	+4·06	+1·96	+0·34	−0·39	−0·34	−0·38	−0·40	−0·60	−0·73	−0·95	11·01	54·88	August ,,
+6·08	+5·03	+3·14	+1·39	+0·32	−0·09	−0·19	−0·48	−0·61	−0·71	−0·87	−1·13	9·76	48·92	September ,,
+4·67	+4·12	+2·89	+1·40	+0·77	+0·38	+0·01	−0·34	−0·82	−1·02	−1·09	−1·17	7·51	39·37	October ,,
+3·23	+2·52	+1·59	+0·99	+0·52	+0·17	−0·13	−0·53	−0·90	−1·19	−1·13	−1·12	4·75	26·58	November ,,
+2·25	+1·79	+1·34	+0·74	+0·27	−0·01	−0·33	−0·68	−0·97	−1·09	−0·99	−0·90	3·34	18·42	December ,,
+4·84	+4·38	+3·14	+1·75	+0·75	+0·19	−0·10	−0·33	−0·53	−0·66	−0·80	−0·95	7·90	41·34	Mean for year (1890 to 1900).
+4·15	+3·54	+2·28	+1·13	+0·38	0·00	−0·18	−0·34	−0·47	−0·54	−0·59	−0·67	6·71	33·15	,, ,, (1890, 1899. 1900)
+5·69	+5·31	+3·98	+2·36	+1·09	+0·39	0·00	−0·35	−0·60	−0·71	−0·95	−1·14	9·37	50·20	,, ,, (1892 to 1895).

Inequality of Inclination.

Afternoon.												Range.	Sum of 24 differences from mean.	
1.	2.	3	4.	5.	6.	7.	8.	9.	10.	11.	12.			
+0′·16	+0′·12	+0′·17	+0′·19	+0′·10	−0′·05	−0′·12	−0′·05	−0′·05	−0′·01	+0′·02	+0′·02	0′·98	4′·53	January (1891 to 1900).
+0·27	+0·15	+0·14	+0·24	+0·15	+0·02	−0·07	−0·19	−0·24	−0·19	−0·17	−0·17	1·01	5·63	February ,,
+0·30	+0·12	+0·03	+0·05	+0·07	−0·09	−0·26	−0·32	−0·28	−0·27	−0·36	−0·33	1·38	8·09	March ,,
+0·49	+0·17	−0·03	−0·17	−0·28	−0·42	−0·45	−0·50	−0·47	−0·47	−0·46	−0·42	1·86	11·30	April ,,
+0·11	−0·03	−0·20	−0·33	−0·51	−0·61	−0·73	−0·64	−0·62	−0·53	−0·51	−0·43	2·05	12·20	May ,,
+0·21	−0·09	−0·27	−0·34	−0·50	−0·65	−0·75	−0·68	−0·62	−0·52	−0·45	−0·36	2·02	12·35	June ,,
+0·28	−0·03	−0·34	−0·34	−0·49	−0·58	−0·67	−0·60	−0·59	−0·52	−0·44	−0·38	2·05	12·40	July ,,
+0·10	−0·08	−0·17	−0·22	−0·29	−0·45	−0·68	−0·69	−0·70	−0·54	−0·58	−0·48	2·15	12·80	August ,,
−0·07	−0·22	−0·15	−0·03	−0·11	−0·28	−0·54	−0·55	−0·54	−0·51	−0·53	−0·46	1·98	11·17	September ,,
+0·39	+0·11	+0·12	+0·16	−0·04	−0·22	−0·34	−0·37	−0·38	−0·35	−0·38	−0·39	1·57	9·67	October ,,
+0·45	+0·28	+0·19	+0·09	−0·13	−0·21	−0·27	−0·23	−0·17	−0·14	−0·11	−0·12	1·27	7·18	November ,,
+0·17	+0·19	+0·15	+0·06	−0·03	−0·11	−0·14	−0·08	−0·03	0·00	+0·03	+0·09	0·63	3·24	December ,,
+0·24	+0·06	−0·03	−0·05	−0·17	−0·30	−0·42	−0·41	−0·39	−0·34	−0·33	−0·29	1·42	8·12	Mean for year (1891 to 1900).

TABLE XIII.—Diurnal Inequality of Horizontal

	Forenoon.											
Hour	1.	2.	3.	4.	5.	6.	7.	8.	9.	10	11.	12.
January (1890 to 1900)	+ 2	+ 3	+14	+35	+50	+58	+61	+ 33	− 23	− 68	− 92	− 74
February ,,	+17	+15	+23	+23	+40	+49	+52	+ 30	− 32	− 89	−115	− 97
March ,,	+43	+45	+42	+40	+58	+60	+42	− 18	−109	−175	−192	−148
April ,,	+66	+58	+56	+53	+54	+51	+21	− 55	−150	−237	−258	−200
May ,,	+69	+46	+41	+29	+15	−23	−88	−166	−219	−234	−210	−142
June ,,	+44	+33	+31	+28	+14	−36	−98	−162	−213	−233	−205	−133
July ,,	+52	+40	+41	+31	+16	−30	−81	−145	−207	−245	−219	−156
August ,,	+73	+61	+55	+44	+22	−15	−81	−167	−232	−252	−210	−123
September ,,	+74	+66	+52	+47	+37	+ 5	−55	−140	−215	−250	−207	−103
October ,,	+53	+48	+53	+56	+68	+62	+36	− 29	−124	−195	−203	−155
November ,,	+18	+19	+28	+44	+61	+68	+49	+ 8	− 64	−127	−132	−107
December ,,	− 9	− 6	+ 6	+23	+34	+42	+44	+ 29	+ 2	− 38	− 62	− 52
Mean for year (1890 to 1900)	+42	+36	+37	+38	+39	+24	− 8	− 65	−132	−179	−175	−124
,, ,, (1890, 1899, 1900)	+33	+26	+30	+30	+32	+15	−10	− 56	−109	−142	−136	− 86
,, ,, (1892 to 1895)	+53	+49	+48	+50	+53	+35	− 6	− 77	−161	−222	−225	−168

TABLE XIV.—Diurnal Inequality of Vertical

	Forenoon.											
Hour	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
January (1891 to 1900)	− 3	− 6	− 8	− 7	−12	−13	−16	−21	−23	− 30	− 32	− 32
February ,,	+ 1	− 9	−10	− 8	−10	−11	−14	−15	−18	− 45	− 54	− 50
March ,,	+17	+12	+ 6	+ 5	+ 4	+ 3	+13	+ 8	−25	− 80	−123	−133
April ,,	+26	+13	+12	+10	+16	+20	+27	+14	−34	− 92	−154	−171
May ,,	+30	+26	+25	+30	+38	+37	+23	−12	−69	−144	−201	−209
June ,,	+ 6	− 2	+ 1	+ 4	+14	+ 7	− 1	−28	−69	−114	−158	−149
July ,,	+15	+ 3	− 6	− 3	+ 7	− 8	−16	−36	−73	−103	−154	−165
August ,,	+18	+11	+ 5	+10	+25	+26	+21	− 7	−55	−111	−143	−150
September ,,	+22	+19	+13	+12	+12	+18	+18	− 9	−55	−112	−138	−135
October ,,	+12	+ 6	+ 4	+ 6	− 3	− 1	+ 7	+ 5	−23	− 74	−103	−101
November ,,	0	0	− 2	− 4	− 5	−13	−18	−11	−18	− 45	− 51	− 40
December ,,	+ 4	+ 2	+ 1	+ 2	+ 3	− 1	− 5	− 9	−20	− 33	− 32	− 31
Mean for year (1891 to 1900)	+12	+ 6	+ 3	+ 5	+ 7	+ 5	+ 3	−10	−40	− 82	−112	−114

Force. (Unit $= 0{\cdot}1\gamma \equiv 1 \times 10^{-6}$ C.G.S.)

Afternoon.												Range.	Sum of 24 differences from mean.	
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.			
− 29	−10	−11	−15	+ 2	+ 19	+ 26	+ 15	+ 12	+ 2	− 2	− 1	153	657	January (1890 to 1900).
− 57	−24	−12	−14	− 2	+ 14	+ 24	+ 37	+ 40	+31	+28	+27	167	892	February ,,
− 82	−30	+ 6	+16	+ 16	+ 36	+ 61	+ 64	+ 57	+56	+58	+51	256	1505	March ,,
−125	−52	+ 8	+41	+ 66	+ 88	+ 99	+ 98	+ 91	+83	+81	+72	357	2163	April ,,
− 76	−22	+23	+63	+103	+129	+147	+127	+114	+97	+91	+75	381	2349	May ,,
− 73	− 3	+47	+71	+102	+136	+153	+137	+122	+96	+76	+61	386	2307	June ,,
− 90	−15	+56	+80	+108	+128	+138	+129	+118	+99	+82	+63	383	2369	July ,,
− 52	+ 1	+33	+55	+ 72	+ 97	+125	+122	+120	+91	+93	+77	377	2273	August ,,
− 23	+18	+23	+23	+ 42	+ 65	+ 95	+ 98	+ 93	+83	+87	+75	348	1976	September ,,
− 87	−36	− 9	− 5	+ 29	+ 51	+ 65	+ 65	+ 69	+61	+63	+62	272	1684	October ,,
− 68	−32	−10	+ 3	+ 33	+ 41	+ 46	+ 37	+ 29	+22	+15	+15	200	1076	November ,,
− 25	−19	− 9	+ 1	+ 6	+ 20	+ 22	+ 13	+ 3	− 3	0	−13	106	481	December ,,
− 66	−19	+12	+27	+ 48	+ 69	+ 83	+ 78	+ 72	+60	+56	+47	262	1536	Mean for year (1890 to 1900).
− 32	+ 4	+20	+21	+ 32	+ 48	+ 63	+ 56	+ 50	+40	+38	+35	205	1144	,, ,, (1890, 1899, 1900).
−100	−39	+ 7	+34	+ 63	+ 91	+104	+100	+ 93	+79	+76	+64	329	1997	,, ,, (1892 to 1895).

Force. (Unit $= 0{\cdot}1\gamma \equiv 1 \times 10^{-6}$ C.G.S.)

Afternoon.												Range.	Sum of 24 differences from mean.	
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.			
− 17	+18	+31	+29	+ 33	+ 31	+ 30	+ 21	+16	+10	+ 3	0	65	442	January (1891 to 1900).
− 38	0	+31	+46	+ 48	+ 43	+ 34	+ 27	+21	+15	+ 8	+10	102	566	February ,,
−101	−44	+13	+58	+ 66	+ 62	+ 59	+ 51	+46	+38	+26	+19	199	1012	March ,,
−140	−67	− 1	+37	+ 63	+ 79	+ 81	+ 71	+60	+50	+43	+33	252	1314	April ,,
−154	−78	+ 1	+52	+ 91	+105	+100	+ 92	+75	+58	+48	+36	314	1734	May ,,
−110	−48	+ 4	+53	+ 90	+100	+107	+101	+78	+56	+36	+24	265	1360	June ,,
−136	−69	0	+60	+105	+118	+117	+103	+91	+68	+48	+31	283	1535	July ,,
−115	−47	+21	+61	+ 79	+ 83	+ 69	+ 60	+52	+39	+28	+20	233	1256	August ,,
− 96	−37	+15	+53	+ 66	+ 62	+ 64	+ 56	+49	+41	+34	+25	204	1161	September ,,
− 72	−38	+19	+45	+ 49	+ 46	+ 42	+ 41	+43	+39	+28	+20	152	827	October ,,
− 16	+18	+39	+42	+ 37	+ 28	+ 23	+ 17	+14	+ 7	0	− 3	93	451	November ,,
− 17	+ 4	+16	+25	+ 23	+ 20	+ 15	+ 10	+ 6	+ 6	+ 6	+ 5	58	296	December ,,
− 84	−32	+16	+47	+ 63	+ 65	+ 62	+ 54	+46	+36	+26	+18	179	948	Mean for year (1891 to 1900).

Table XV.—Diurnal Inequality of Northern

	Forenoon.											
Hour	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
December (1890 to 1900)	0	− 1	+ 9	+26	+37	+47	+52	+40	+ 14	− 37	− 75	− 78
March ,, ...	+57	+58	+57	+58	+76	+83	+76	+35	− 52	−141	−204	−207
June ,, ...	+54	+47	+49	+58	+67	+38	−14	−79	−146	−203	−222	−197
Mean for year (1890 to 1900)	+54	+48	+51	+57	+65	+59	+37	−14	− 86	−160	−194	−180
,, ,, (1890, 1899, 1900). . .	+41	+35	+41	+45	+53	+44	+27	−13	− 72	−128	−155	−137
,, ,, (1892 to 1895)	+68	+65	+66	+73	+85	+79	+48	−15	−105	−197	−244	−231

Table XVI.—Diurnal Inequality of Western

	Forenoon.											
Hour	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
December (1890 to 1900)	−31	−17	−10	− 5	− 3	− 11	− 19	− 31	− 40	− 11	+31	+ 77
March ,, ...	−37	−34	−42	−52	− 48	− 63	−101	−175	−201	−135	+10	+168
June ,, ...	−24	−40	−53	−93	−169	−244	−284	−292	−248	−132	+22	+185
Mean for year (1890 to 1900)	−33	−36	−40	−54	− 78	−110	−145	−175	−168	− 90	+35	+162
,, ,, (1890, 1899, 1900). . .	−22	−24	−30	−43	− 64	− 91	−121	−147	−137	− 67	+41	+152
,, ,, (1892 to 1895)	−41	−45	−52	−66	− 95	−135	−174	−210	−203	−116	+26	+176

Table XVII.—Diurnal Inequality of Total

	Forenoon.											
Hour	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
December (1890 to 1900)	0	0	+ 2	+11	+16	+15	+12	+ 3	− 18	− 45	− 53	− 49
March ,, ...	+32	+28	+22	+20	+27	+27	+28	+ 1	− 65	−141	−186	−177
June ,, ...	+26	+14	+14	+16	+19	− 9	−42	−91	−150	−200	−225	−190
Mean for year (1890 to 1900)	+27	+19	+17	+19	+22	+14	0	−34	− 88	−145	−171	−153

Component. (Unit = $0{\cdot}1\gamma \equiv 1 \times 10^{-6}$ C.G.S.)

Afternoon.												Range.	Sum of 24 differences from mean.	
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.			
− 60	− 47	−30	−11	+ 1	+ 19	**+ 26**	+ 23	+ 18	+14	+16	+ 2	130	683	December (1890 to 1900).
−165	−111	−52	−12	+ 8	+ 34	+ 64	+ 69	+ 65	+67	**+70**	+65	290	1886	March ,,
−160	− 90	−26	+17	+69	+114	**+140**	+128	+116	+90	+77	+67	362	2268	June ,,
−140	− 87	−38	− 2	+34	+ 63	**+ 81**	+ 80	+ 77	+68	+66	+60	275	1801	Mean for year (1890 to 1900).
− 96	− 52	−17	+ 2	+25	+ 46	**+ 63**	+ 59	+ 55	+47	+46	+44	218	1343	,, ,, (1890, 1899, 1900).
−185	−121	−56	− 5	+43	+ 81	+ 99	**+101**	+ 98	+87	+87	+79	345	2318	,, ,, (1892 to 1895).

Component. (Unit = $0{\cdot}1\gamma \equiv 1 \times 10^{-6}$ C.G.S.)

Afternoon.												Range.	Sum of 24 differences from mean.	
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.			
+107	+ 85	+ 65	+ 38	+ 15	+ 5	−10	−31	−48	**−56**	−50	−50	163	846	December (1890 to 1900).
+255	**+257**	+187	+ 92	+ 28	+12	0	− 6	−18	−28	−31	**−38**	458	2018	March ,,
+263	**+279**	+242	+184	+123	+91	+65	+50	+39	+36	+ 9	−10	571	3177	June ,,
+226	+217	+163	+ 97	+ 52	+30	+20	+ 6	− 5	−16	−24	−34	401	2016	Mean for year (1890 to 1900).
+201	+181	+122	+ 64	+ 29	+14	+ 9	0	− 9	−15	−19	−24	348	1626	,, ,, (1890, 1899, 1900).
+259	+258	+204	+130	+ 74	+47	+31	+12	− 3	−13	−26	−37	469	2433	,, ,, (1892 to 1895).

Force. (Unit = $0{\cdot}1\gamma \equiv 1 \times 10^{-6}$ C.G.S.)

Afternoon.												Range.	Sum of 24 differences from mean.	
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.			
− 25	− 4	+11	+23	+ 24	**+ 26**	+ 22	+ 14	+ 7	+ 4	+ 5	0	79	389	December (1890 to 1900).
−120	−52	+14	+60	+ 65	+ 69	**+ 77**	+ 71	+ 63	+54	+44	+37	263	1480	March ,,
−130	−45	+21	+77	+121	+144	**+158**	+145	+120	+92	+65	+48	383	2162	June ,,
−103	**−37**	+19	+54	+ 77	+ 87	**+ 89**	+ 80	+ 70	+56	+46	+35	260	1462	Mean for year (1890 to 1900).

Declination.

§ 22. A remark applicable to most if not all of the diurnal inequalities is that turning points, whether maxima or minima, which occur near noon are much less variable in the time of their appearance than those which occur early or late in the day. A particularly good instance of this is afforded by the chief maximum in D. It will be seen in Table XI. that the largest hourly value appears at 1 P.M. in 11 out of the 12 months. The uniformity in the time of appearance of the maximum is perhaps even better shown in the curves in fig. 2, which represent the D inequality for December, March and June. In the 6 months, October to March, the D inequality shows two distinct maxima and minima, and in every month of the year, with the exception of September, Table XI. shows at least a suggestion of a second maximum and minimum.

There is in all months a well marked morning minimum which, except in January and December, is the chief minimum of the day. Its time of occurrence shows a pronounced seasonal change, varying from 7 A.M. in summer to 9 A.M. in winter. This is well brought out in fig. 2, which also shows the rapid swing from east to west between 9 A.M. and 1 P.M. so characteristic of the declination needle. It would require a very large number of years' records, and possibly the employment of greater sensitiveness, to settle definitely the times of occurrence of the second maximum and minimum, and to place their occurrence or non-occurrence in summer in a position of certainty.

In the mean inequality for the year, we have the somewhat curious phenomenon of a maximum and minimum presenting themselves at adjacent hours, viz., 1 A.M. and midnight. As this occurs in the inequalities for the two sub-groups of years, as well as in that for the whole period, it is presumably a natural phenomenon.

It will be noticed that though the amplitudes of the mean inequalities for the year are widely different for the two groups of years, the hours of occurrence of the maxima and minima are alike. A minute comparison of the figures shows, however, a slight tendency for definite features of the inequality to be later in the day in the case of the second group of years (sun-spot maximum). More definite evidence in this point is adduced later (see § 46).

The month of the year in which the amplitude of the inequality is least is unmistakably December, but the ranges for January, February and November are also very small. There is a very rapid increase of range in March, and correspondingly rapid decrease in October, whilst in the six months April to September there is comparatively little change. The sum of the 24 hourly differences, however, is decidedly less for April and September than for the four mid-summer months. The range appears slightly larger in May and August than in June and July, so that the annual variation of the range seemingly presents two nearly equal maxima, respectively in early and late summer, with an intermediate inconspicuous minimum at midsummer, and a very prominent minimum at midwinter.

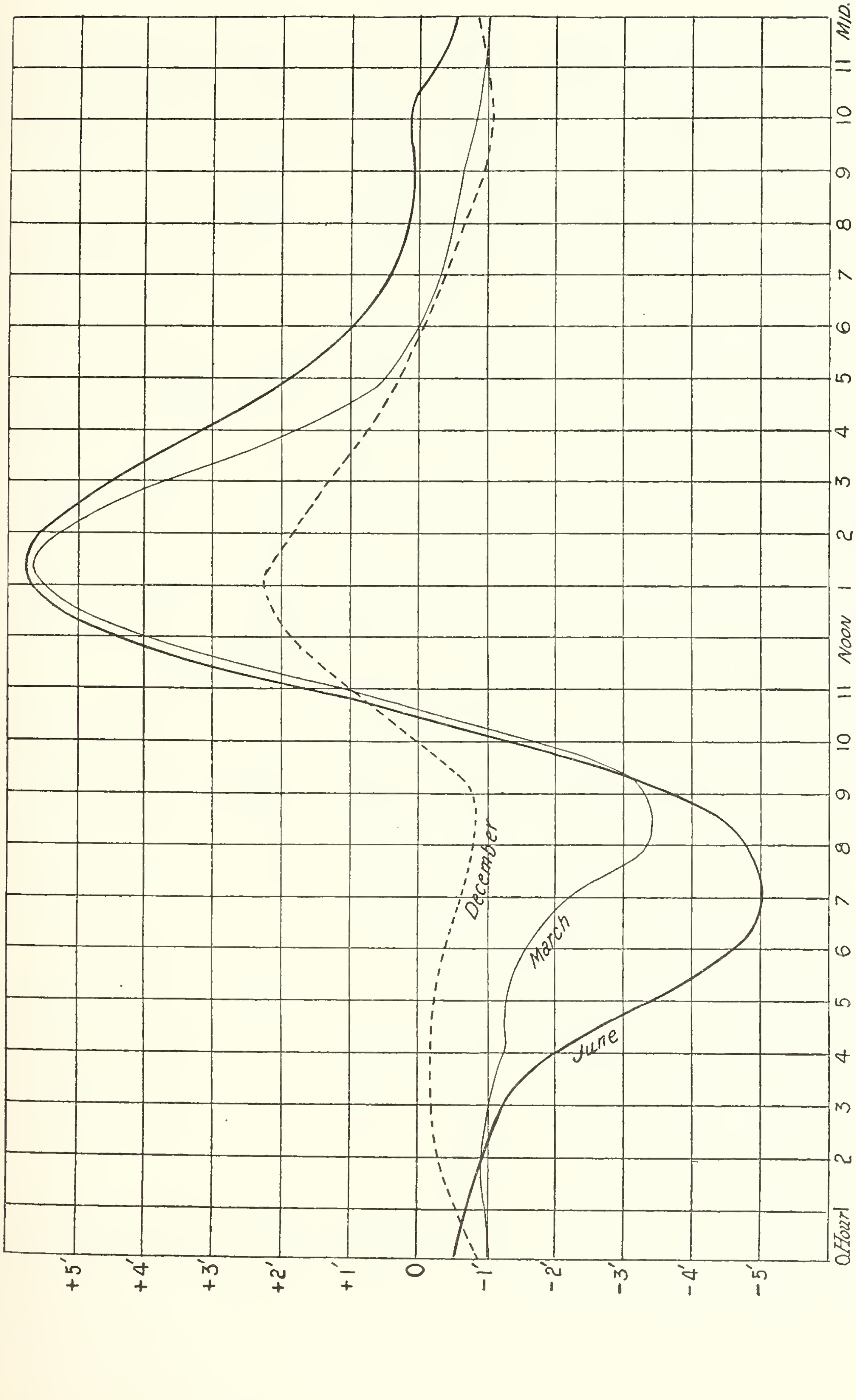

Fig. 2. Diurnal inequality of declination.

Inclination.

§ 23. The most distinct phenomenon in the diurnal inequality (see Table XII. and fig. 3) is the maximum between 9 and 11 A.M., its occurrence being earlier in summer than in winter. It is difficult to speak with certainty as to the number of maxima and minima in several months. In the 5 months April to August, there appears to be only one maximum and minimum, the latter occurring between 7 and 9 P.M.

In most of the other months there are at least two distinct maxima and minima, and sometimes suggestions of a third pair (see fig. 3). In the six months October to March, the principal minimum of the day is found in the morning between 5 and 7 A.M.

In the late evening the value is so nearly stationary in most months, that a very long series of observations might be necessary to elucidate the exact details.

The mean inequality for the year shows clearly only one maximum (at 10 A.M.), and one minimum (at 7 P.M.); but from 1 to 5 A.M. the value is practically stationary.

As regards the range, the phenomena are similar to those noted in the declination, but the existence of two maxima in summer with an intervening minimum is far from clearly shown. The minimum in December is very strongly marked.

The sum of the 24 differences also shows the December minimum clearly, but the value increases uniformly, though slightly from May to August.

Horizontal Force.

§ 24. Here two distinct maxima and minima appear in the 6 winter months, October to March, but only one is *clearly* shown in the summer months. In the mean inequality for the year two maxima and minima are distinctly recognisable.

Of the turning points the forenoon minimum is the best marked (*cf.* fig. 4). Its time of occurrence varies only from about 10 to 11 A.M., being earlier in summer than in winter. The afternoon maximum is less prominent, especially in winter, but is on the whole fairly definite. In summer and at midwinter it appears about 7 P.M., but in some of the equinoctial and winter months it is an hour, or even two, later.

The range and the sum of the 24 hourly differences from the mean both show a conspicuous minimum in December. In the 4 midsummer months it is now the sum of the 24 differences that shows two maxima and an intermediate badly-defined minimum. The range shows only one maximum, in June. The variation, however, in both cases is so small, from May to August, that the exact nature of the phenomena remains open to doubt.

Vertical Force.

§ 25. Here the principal minimum presents itself in the late forenoon. In the summer months the smallest hourly value usually occurs at noon; in the winter months it occurs earlier, usually at 11.

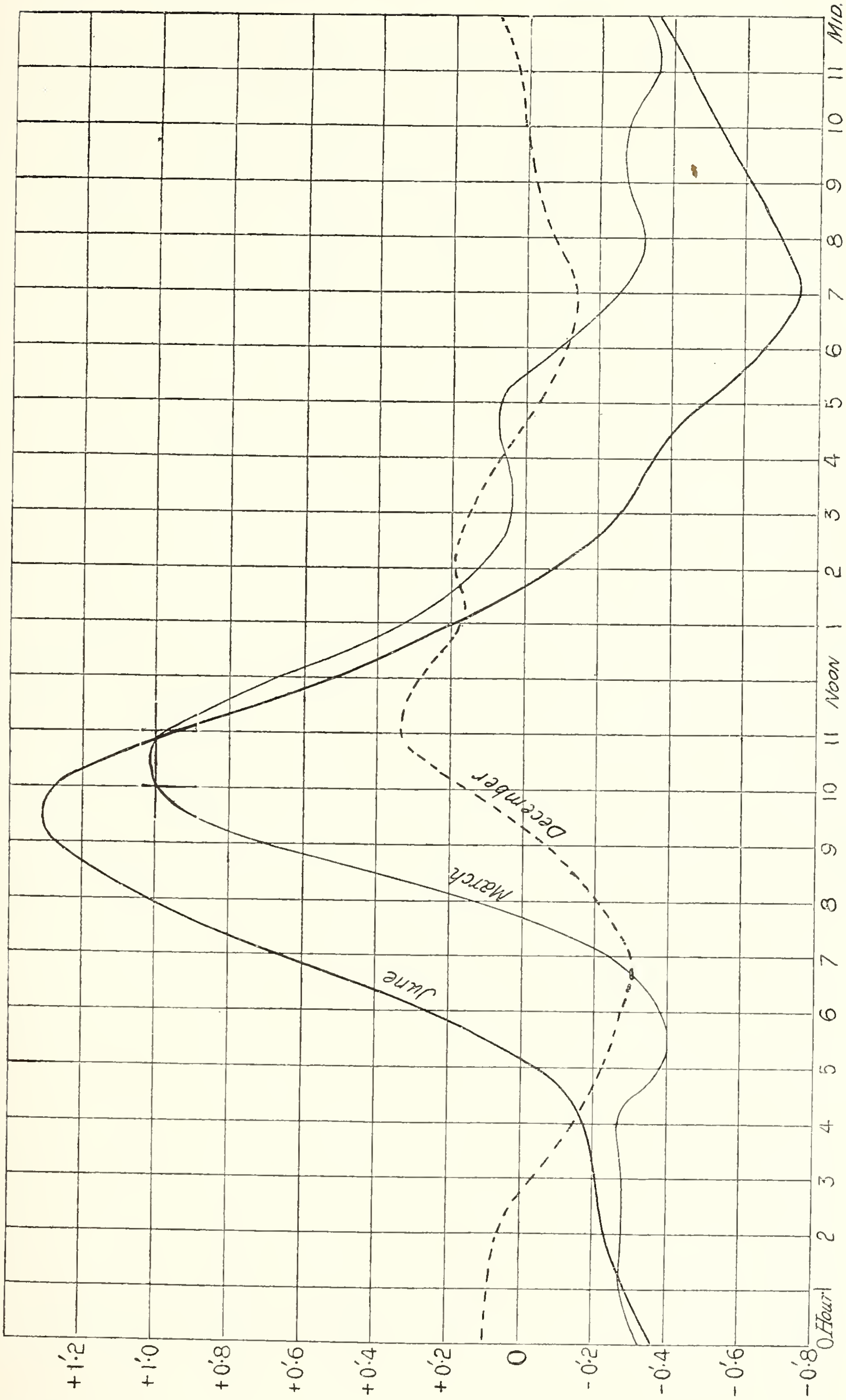

Fig. 3. Diurnal inequality of inclination.

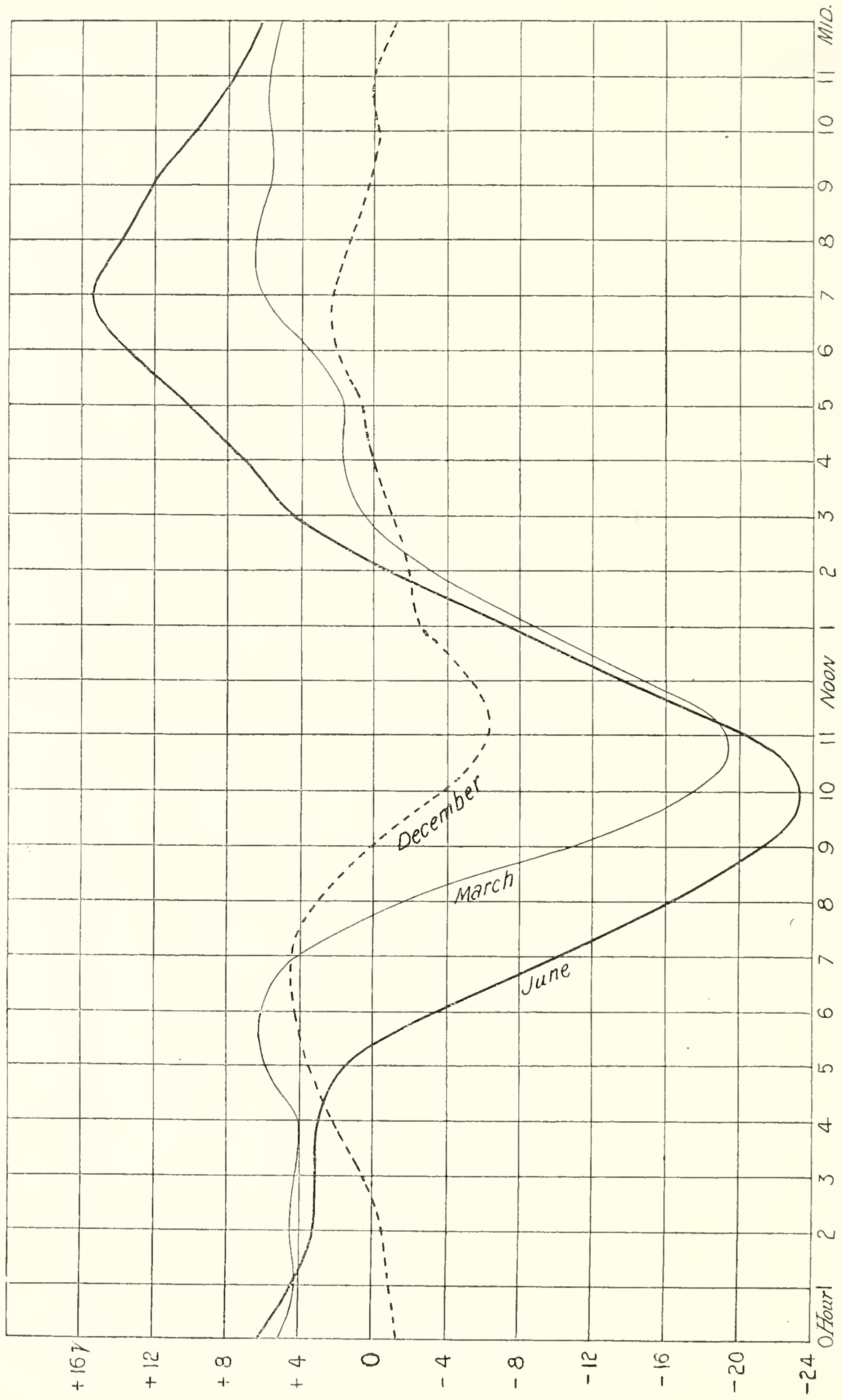

Fig. 4. Diurnal inequality of horizontal force.

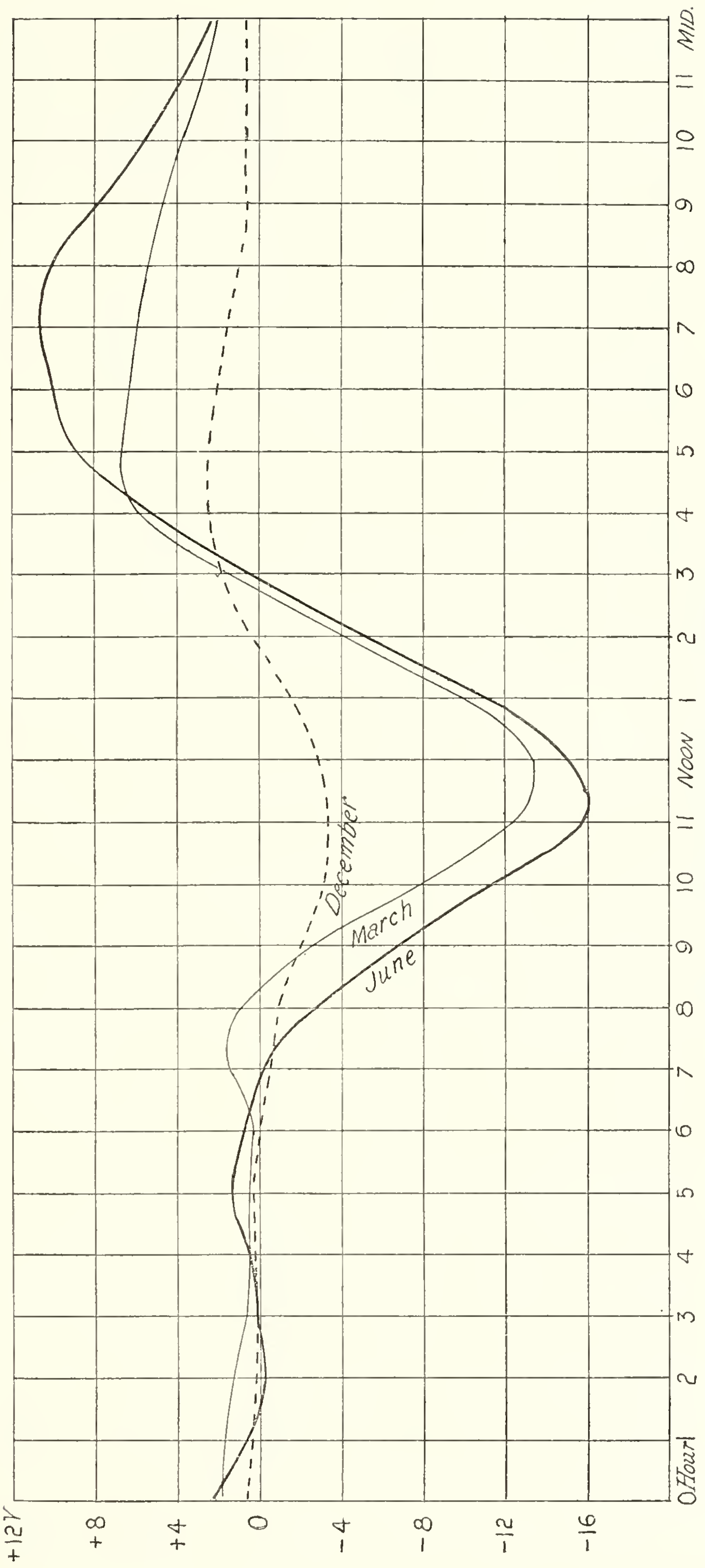

Fig. 5. Diurnal inequality of vertical force.

The principal maximum is found in the afternoon; the time varies from 4 to 7 P.M., and, as with the minimum, is earlier in winter than in summer (see fig. 5).

Normally there would seem to be 2 maxima and minima, the second maximum and minimum occurring in the early morning within a few hours of one another. This is shown, though faintly, even in the mean inequality for the year. In the winter months, however, the values in the earlier morning hours become so nearly stationary that the true nature of the phenomena is uncertain.

The ranges and the sum of the 24 hourly differences from the mean both show two maxima in summer, in May and July, the intervening minimum being more clearly marked than in the other elements. The winter minimum in December, on the other hand, is somewhat less clearly marked than in H or I.

Northerly and Westerly Components.

§ 26. All the months included in Table XV. show 2 maxima and minima in the diurnal inequality of N, and the same is true of the mean inequality for the year (*cf.* fig. 6). As with H, the most conspicuous turning point is the forenoon minimum; but its time of occurrence is an hour or so later than in H, varying from 11 A.M. to noon. In December and March the forenoon maximum is the larger; but in June, and in the mean inequality for the year, the afternoon maximum—occurring usually at 7 or 8 P.M.—is decidedly the larger of the two. The early morning minimum, though not very conspicuous, seems to have a very uniform time of occurrence.

The phenomena met with in the case of W (Table XVI., fig. 6) naturally resemble those met with in D. The maximum at 1 or 2 P.M., and the minimum at 8 or 9 A.M., are somewhat later than the corresponding turning points in the declination. In June there is no trace of a second maximum and minimum, and in the mean inequality for the year their presence is at least doubtful. In December the evening minimum is the more prominent of the two.

Total Force.

§ 27. The diurnal inequality of T (see Table XVII., figs. 6 and 7) shows 2 maxima and minima, of which the afternoon maximum at 6 or 7 P.M. and the forenoon minimum at about 11 A.M. are the most important. The early morning maximum and minimum occur pretty close together, and their difference is generally small.

The T inequality curves appear exceptionally regular, which is hardly what one would have expected, considering that variations in both H and V are involved.

From a mathematical standpoint, T is most naturally regarded as the resultant of W, N, and V, and so mean inequalities for the year for these elements are shown alongside of the corresponding inequality for T in fig. 6.

It will be observed in Tables XI. to XVII. that the range and the sum of the 24 differences in March generally resemble closely the corresponding quantities from the

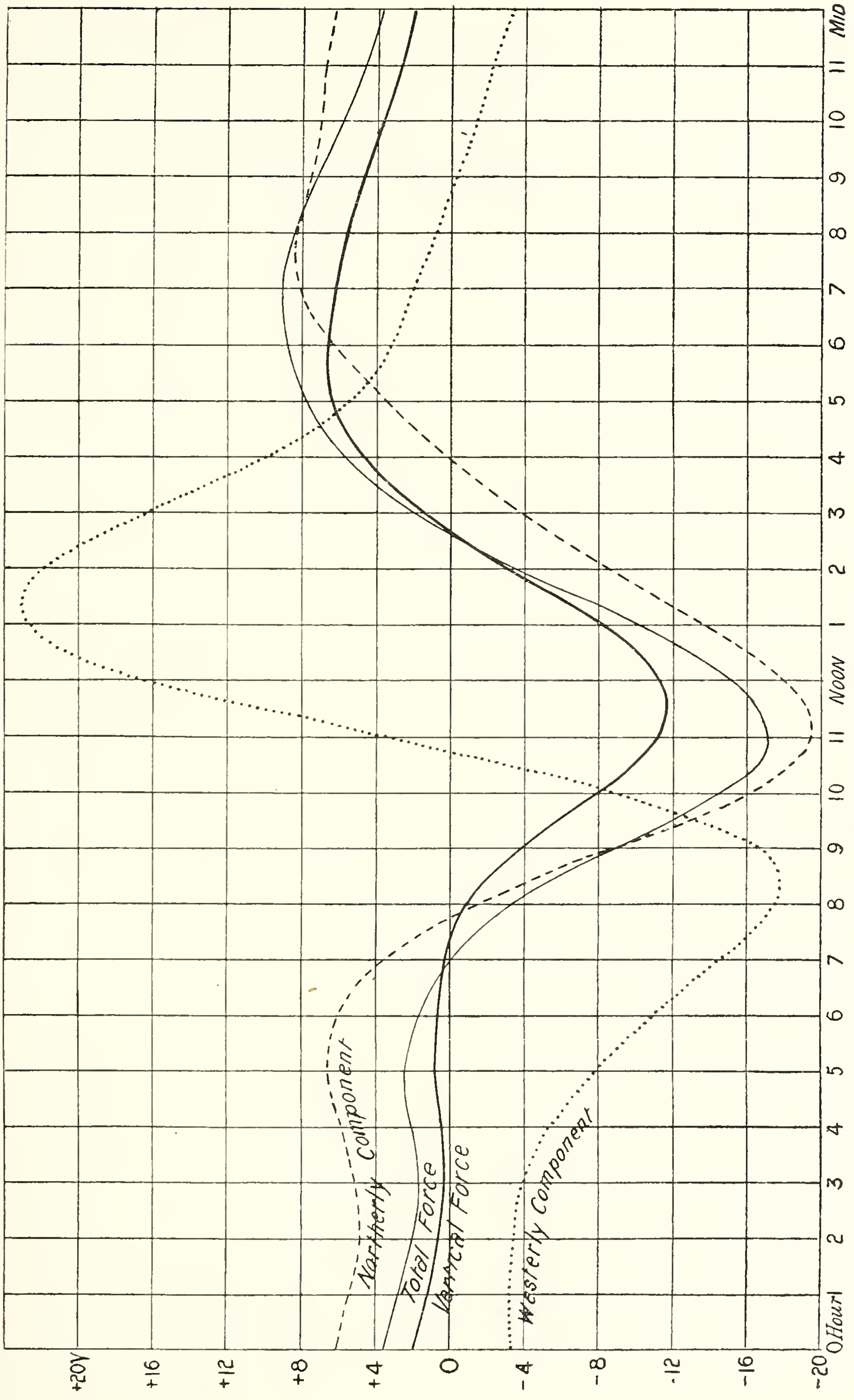

Fig. 6. Mean diurnal inequality for year.

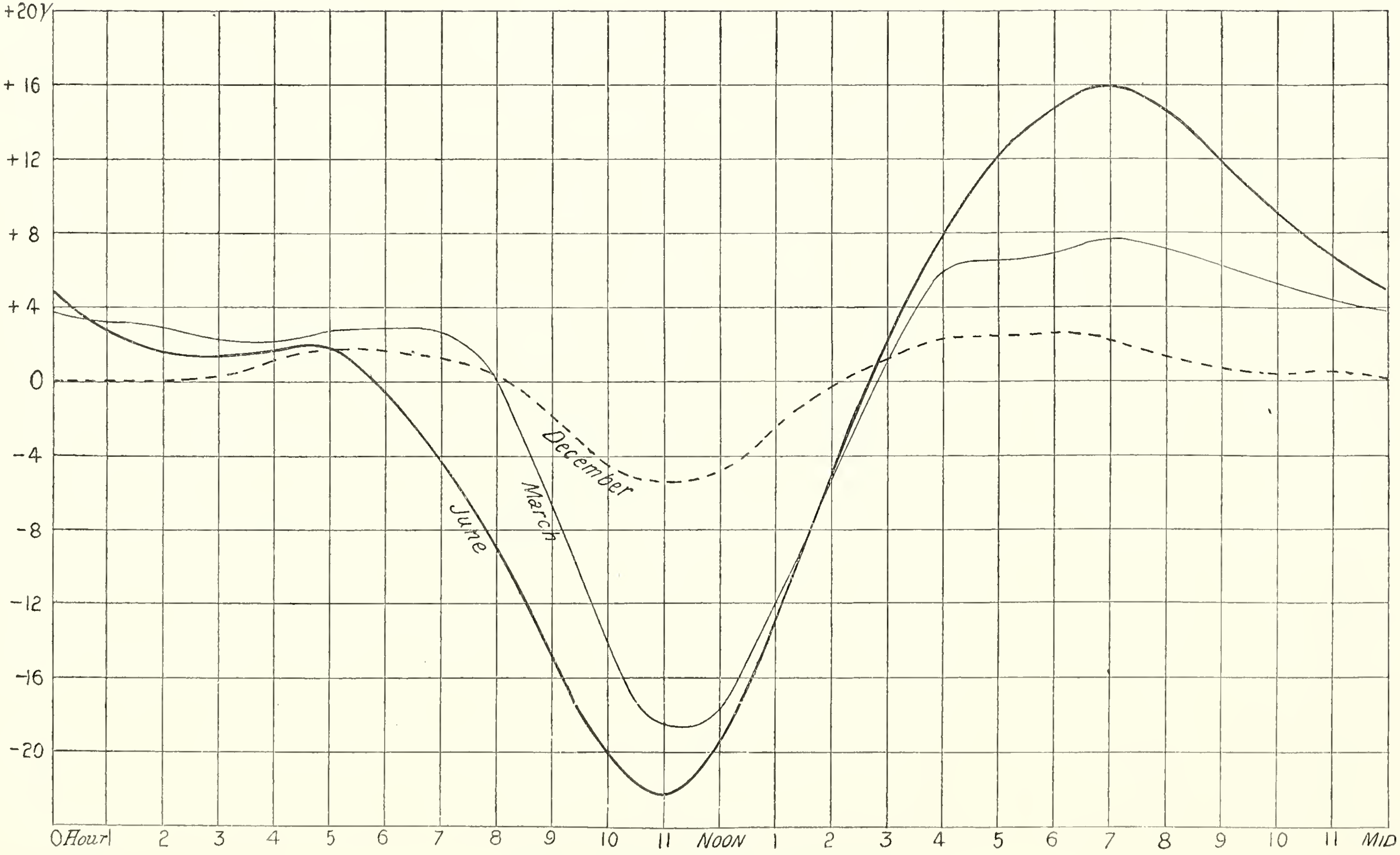

Fig. 7. Diurnal inequality of total force.

mean inequality for the year. In fact, the data from March give a better general idea of the phenomena than those from any other month.

§ 28. To facilitate comparison of the law of variation throughout the year of the range and the sum of the 24 differences in the diurnal inequalities of D, I, H, and V, I give a synopsis of the whole of the data in Table XVIII. Here each quantity dealt with is expressed as a percentage of its mean value for the 12 months. This enables us to see more readily points of agreement and difference. It will be observed that there is a close resemblance between the annual variations in D, I, and H, and that the mean of the results from these three elements for the range and for the sum of the 24 differences are very similar. On the whole, the sum of the 24 differences has the more accentuated annual variation.

The annual variation seems somewhat greater in V than in the other elements, the maximum in May being exceedingly prominent.

TABLE XVIII.—Monthly Relative Values. (100 ≡ Mean from 12 Months.)

	Range.					Sum of 24 differences from mean.				
	D.	I.	H.	V.	Mean of D, I, H.	D.	I.	H.	V.	Mean of D, I, H.
January . . .	51	62	54	35	55	57	49	40	44	49
February . . .	59	64	59	55	61	74	61	54	57	63
March	110	87	91	108	96	106	88	92	102	96
April	132	118	127	136	126	120	123	132	132	125
May	136	130	135	170	134	128	132	143	174	134
June	132	128	137	143	132	136	134	140	137	137
July	127	130	136	153	131	128	135	144	154	136
August . . .	137	136	134	126	136	132	139	138	126	136
September . .	122	125	123	110	123	117	121	120	117	119
October . . .	93	99	96	82	96	94	105	102	83	100
November . .	59	80	71	50	70	64	78	66	45	69
December . .	42	40	37	31	40	44	35	29	30	36

§ 29. Figs. 2 to 7 should give an adequate pictorial idea of the general character of the diurnal inequality in individual elements.

A more complete idea of the phenomenon as a whole can be obtained from two other types of curves. The first type, commonly known as the "vector diagram," has been used by LLOYD, AIRY and others. It represents the variation throughout the 24 hours of the disturbing force to which may be ascribed the changes in the horizontal component of magnetic force. The radius vector from a fixed point represents the horizontal component of the disturbing force in magnitude and direction. When inequalities for N and W have been calculated, the simplest way to draw the diagram is to take the hourly values of the N and W inequalities as co-ordinates, employing rectangular axes, one in, the other perpendicular to, the astronomical meridian. This has been done in drawing the vector diagrams for December, June, March and the whole year—all for the entire period 1890 to 1900—which are represented in figs. 8 to 11.

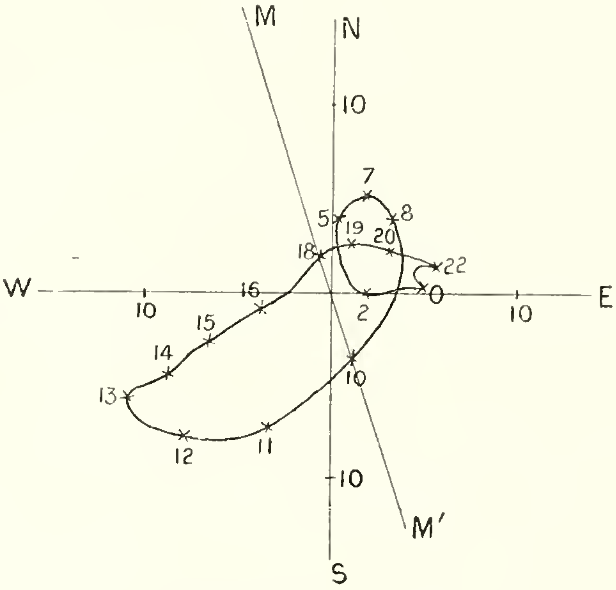

Fig. 8. December.

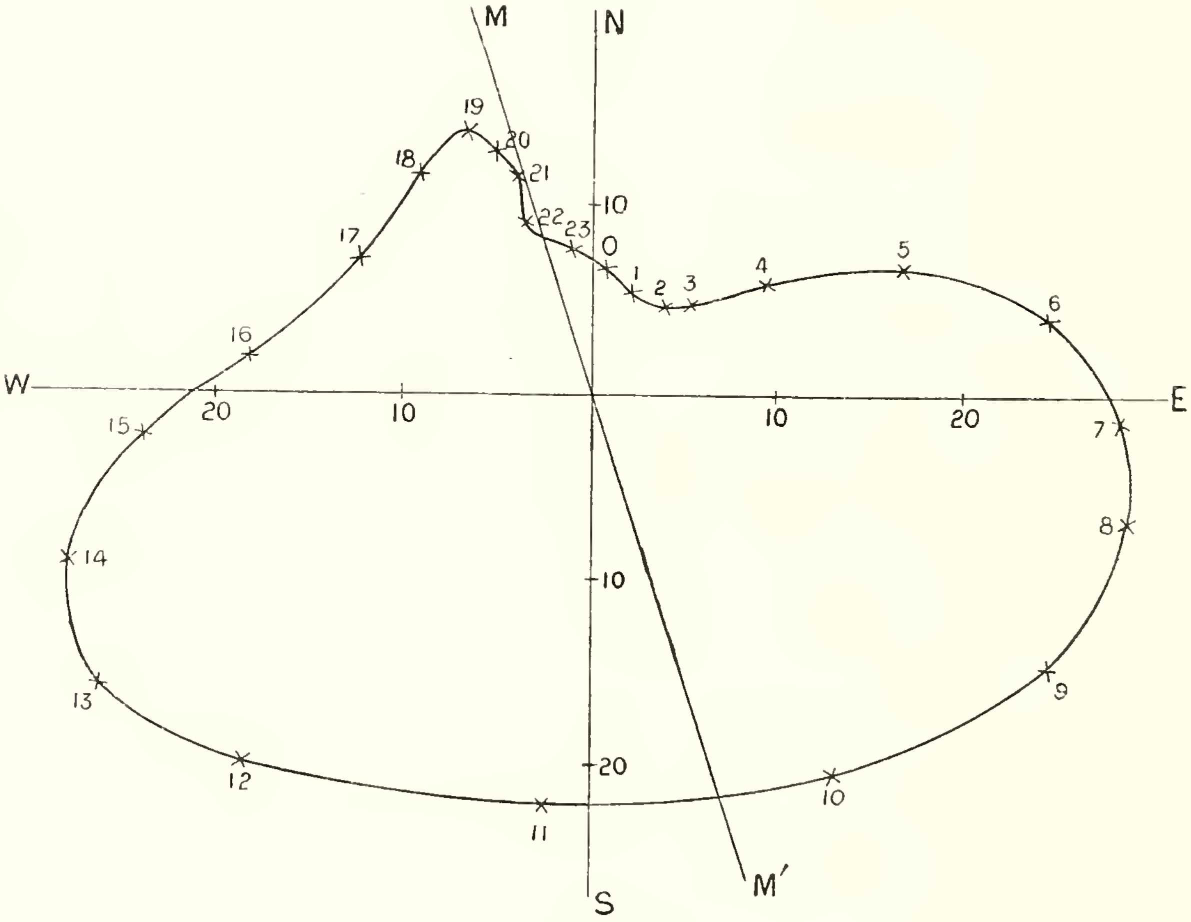

Fig. 9. June.

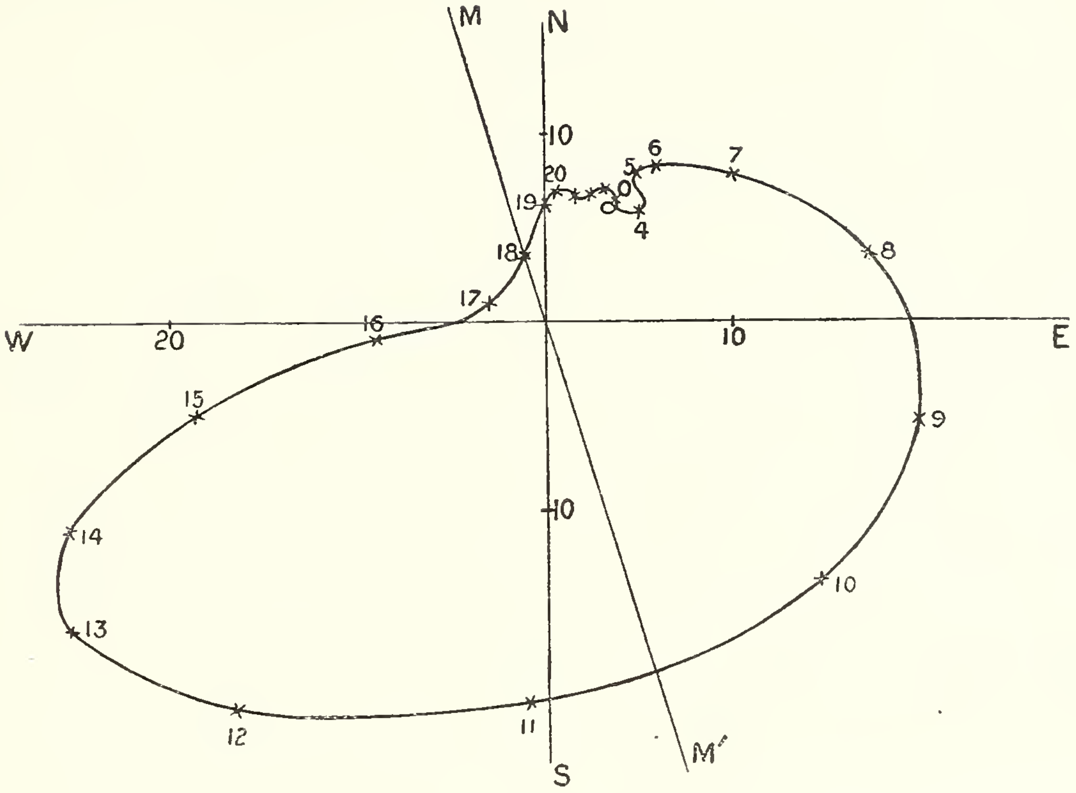

Fig. 10. March.

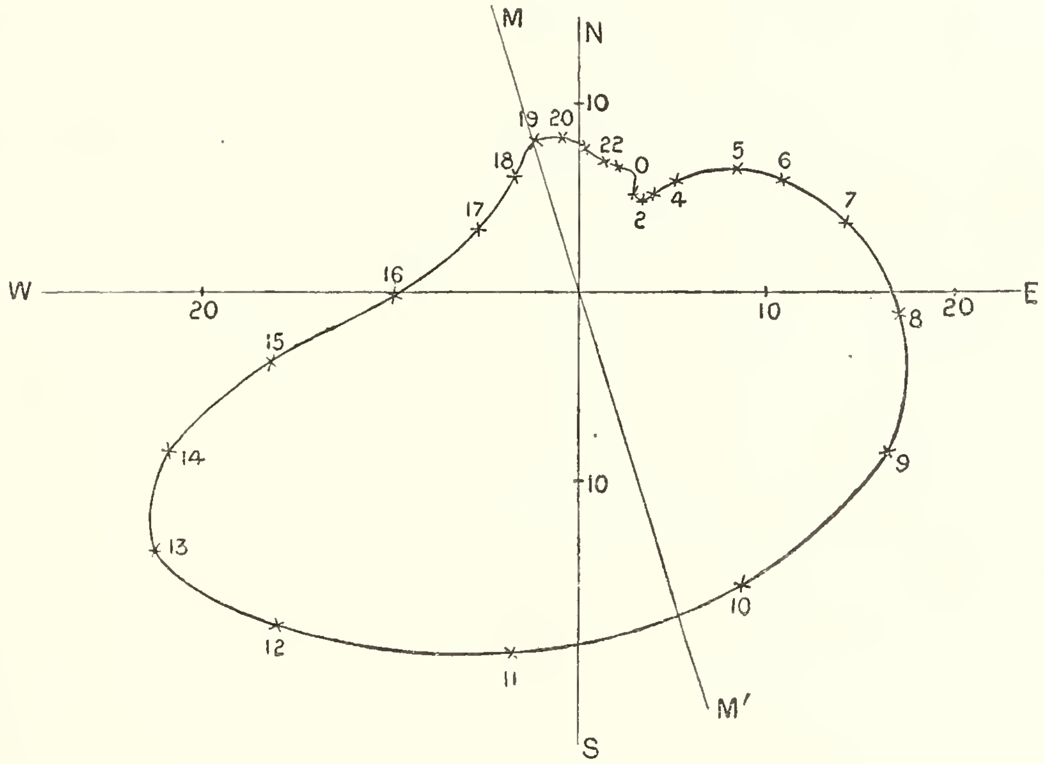

Fig. 11. Year.

In all the figures, NS represents the astronomical meridian, MM′ the mean magnetic meridian for the period, the two being inclined at an angle of 17° 18′·8. The hours to which the individual observations refer are shown in the figures, all being reckoned from midnight as 0.

When N and W inequalities are not available, the vector diagram can be readily constructed by taking axes in and perpendicular to the magnetic meridian, employing for co-ordinates δH and δD, the latter converted into absolute measure. This was the method which I employed in the 'B. A. Report' for 1895.

The difference between the vector diagrams for December and June is very striking, the area described by the radius vector in the latter curve being about 16 times that described in the former. The diagram for March pretty closely resembles that for the whole year, but encloses a somewhat larger area. In December the portion of the curve answering to the hours near midnight forms a regular closed loop—also seen in other midwinter months. The March curve shows a very tiny loop, and forms a transition to the June curve, where no loop appears, though the portion of the curve answering to the hours from 7 or 8 P.M. to 3 A.M. is still markedly indented.

The longest radius vector, and so the largest value of the disturbing force, answers to about 1 P.M. in all the curves. The shortest radius vector answers either to about 2 A.M. or 5 P.M. In all the curves the radius vector passes through astronomical south between 10 and 11 A.M., the time of crossing being somewhat earlier in December than in March or June.

§ 30. The second form of curve, illustrated by figs. 12 to 15, shows the change throughout the day in the direction of an imaginary magnet freely suspended as described in § 8. The curve may be supposed drawn by a style carried by the dipping end of the magnet, on a plane perpendicular to the mean position of the magnet throughout the day. MM′ is the trace of the *magnetic* meridian in this plane.

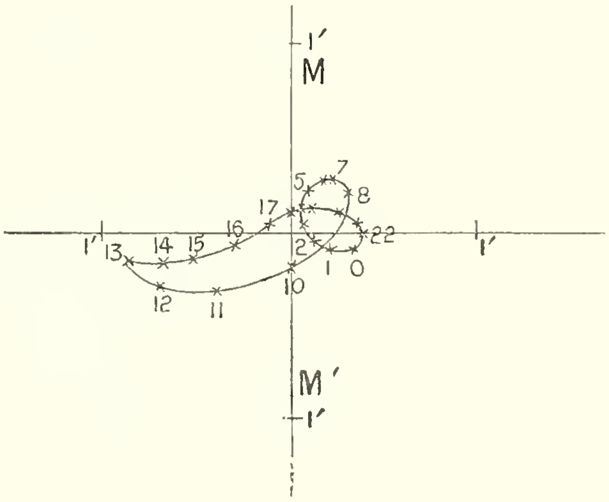

Fig. 12. December.

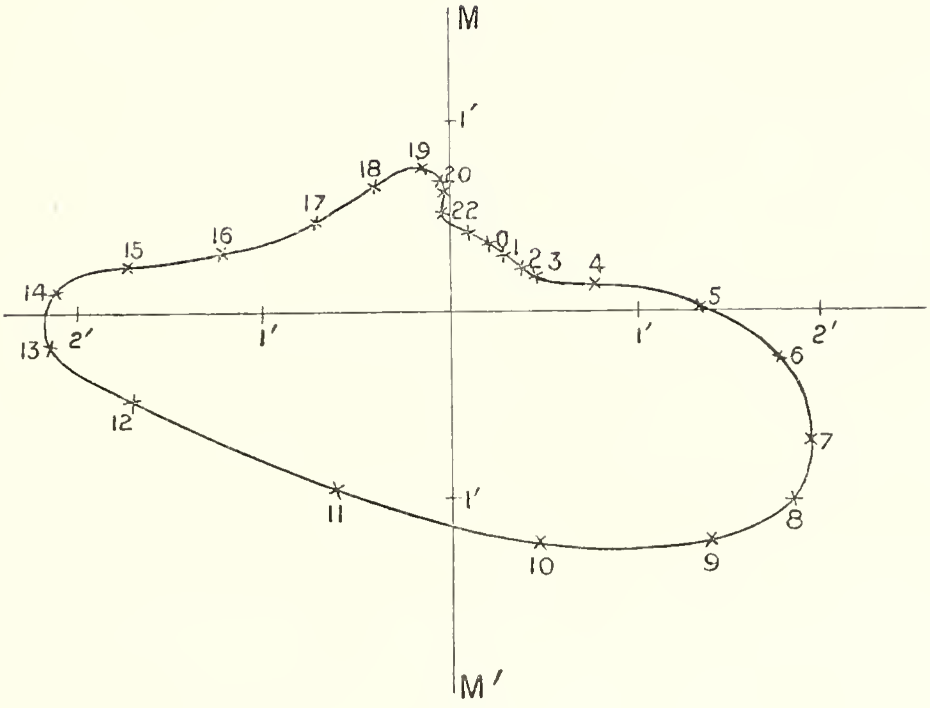

Fig. 13. June.

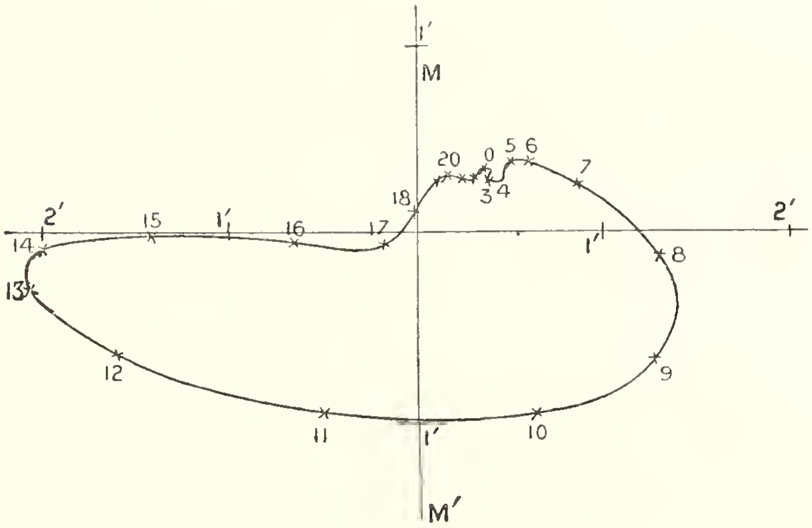

Fig. 14. March.

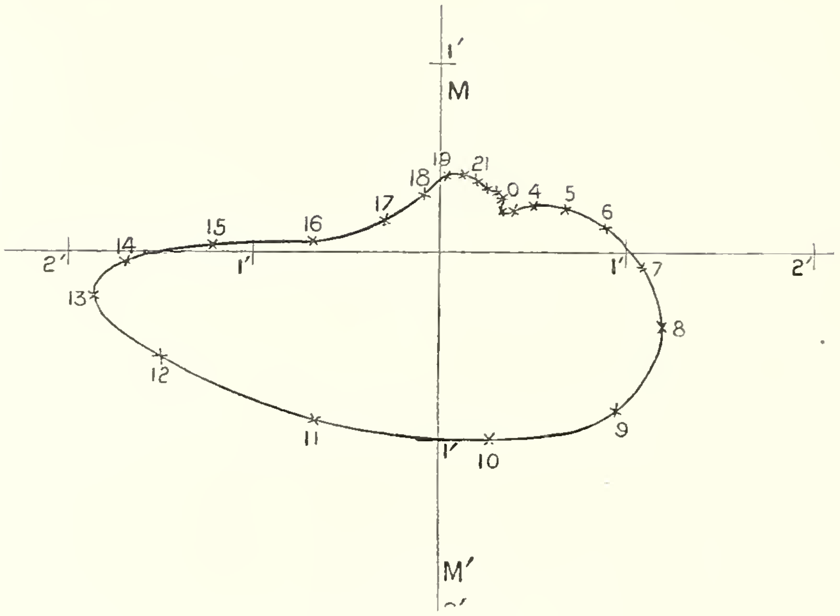

Fig. 15. Year.

The curve is really drawn from Cartesian co-ordinates, δI parallel to MM′, and $\cos I\ \delta D$ (or here $\cdot 385\ \delta D$) perpendicular to MM′. Increasing I answers to movement towards the foot of the paper, increasing D to movement towards the reader's left hand. The hours are counted and marked as in figs. 8, 9, 10 and 11, to which the figures now under discussion bear a general resemblance.

The angular distance of the needle from its mean position for the day is seen to be greatest about 1 P.M., though in June the distance at 8 A.M. is nearly as great. The approach to the mean position is closest shortly after midnight, or else about 5.30 P.M.

The movement perpendicular to the magnetic meridian is considerably larger than that in the meridian. The curves for March and for the year are oriented, so to speak, approximately magnetic east and west. The orientations of the June and December curves are almost equally inclined to this direction, but on opposite sides.

The curves of the second type were employed by the late Admiral CAPELLO in a paper in the 'B. A. Report' for 1898, p. 750, dealing with diurnal inequalities at a variety of stations. They were also used by Sir A. RÜCKER in a Rede Lecture to illustrate the actual motion of a freely suspended needle on a magnetic quiet day, showing the average non-cyclic effect experienced at Kew. In the present case the curves of both types answer to the strictly *periodic* part of the diurnal motion.

Analysis of Diurnal Inequality in Fourier Series.

§ 31. The diurnal inequality of an element may be expressed in either of the two equivalent forms

$$a_1 \cos t + b_1 \sin t + a_2 \cos 2t + b_2 \sin 2t + \ldots,$$

$$c_1 \sin (t + \alpha_1) + c_2 \sin (2t + \alpha_2) + \ldots$$

where t represent G.M.T. counted from the first midnight of the day, an hour being taken as equivalent to 15°; whilst a_1, b_1, c_1, α_1 . . . are constants. Between the constants of the two expressions there exist the relations

$$\alpha_n = \tan^{-1}(a_n/b_n), \quad c_n = \sqrt{a_n^2 + b_n^2}.$$

The constants with suffix n occur in terms in which the period is $24/n$ hours. The periods of the terms in the above expressions are respectively 24, 12, 8, 6 hours. In a previous paper dealing with Kew data I explained that terms with periods shorter than 6 hours were so small as to be of little account, and similar conclusions have been reached elsewhere. Thus attention will be confined to the first four periods. The values of a_n, b_n have been found by calculation from the well known formulæ; the values so obtained are, it should be noticed, independent of whether terms of the higher orders are neglected or not.

The data employed in the calculations refer to G.M.T. If results are wanted relating to local solar time, all that is necessary is the application of a table of corrections to the values found for the angles α_1, α_2, &c. In the case of α_1, the correction simply represents the angular equivalents of the equation of time and the longitude of the place of observation. The corrections to α_2, α_3, and α_4 are obtained by multiplying those for α_1 by 2, 3, and 4 respectively. The corrections for the individual months and seasons of the year applicable to Kew are given in Table XIX. They represent the mean of the results given in the 'Greenwich Magnetical and Meteorological Observations' for the four years 1892 to 1895, with the addition required to allow for the longitude of Kew, viz., 19′ W. The corrections to α_1—omitting of course the 19′—are in close agreement with corresponding results given by General STRACHEY,* there being sensible differences only in August and September. In these months, however, they are in good agreement with results given more recently by ANGOT.†

There are probably for a mean year errors of 1′ in the values of α_1 in the table, and these of course multiply up for α_2, α_3, and α_4; but the results are probably sufficiently exact for all practical purposes.

For the seasons, the use of local solar time fortunately makes but little difference; but in several months, notably February and November, the distinction between local solar time and G.M.T. is very appreciable.

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* 'Phil. Trans.' A, for 1893, p. 646.

† 'Ann. du Bureau Central Météorologique de France,' 1899, "Mémoires," p. B. 98.

Table XIX.—Corrections to be applied to Angles in Fourier Expansions when G.M.T. replaced by Kew Solar Time.

Angle	α_1.	α_2.	α_3.	α_4.
January	+2° 42′	+5° 24′	+ 8° 6′	+10° 48′
February.	+3 48	+7 36	+11 24	+15 12
March	+2 28	+4 56	+ 7 24	+ 9 52
April	+0 20	+0 40	+ 1 0	+ 1 20
May	−0 33	−1 6	− 1 39	− 2 12
June	+0 25	+0 50	+ 1 15	+ 1 40
July	+1 41	+3 22	+ 5 3	+ 6 44
August	+1 15	+2 30	+ 3 45	+ 5 0
September	−0 58	−1 56	− 2 54	− 3 52
October	−3 12	−6 24	− 9 36	−12 48
November	−3 20	−6 40	−10 0	−13 20
December	−0 40	−1 20	− 2 0	− 2 40
Year	+0 19	+0 38	+ 0 57	+ 1 16
Winter	+0 37	+1 14	+ 1 51	+ 2 28
Equinox	−0 21	−0 42	− 1 3	− 1 24
Summer	+0 42	+1 24	+ 2 6	+ 2 48

§ 32. Tables XX. to XXIII. give the values of the two sets of Fourier constants a, b, and c, α—using G.M.T.—for D, I, H, and V. Values are given for the inequalities for the several months, for the year as a whole, and for winter, equinox, and summer, each representing, as before, a group of 4 months.

The D and H results are based on the 11 years 1890 to 1900, the I and V results on the 10 years 1891 to 1900.

An a or b coefficient for a group of i months is the arithmetic mean of the a's or b's for the individual i months; but this is not in general true of the c's or α's. For instance, the arithmetic mean of the 12 values of c_1 for individual months of the year, in Table XX. is 2·371, the mean of the three values for c_1 for the three seasons is 2·356, whilst the value of c_1 from the mean inequality for the year is 2·322. The more variable the angle α throughout the season dealt with, the greater is the difference between the corresponding c for that season and the arithmetic mean of the c's for the individual months composing it.

In all probability it would require a very large number of years' data to supply smooth values for the coefficients of the 8-hour and 6-hour terms, and much weight cannot be assigned to apparent irregular fluctuations in the values of these coefficients from month to month. This is really one of the principal reasons for grouping the months into seasons. The four mid-winter months stand out rather noticeably from the two adjacent months March and October, so that separation into three seasons seems better for the present purpose than the more usual separation into two 6-month periods.

The values of the a, b, c constants were really calculated to at least one figure farther than appears in the tables, but the retention of the extra figure seemed more likely to mislead than to serve any useful purpose. It would have been more logical to have similarly restricted the values of the angles, but I have followed the example of the annual Greenwich Tables and given them to minutes. When it comes to comparing one season or one year with another, the minutes may possibly possess a real significance, but the uncertainties in the monthly data represent degrees rather than minutes.

TABLE XX.—Coefficients and Angles in Fourier Series

	Period, 24 hours.				Period, 12 hours.			
	a_1.	b_1.	c_1.	α_1.	a_2.	b_2.	c_2.	α_2.
January	−1′·18	−0′·61	1′·33	242° 40′	+0′·39	+0′·75	0′·84	27° 43′
February	−1·43	−1·06	1·78	233 38	+0·52	+0·86	1·01	31 3
March	−1·65	−1·66	2·34	224 55	+1·21	+1·59	2·00	37 12
April	−1·51	−2·29	2·75	213 26	+1·47	+1·88	2·39	38 0
May	−1·84	−2·46	3·07	216 47	+2·14	+1·50	2·61	55 3
June	−1·57	−3·03	3·42	207 24	+1·81	+1·66	2·45	47 23
July	−1·65	−2·75	3·21	210 58	+1·81	+1·57	2·39	49 0
August	−2·22	−2·23	3·15	224 55	+2·17	+1·37	2·57	57 52
September . . .	−2·11	−1·83	2·79	229 2	+1·82	+1·16	2·16	57 27
October	−1·55	−1·44	2·12	227 12	+0·94	+1·31	1·61	35 34
November . . .	−1·26	−0·72	1·45	240 26	+0·56	+0·85	1·02	33 33
December . . .	−0·99	−0·32	1·04	251 53	+0·36	+0·68	0·77	27 54
Mean of 12 monthly values . . .	−1·582	−1·700	—	—	+1·266	+1·264	—	—
Inequality for—								
Year	—	—	2·322	222 57	—	—	1·789	45 3
Winter	−1·217	−0·677	1·393	240 55	+0·458	+0·784	0·908	30 18
Equinox . . .	−1·707	−1·805	2·484	223 24	+1·358	+1·486	2·013	42 25
Summer . . .	−1·822	−2·620	3·191	214 49	+1·981	+1·523	2·499	52 27

TABLE XXI.—Coefficients and Angles in Fourier Series

	Period, 24 hours.				Period, 12 hours.			
	a_1.	b_1.	c_1.	α_1.	a_2.	b_2.	c_2.	α_2.
January	−0′·176	−0′·134	0′·221	232° 41′	+0′·219	−0′·016	0′·220	94° 17′
February	−0·283	−0·087	0·296	252 50	+0·171	+0·020	0·172	83 25
March	−0·477	+0·044	0·479	275 13	+0·212	−0·141	0·254	123 44
April	−0·651	+0·236	0·693	289 54	+0·305	−0·210	0·370	124 34
May	−0·569	+0·566	0·803	314 52	+0·099	−0·279	0·296	160 27
June	−0·560	+0·566	0·796	315 18	+0·185	−0·277	0·333	146 19
July	−0·588	+0·509	0·778	320 53	+0·179	−0·294	0·345	148 41
August	−0·656	+0·511	0·832	307 56	+0·083	−0·316	0·327	165 15
September . . .	−0·594	+0·385	0·708	302 57	+0·055	−0·317	0·322	170 6
October	−0·566	+0·075	0·571	277 32	+0·249	−0·151	0·292	121 10
November . . .	−0·363	−0·040	0·365	263 45	+0·312	−0·063	0·318	101 24
December. . . .	−0·081	−0·073	0·109	228 4	+0·189	+0·041	0·193	77 45
Mean of 12 monthly values . . .	−0·4636	+0·2132	—	—	+0·1881	−0·1670	—	—
Inequality for—								
Year	—	—	0·5103	294 42	—	—	0·2515	131 36
Winter	−0·2256	−0·0835	0·2405	249 41	+0·2225	−0·0047	0·2225	91 13
Equinox . . .	−0·5720	+0·1848	0·6010	287 54	+0·2052	−0·2046	0·2898	134 55
Summer . . .	−0·5933	+0·5382	0·8009	312 12	+0·1365	−0·2916	0·3220	154 55

Expansion of Diurnal Inequality of Declination (1890 to 1900).

Period, 8 hours.				Period, 6 hours.				
a_3.	b_3.	c_3.	α_3.	a_4.	b_4.	c_4.	α_4.	
−0′·43	−0′·18	0′·47	246° 51′	+0′·23	+0′·13	0′·27	61° 31′	January.
−0·47	−0·36	0·59	232 44	+0·17	+0·21	0·27	38 0	February.
−0·82	−0·91	1·23	222 13	+0·38	+0·35	0·52	46 48	March.
−0·94	−0·98	1·36	223 43	+0·32	+0·20	0·38	57 19	April.
−1·01	−0·44	1·10	246 41	+0·16	+0·04	0·17	76 48	May.
−0·77	−0·38	0·86	243 58	+0·05	+0·02	0·05	70 30	June.
−0·71	−0·58	0·92	230 25	−0·05	+0·19	0·20	−15 11	July.
−1·04	−0·53	1·17	243 14	+0·15	+0·12	0·19	49 42	August.
−1·08	−0·49	1·18	245 45	+0·50	+0·12	0·52	76 51	September.
−0·82	−0·57	1·00	235 9	+0·43	+0·23	0·49	61 17	October.
−0·56	−0·23	0·61	247 46	+0·30	+0·15	0·33	63 45	November.
−0·32	−0·13	0·35	248 12	+0·15	+0·10	0·18	56 24	December.
−0·748	−0·481	—	—	+0·231	+0·155	—	—	Mean of 12 monthly values.
								Inequality for—
—	—	0·889	237 16	—	—	0·278	56 8	Year.
−0·446	−0·225	0·499	243 14	+0·211	+0·146	0·257	55 19	Winter.
−0·915	−0·736	1·174	231 11	+0·407	+0·228	0·466	60 45	Equinox.
−0·883	−0·481	1·006	241 26	+0·076	+0·091	0·119	39 52	Summer.

Expansion of Diurnal Inequality of Inclination (1891 to 1900).

Period, 8 hours.				Period, 6 hours.				
a_3.	b_3.	c_3.	α_3.	a_4.	b_4.	c_4.	α_4.	
−0′·019	+0′·105	0′·107	−10° 3′	−0′·017	−0′·094	0′·095	190° 6′	January.
−0·049	+0·141	0·150	−19 5	+0·007	−0·103	0·103	175 49	February.
−0·028	+0·207	0·209	− 7 48	−0·041	−0·116	0·123	199 31	March.
−0·059	+0·193	0·202	−16 53	−0·028	−0·101	0·105	195 39	April.
+0·113	+0·112	0·159	+45 14	−0·085	−0·018	0·087	258 6	May.
+0·109	+0·117	0·159	+43 3	−0·053	−0·023	0·057	246 15	June.
+0·051	+0·134	0·143	+20 51	−0·021	−0·043	0·047	207 6	July.
+0·148	+0·181	0·233	+39 14	−0·073	−0·069	0·101	226 37	August.
+0·142	+0·241	0·280	+30 33	−0·091	−0·121	0·151	216 50	September.
−0·009	+0·210	0·210	− 2 19	−0·060	−0·120	0·134	206 36	October.
−0·033	+0·114	0·119	−16 5	−0·054	−0·073	0·091	216 26	November.
−0·021	+0·035	0·041	−30 23	−0·007	−0·029	0·030	193 3	December.
+0·0288	+0·1491	—	—	−0·0435	−0·0758	—	—	Mean of 12 monthly values.
								Inequality for—
—	—	0·1518	+10 56	—	—	0·0874	209 51	Year.
−0·0303	+0·0991	0·1036	−17 0	−0·0174	−0·0745	0·0765	193 9	Winter.
+0·0117	+0·2125	0·2129	+ 3 9	−0·0551	−0·1146	0·1271	205 41	Equinox.
+0·1051	+0·1358	0 1718	+37 44	−0·0581	−0·0383	0·0696	236 36	Summer.

TABLE XXII.—Coefficients and Angles in Fourier Series Expansion

	Period, 24 hours.				Period, 12 hours.			
	a_1.	b_1.	c_1.	α_1.	a_2.	b_2.	c_2.	x_2.
January	+ 2·70	+ 1·06	2·90	68° 32′	−3·73	+0·47	3·76	277° 15′
February	+ 4·77	+ 0·37	4·79	85 36	−3·44	0·00	3·44	269 58
March	+ 8·65	− 1·72	8·82	101 14	−4·99	+2·15	5·44	293 17
April	+12·17	− 4·38	12·94	109 48	−6·85	+3·04	7·49	293 56
May	+11·74	− 9·51	15·11	129 1	−4·32	+4·23	6·05	314 23
June	+10·75	−10·26	14·86	133 39	−4·56	+4·18	6·19	312 29
July	+11·31	− 9·70	14·90	130 38	−5·06	+4·39	6·70	310 57
August	+11·72	− 8·67	14·58	126 29	−3·39	+5·10	6·12	326 21
September . . .	+10·77	− 6·55	12·61	121 18	−2·64	+5·14	5·77	332 50
October	+ 9·82	− 1·83	9·99	100 32	−5·27	+2·41	5·80	294 35
November . . .	+ 5·45	− 0·30	5·46	93 11	−5·12	+1·40	5·31	285 15
December . . .	+ 1·43	+ 0·75	1·62	62 18	−3·07	−0·07	3·07	268 38
Mean of 12 monthly values . . .	+ 8·441	− 4·229	—	—	−4·370	+2·702	—	—
Inequality for—								
Year	—	—	9·443	116 37	—	—	5·138	301 44
Winter	+ 3·588	+ 0·469	3·619	82 33	−3·840	+0·448	3·865	276 39
Equinox . . .	+10·353	− 3·619	10·967	109 16	−4·937	+3·184	5·875	302 49
Summer . . .	+11·381	− 9·536	14·849	129 58	−4·334	+4·474	6·230	315 55

TABLE XXIII.—Coefficients and Angles in Fourier Series Expansion

	Period, 24 hours.				Period, 12 hours.			
	a_1.	b_1.	c_1.	α_1.	a_2.	b_2.	c_2.	α_2.
January	+0·80	−2·43	2·56	161° 43′	−1·15	+0·71	1·35	301° 36′
February	+1·53	−2·80	3·19	151 27	−1·99	+0·60	2·08	286 51
March	+4·97	−2·84	5·10	119 43	−4·64	+0·13	4·64	271 36
April	+6·99	−2·71	7·50	111 12	−5·90	−0·62	5·93	264 1
May	+9·12	−3·78	9·87	112 30	−7·69	+0·57	7·71	274 15
June	+6·75	−5·11	8·46	127 8	−6·07	−0·02	6·07	269 46
July	+7·55	−5·89	9·58	127 57	−6·15	−0·51	6·17	265 14
August	+5·96	−3·34	6·83	119 16	−5·89	+0·76	5·94	277 24
September . . .	+5·86	−3·08	6·62	117 44	−4·86	+0·90	4·94	280 32
October	+4·12	−2·50	4·82	121 13	−3·39	+0·13	3·39	272 15
November . . .	+0·96	−2·34	2·53	157 38	−1·50	+1·23	1·94	309 28
December. . . .	+1·09	−1·25	1·66	138 54	−1·12	+0·81	1·38	305 42
Mean of 12 monthly values . . .	+4·64	−3·17	—	—	−4·20	+0·39	—	—
Inequality for—								
Year	—	—	5·62	124·21	—	—	4·21	275 19
Winter. . . .	+1·10	−2·21	2·46	153·35	−1·44	+0·84	1·67	300 11
Equinox . . .	+5·49	−2·78	6·15	116·53	−4·70	+0·14	4·70	271 40
Summer . . .	+7·34	−4·53	8·63	121·40	−6·45	+0·20	6·45	271 47

of Diurnal Inequality of Horizontal Force (1890 to 1900). Unit = 1γ.

Period, 8 hours.				Period, 6 hours.				
a_3.	b_3.	c_3.	α_3.	a_4.	b_4.	c_4.	α_4.	
+0·62	-1·70	1·81	159° 47′	+0·18	+1·36	1·38	7° 29′	January.
+1·23	-2·00	2·35	148 25	-0·31	+1·39	1·42	-12 32	February.
+1·44	-3·14	3·45	155 25	+0·01	+1·79	1·79	0 15	March.
+1·92	-2·92	3·50	146 38	+0·18	+1·64	1·65	6 6	April.
-0·66	-1·80	1·91	200 3	+1·13	+0·60	1·28	62 3	May.
-1·01	-2·04	2·28	206 20	+0·32	+0·59	0·67	28 10	June.
0·00	-2·20	2·20	180 0	+0·11	+0·55	0·56	11 9	July.
-1·25	-2·91	3·17	203 16	+0·86	+1·20	1·48	35 35	August.
-1·24	-3·77	3·96	198 10	+1·18	+1·96	2·28	31 5	September.
+1·01	-3·10	3·26	162 1	+0·50	+1·74	1·81	16 10	October.
+0·85	-1·91	2·09	155 59	+0·48	+1·14	1·24	22 58	November.
+0·60	-0·85	1·04	144 33	0·00	+0·64	0·64	0 0	December.
+0·293	-2·361	—	—	+0·386	+1·216	—	—	Mean of 12 monthly values.
								Inequality for—
—	—	2·382	172 56	—	—	1·276	17 37	Year.
+0·828	-1·614	1·814	152 51	+0·089	+1·131	1·134	4 30	Winter.
+0·782	-3·230	3·321	166 23	+0·466	+1·781	1·840	14 40	Equinox.
-0·730	-2·238	2·354	198 4	+0·604	+0·736	0·952	39 22	Summer.

of Diurnal Inequality of Vertical Force (1891 to 1900). Unit = 1γ.

Period, 8 hours.				Period, 6 hours.				
a_3.	b_3.	c_3.	α_3.	a_4.	b_4.	c_4.	α_4.	
+0·50	-0·21	0·54	113° 10′	-0·37	+0·09	0·38	283° 20′	January.
+1·27	-0·11	1·27	94 50	-0·42	-0·10	0·43	256 23	February.
+2·64	-0·03	2·64	90 40	-1·10	+0·15	1·12	277 50	March.
+2·92	-0·09	2·92	91 46	-0·94	+0·38	1·01	291 42	April.
+2·78	-0·57	2·84	101 40	-0·73	+0·40	0·83	298 34	May.
+1·56	-0·52	1·65	108 20	-0·43	+0·32	0·53	306 48	June.
+1·94	+0·28	1·96	81 41	-0·45	-0·34	0·57	233 15	July.
+2·57	-0·64	2·65	103 57	-0·51	+0·16	0·53	287 23	August.
+2·29	-0·79	2·42	109 10	-0·60	+0·50	0·78	309 30	September.
+2·10	-0·43	2·14	101 27	-0·95	+0·12	0·96	276 58	October.
+0·91	-0·39	0·99	113 6	-0·73	+0·23	0·77	287 30	November.
+0·62	-0·27	0·67	113 54	-0·13	+0·03	0·13	283 4	December.
+1·84	-0·31	—	—	-0·61	+0·16	—	—	Mean of 12 monthly values.
								Inequality for—
—	—	1·87	99 40	—	—	0·63	284 38	Year.
+0·82	-0·25	0·86	106 37	-0·41	+0·06	0·42	278 35	Winter.
+2·49	-0·34	2·51	97 40	-0·90	+0·28	0·94	287 34	Equinox.
+2·22	-0·36	2·24	99 17	-0·53	+0·13	0·55	284 13	Summer.

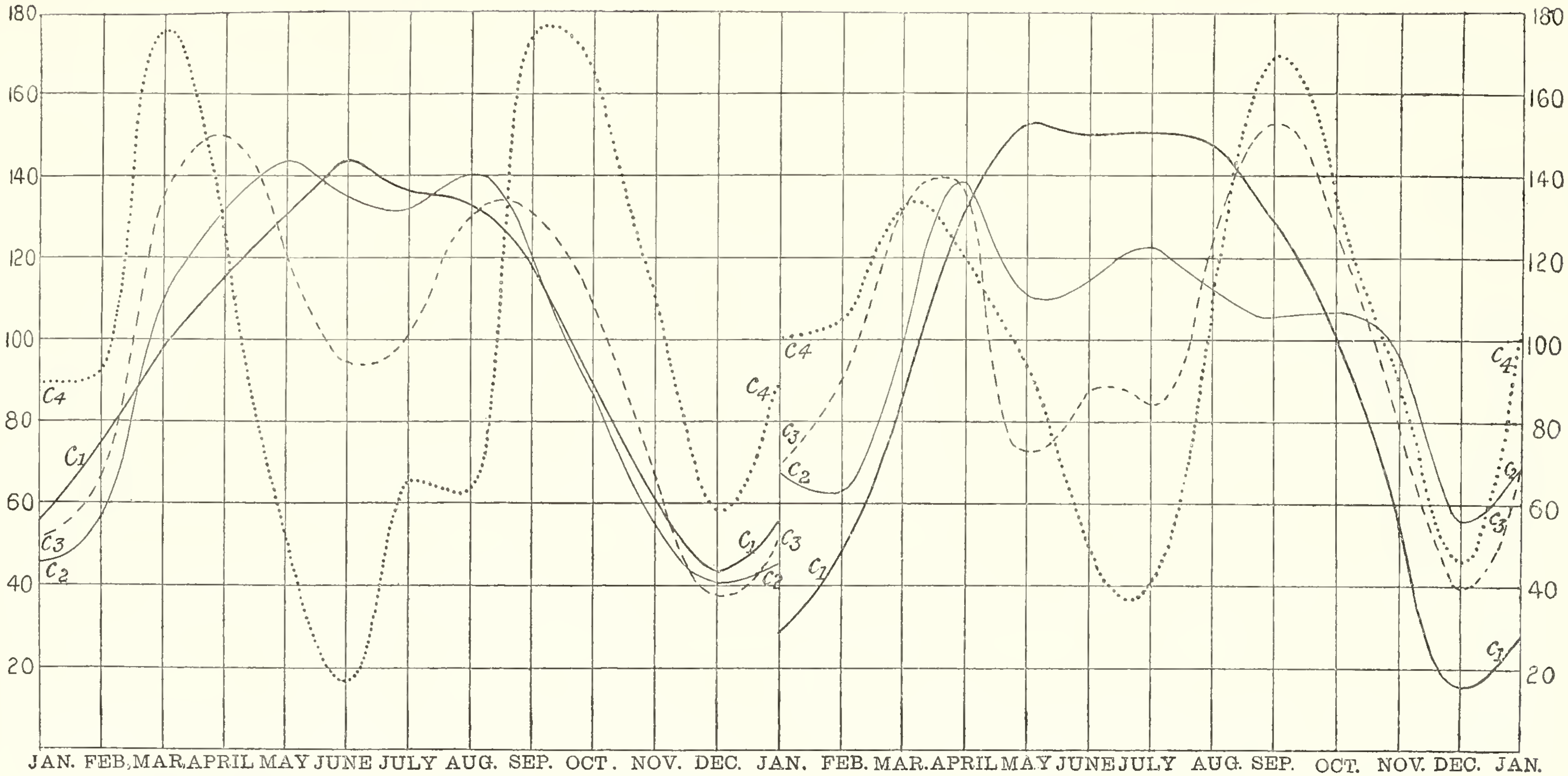
§ 33. The mode of variation of the c coefficients throughout the year is of importance, as its comparison with other phenomena seems one of the most promising methods of investigating the source of diurnal inequality. To facilitate inter-comparisons, I have expressed each monthly value of a "c" as a percentage of the mean value for the 12 months. The results appear in Tables XXIV. and XXV. The tables give also percentage values for the three seasons; these are based on the seasonal diurnal inequalities, 100 representing in their case the arithmetic mean of the values for the three seasons. The mode of annual variation of the c's is also shown graphically in figs. 16 and 17.

It will be readily seen, either from the tables or the curves, that the mode of variation of corresponding c coefficients is fairly similar in all the elements. The coefficient c_1 has an annual variation very similar to that shown by the range of the diurnal inequality (see Table XVIII.). There is the same very pronounced minimum at midwinter, with at least a suggestion of two nearly equal maxima in summer.

The annual variation in c_2 is fairly similar to that in c_1, but the existence of a secondary minimum in summer is usually indicated more clearly. In c_3 the summer minimum is prominent, and in c_4 it is in some cases the chief minimum of the year. The two maxima in c_3 and c_4 are very prominent, and the interval between their occurrence is so much greater than in c_2 or c_1 that they fall approximately at the equinoxes. This question is further dealt with in § 37.

TABLE XXIV.—Variation of Fourier Coefficients throughout the Year.
Kew, 11 Years.

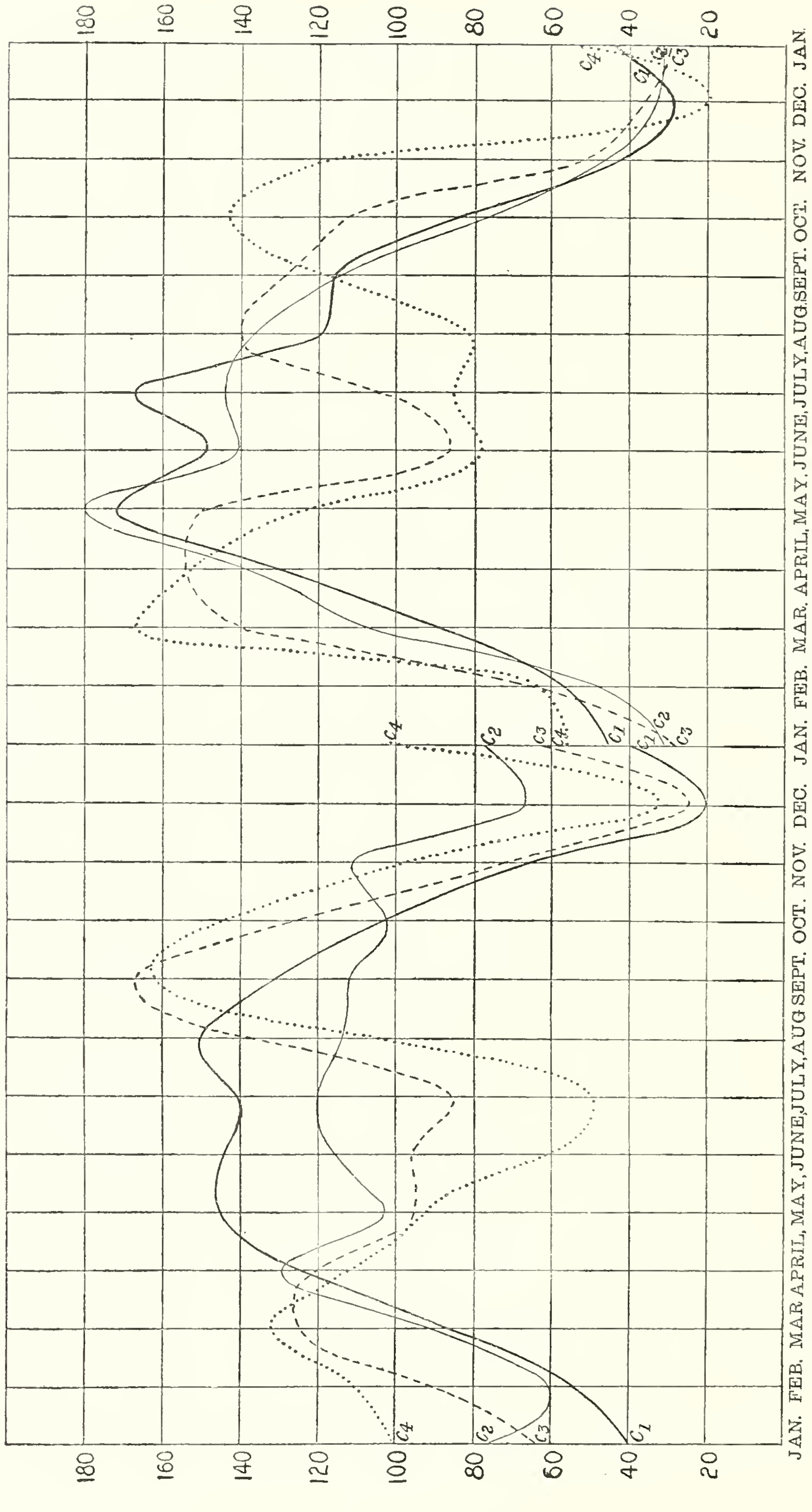
	Declination.				Horizontal force.			
	c_1.	c_2.	c_3.	c_4.	c_1.	c_2.	c_3.	c_4.
January	56	46	52	90	29	69	70	102
February	75	56	66	92	48	63	91	105
March	99	110	136	175	89	100	133	133
April	116	131	150	128	131	138	135	122
May	130	144	122	56	153	111	74	95
June	144	135	95	17	150	114	88	50
July	136	132	101	66	151	123	85	41
August	133	141	130	64	148	113	123	110
September	118	119	131	175	128	106	153	169
October	89	88	111	165	101	107	126	134
November	61	56	68	112	55	98	81	92
December	44	42	38	59	16	56	40	47
Winter	59	50	56	92	37	73	73	87
Equinox	105	111	131	166	112	110	133	141
Summer	135	138	113	42	151	117	94	73



Annual variation of the amplitudes of the principal terms of the Fourier series for the diurnal inequalities (percentage values).

Declination. Horizontal force.

Fig. 16.



Annual variation of the amplitudes of the principal terms of the Fourier series for the diurnal inequalities (percentage values).

Inclination.

Vertical force.

Fig. 17.

Table XXV.—Variation of Fourier Coefficients throughout the Year.
Kew, 10 Years.

	Inclination.				Vertical force.			
	c_1.	c_2.	c_3.	c_4.	c_1.	c_2.	c_3.	c_4.
January	40	77	64	101	45	31	29	56
February	53	60	90	110	56	48	67	64
March	86	89	124	132	89	108	140	167
April	125	129	120	112	131	138	154	152
May	145	103	95	93	172	180	150	124
June	144	116	95	61	148	141	87	79
July	140	120	85	50	167	144	104	85
August	150	114	139	107	119	138	140	80
September	128	112	167	162	116	115	128	117
October	103	102	125	143	84	79	113	143
November	66	111	71	97	44	45	52	115
December	20	67	25	32	29	32	36	19
Winter	44	80	64	84	43	39	46	65
Equinox	110	104	131	140	107	110	134	149
Summer	146	116	105	76	150	151	120	86

§ 34. Table XXVI. shows the relative importance of the four leading terms of the Fourier series in the case of the mean diurnal inequality for the year. The importance of the 12-hour term as compared to the 24-hour term appears decidedly greater in D, W, and V, which present remarkably similar features, than in H, N or I, which resemble one another.

Table XXVII. shows how the importance of the higher Fourier terms, as compared to the first, varies with the season of the year. In I and H the relative importance of the higher terms diminishes largely as we pass from winter to equinox, and also conspicuously as we pass from equinox to summer.

In D and V, on the other hand, c_2/c_1 and c_3/c_1 are greatest at the equinox, and c_2/c_1 is decidedly greater in summer than in winter. The summer value of c_4/c_1 is as conspicuously small in D and V as in the other elements, but the equinoctial value is closely similar to the winter value.

TABLE XXVI.—Relations between Fourier Coefficients in mean Diurnal Inequality for the Year.

		c_2/c_1.	c_3/c_1.	c_4/c_1.
Declination	(11 years)	·77	·38	·12
Westerly component	,,	·78	·43	·15
Horizontal force	,,	·54	·25	·14
Northerly component	,,	·58	·19	·09
Inclination	(10 years)	·49	·30	·17
Vertical force	,,	·75	·33	·11
Total force		·65	·25	·08

TABLE XXVII.—Relation between Fourier Coefficients in Diurnal Inequalities for the Seasons (from 11 or 10 years at Kew).

	c_2/c_1.			c_3/c_1.			c_4/c_1.		
	Winter.	Equinox.	Summer.	Winter.	Equinox.	Summer.	Winter.	Equinox.	Summer.
Declination	·65	·81	·78	·36	·47	·32	·18	·19	·04
Inclination	·92	·48	·40	·43	·35	·17	·32	·21	·09
Horizontal force	1·07	·54	·42	·50	·30	·16	·31	·17	·06
Vertical force	·68	·76	·75	·35	·41	·26	·17	·15	·06

§ 35. Taking the 24-hour term, we see in D, I, H and V (see Tables XX. to XXIII.) a fairly regular annual variation of considerable amplitude in the angle α_1. In D and V, α_1 is larger in winter than in summer; in I and H it is the other way about. A larger value of α_1 means an earlier hour for the occurrence of the maximum, an increase of 15° representing an advance of one hour. The angle α_2 increases fairly regularly in passing from winter to summer in the case of D, I and H; but in V the winter value is the largest. The angles α_3 and α_4 show a fairly regular increase from winter to summer in I and H, but in D and V the annual variation seems small.

§ 36. Table XXVIII. gives an analysis of the values of α for the seasonal inequalities when local solar time is used; the corresponding hours of occurrence of the first maximum of the day are shown in Table XXIX. The hours are counted from 0 to 24, with 0 representing true local midnight. The table goes only to tenths of hours, but suffices to show the much greater variability in the time of occurrence of the maximum of the 24-hour wave than in the maxima of the waves of shorter periods. The variability appears greater in I and H than in D or V.

TABLE XXVIII.—Seasonal Values of the Angles in Fourier Coefficient Expansions of Diurnal Inequality when Kew Solar Time used.

Angle.	Declination.			Inclination.			Horizontal force.			Vertical force.		
	Winter.	Equinox.	Summer.	Winter.	Equinox.	Summer.	Winter.	Equinox.	Summer.	Winter.	Equinox.	Summer.
α_1	241° 32′	223° 3′	215° 31′	250° 18′	287° 33′	312° 54′	83° 10′	108° 55′	130° 40′	154° 12′	116° 32′	122° 22′
α_2	31 32	41 43	53 51	92 27	134 13	156 19	277 53	302 7	317 19	301 25	270 58	273 11
α_3	245 5	230 8	243 32	− 15 9	2 6	39 50	154 42	165 20	200 10	108 28	96 37	101 23
α_4	57 47	59 21	42 40	195 37	204 17	239 24	6 58	13 16	42 10	281 3	286 10	287 1

TABLE XXIX.—Time of Occurrence of First Maximum in the Terms of the First 4 Orders in Fourier Expressions for Diurnal Inequality.

Period of Fourier term.	Declination.			Inclination.			Horizontal force.			Vertical force.		
	Winter.	Equinox.	Summer.	Winter.	Equinox.	Summer.	Winter.	Equinox.	Summer.	Winter.	Equinox.	Summer.
	h.	h.	h.	h.	h.	h.	h.	h.	h.	h.	h.	h.
24 hours . .	13·9	15·1	15·6	13·3	10·8	9·1	1·1	22·7	21·3	19·7	22·2	21·8
12 ,, . .	1·9	1·6	1·2	11·9	10·5	9·8	5·7	4·9	4·4	5·0	6·0	5·9
8 ,, . .	4·6	4·9	4·6	2·3	2·0	1·1	6·6	6·3	5·6	7·6	7·9	7·7
6 ,, . .	0·5	0·5	0·8	4·2	4·1	3·5	1·4	1·3	0·8	2·8	2·7	2·7

A reference to Table XI., or fig. 2, shows that the most prominent turning-point in the diurnal inequality for D is the maximum about 1 P.M. (or 13 h.). It will be seen that this comes near the time of occurrence of the single maximum in the 24-hour term, of the second maximum in the 12-hour and 8-hour terms, and of the third maximum in the 6-hour term. A similar coincidence will be found in the case of the most prominent turning-points in I, H, and V.

Variation throughout the Year (*Fourier Series*).

§ 37. Fourier series may be employed to assist in investigating the variation throughout the year of the diurnal range, or the sum of the 24 hourly differences from the mean, or the values of the c coefficients in the Fourier series representing the diurnal inequalities. A variety of these annual variation series have been calculated and the results appear in Table XXX. In the formulæ t represents an angle increasing at the rate of 30° per *month*, $t = 0$ answering to the *beginning* of January. In the calculations, the results from the monthly inequalities have been treated as corresponding exactly to the middle of the months, and as separated by equal intervals of time. Neither assumption is exactly true. In the selection of the 5 days a month one of the objects kept in view has been that the mean of the 5 days should come near the middle of the month, but in general of course only an approximation is possible. Again, calendar months are unequal in length. Still the mean day of a calendar month seldom differs by more than 24 hours from the position it would occupy if each month were strictly the twelfth of a year, and unless one is dealing with a very long series of years, or with observational data of exceptional accuracy, very little is likely to be gained by replacing calendar months by any theoretically more perfect scheme of days.

In addition to the Fourier series formulæ actually found for the annual variation, Table XXX. gives the ratio existing between :

(i.) P_1, the amplitude of the *annual* term, and M the mean of the 12 monthly values of the quantity considered ;

(ii.) P_2, the amplitude of the *semi-annual* term, and M ;

(iii.) The amplitudes P_2 and P_1.

The final column in the table gives the mean difference, irrespective of sign, between the observed and calculated values of each quantity for the 12 months, expressed as a percentage of the mean observed value M. In the table, unity represents 1′ in the case of angles and 1γ in the case of force components.

TABLE XXX.—Diurnal Inequalities, Annual Variation in Fourier Series.

		Formulæ.	P_1/M.	P_2/M.	P_2/P_1.	Mean percentage difference between calculated and observed values.
Ranges	D	$8{\cdot}03 + 3{\cdot}81 \sin (t+275^\circ) + 1{\cdot}22 \sin (2t+273^\circ)$	·47	·15	0·32	4
	I	$1{\cdot}58 + 0{\cdot}67 \sin (t+264^\circ) + 0{\cdot}16 \sin (2t+269^\circ)$	·42	·10	0·24	5
	H	$28{\cdot}2 + 13{\cdot}6 \sin (t+269^\circ) + 3{\cdot}0 \sin (2t+261^\circ)$	·48	·11	0·22	3
	V	$18{\cdot}5 + 11{\cdot}7 \sin (t+282^\circ) + 2{\cdot}2 \sin (2t+242^\circ)$	·63	·12	0·19	5
Sum of 24 differences from mean	D	$41{\cdot}68 + 17{\cdot}54 \sin (t+274^\circ) + 4{\cdot}97 \sin (2t+291^\circ)$	·42	·12	0·28	2
	I	$9{\cdot}21 + 4{\cdot}39 \sin (t+264^\circ) + 1{\cdot}15 \sin (2t+263^\circ)$	·48	·12	0·26	4
	H	$164{\cdot}4 + 92{\cdot}4 \sin (t+269^\circ) + 22{\cdot}5 \sin (2t+256^\circ)$	·56	·14	0·24	4
	V	$99{\cdot}6 + 61{\cdot}9 \sin (t+281^\circ) + 10{\cdot}3 \sin (2t+252^\circ)$	·62	·10	0·17	7
c_1	D	$2{\cdot}37 + 1{\cdot}09 \sin (t+274^\circ) + 0{\cdot}17 \sin (2t+304^\circ)$	·45	·07	0·16	2
	I	$0{\cdot}554 + 0{\cdot}331 \sin (t+266^\circ) + 0{\cdot}079 \sin (2t+266^\circ)$	·60	·14	0·24	5
	H	$9{\cdot}88 + 6{\cdot}65 \sin (t+269^\circ) + 1{\cdot}47 \sin (2t+261^\circ)$	·67	·15	0·22	3
	V	$5{\cdot}73 + 3{\cdot}75 \sin (t+279^\circ) + 0{\cdot}38 \sin (2t+222^\circ)$	·65	·07	0·10	9
c_2	D	$1{\cdot}82 + 0{\cdot}94 \sin (t+276^\circ) + 0{\cdot}25 \sin (2t+271^\circ)$	·52	·13	0·26	5
	I	$0{\cdot}287 + 0{\cdot}067 \sin (t+254^\circ) + 0{\cdot}032 \sin (2t+222^\circ)$	·24	·11	0·47	9
	H	$5{\cdot}43 + 1{\cdot}47 \sin (t+270^\circ) + 0{\cdot}78 \sin (2t+241^\circ)$	·27	·14	0·53	8
	V	$4{\cdot}30 + 2{\cdot}85 \sin (t+281^\circ) + 0{\cdot}62 \sin (2t+246^\circ)$	·66	·14	0·22	7
c_3	D	$0{\cdot}90 + 0{\cdot}30 \sin (t+281^\circ) + 0{\cdot}32 \sin (2t+274^\circ)$	·33	·35	1·06	6
	I	$0{\cdot}168 + 0{\cdot}044 \sin (t+251^\circ) + 0{\cdot}072 \sin (2t+293^\circ)$	·27	·43	1·62	7
	H	$2{\cdot}58 + 0{\cdot}39 \sin (t+241^\circ) + 1{\cdot}05 \sin (2t+290^\circ)$	·15	·41	2·69	8
	V	$1{\cdot}89 + 0{\cdot}82 \sin (t+284^\circ) + 0{\cdot}80 \sin (2t+276^\circ)$	·43	·42	0·98	9
c_4	D	$0{\cdot}30 + 0{\cdot}07 \sin (t+115^\circ) + 0{\cdot}18 \sin (2t+279^\circ)$	·24	·59	2·47	15
	I	$0{\cdot}094 + 0{\cdot}007 \sin (t+146^\circ) + 0{\cdot}043 \sin (2t+286^\circ)$	·08	·46	5·77	12
	H	$1{\cdot}35 + 0{\cdot}12 \sin (t+126^\circ) + 0{\cdot}64 \sin (2t+285^\circ)$	·09	·47	5·25	12
	V	$0{\cdot}67 + 0{\cdot}12 \sin (t+303^\circ) + 0{\cdot}26 \sin (2t+259^\circ)$	·18	·39	2·12	16

§ 38. Considering first the last column of Table XXX., we see that the agreement between the observed and calculated monthly values is on the whole best for D and H, and worst for V. This is in accordance with what we would expect from instrumental considerations. Even for V the agreement is very good. Except in the case of c_4, the mean percentage error does not exceed 9, while in the case of the ranges and the sum of the 24 hourly differences from the mean, it does not exceed 7. In the case of c_4 the quantities concerned are so small that an error of 15 per cent. represents but a small fraction of $0'\cdot1$ or 1γ, the least quantities actually measured. This shows that annual and semi-annual terms suffice to give a very accurate representation of the annual variation, and that little would be gained by introducing higher terms in the Fourier series.*

Coming next to the ratios, we see that in the case of the ranges, the 24 hourly differences, and c_1, the phenomena presented are fairly similar in all the elements; we have P_1/M varying only from 0·42 to 0·67, and P_2/M varying only from 0·07 to 0·15.

In the case of c_2 the value of P_2/M is nearly the same for all the elements; but, compared to the annual term, the semi-annual term is relatively much more important in I and H than in D and V.

The relative importance of the semi-annual term is much greater in c_3 than in c_1 or c_2; and in c_4 the semi-annual term is much the more important of the two, especially in the case of I and H.

It will be noticed that, speaking generally, the values of P_2/M differ less in the several elements than do the values of P_1/M, and that there is a close resemblance between the phenomena in D and V, and again between the phenomena in I and H.

Coming next to the phase angles, we see that excluding c_4 the different quantities considered show pretty similar results, and that the angles in the annual and semi-annual terms do not differ much. It is probably most instructive to consider not so much the angles themselves, as the results deduced from them for the times of occurrence of the maxima in the several terms. In the case of the annual terms there is only one maximum. Taking, for example, the declination range, we find the angle corresponding to the maximum of the annual term from the equation

$$t + 275° = 450°, \quad \text{or} \quad t = 175°.$$

This answers to 177 days from the beginning of the year, going only to the nearest whole day, and may be taken as answering to June 26. The minimum occurs six months later.

A semi-annual term has of course two maxima separated by six months, with two minima, at three months intervals from the maxima. In the case of the declination range, for instance, the first maximum would answer to

$$2t + 273° = 450°, \quad \text{or} \quad t = 88°\cdot5.$$

This may be taken as representing 89 days from the beginning of the year.

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* See 'Brit. Assoc. Report' for 1895, p. 223.

The results thus obtained appear in Table XXXI. They should be regarded as affected by an uncertainty of the order of a day through the treatment of the months as of uniform length.

The maximum in the annual term appears in general near midsummer, and would seem somewhat earlier in D and V than in I and H. The first maximum in the semi-annual term appears generally late in March or early in April.

TABLE XXXI.—Annual Variation. Date of Occurrence of First Maximum.

	Annual term.				Semi-annual term.			
	D.	I.	H.	V.	D.	I.	H.	V.
Ranges	June 26	July 8	July 3	June 19	March 30	April 1	April 6	April 16
24 differences . .	,, 27	,, 8	,, 3	,, 20	,, 21	,, 4	,, 8	,, 10
c_1	,, 27	,, 6	,, 3	,, 22	,, 15	,, 3	,, 6	,, 26
c_2	,, 25	,, 18	,, 2	,, 20	April 1	,, 26	,, 16	,, 13
c_3	,, 20	,, 21	,, 31	,, 17	March 30	March 20	March 22	March 29
c_4	Dec. 6	Nov. 5	Nov. 25	May 29	,, 27	,, 24	,, 24	April 7

"*Variability*" *of the Declination.*

§ 39. In discussing magnetic observations made during the recent "Southern Cross" Antarctic Expedition,* I made a comparison of what I called the "Variability of the Declination" at Cape Adare and at Kew in 1899. I have made a similar investigation into the data at Kew during the remainder of the period 1890 to 1900, partly with a view to seeing whether the phenomenon is of sufficient definiteness and regularity to afford a satisfactory basis for inter-comparison of stations.

It is customary at Kew, during absolute observations, to take two declination readings with the magnet's scale erect, and three with it inverted. These readings show the changes taking place in D during three intervals in which the magnet has remained untouched, the length of an average interval being about 4 minutes. The observations have mostly been made at a time of the day when the regular diurnal change is slow. The same instrument has been in use throughout, the procedure has varied but little, and the same observer has been responsible for the great majority of the observations. Thus the results for different months and years are fairly comparable.

The plan I have adopted has been to sum up all the changes in reading in a year,

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* 'Magnetic and Meteorological Observations made by the "Southern Cross" Antarctic Expedition 1898–1900,' p. 24.

or in one month of the 11 years, irrespective of sign, and divide them by the sum of the intervals in minutes between successive readings. The resulting quantity, measured in seconds of arc, I have called the "mean change per minute." The results so found for the several years, and the several months of the year, are given in Table XXXII.

TABLE XXXII.—Variability of the Declination.

Year.	Mean change per minute.	Month.	Mean change per minute.
1890	4″·91	January	3″·39
1891	4·44	February	4·97
1892	5·83	March	4·46
1893	3·91	April	4·21
1894	4·95	May	3·03
1895	4·46	June	3·29
1896	3·24	July	3·68
1897	3·43	August	3·34
1898	2·93	September	4·28
1899	2·95	October	4·27
1900	2·22	November	4·35
		December	3·67
Mean	3·93		

§ 40. If we divide the sum of the changes of reading during the whole eleven years by the sum of the intervals between the successive readings, we find for the "mean change per minute" the value 3″·927, which is in practical agreement with the arithmetic mean of the means for the eleven individual years in Table XXXII.

No observation has been omitted owing to abnormal disturbance, though some 400 to 500 observation days are included in the table. At a polar station no doubt there would be much greater uncertainty on this ground.

The mean values vary on the whole in a fairly regular way from year to year. They have certainly been smaller since 1896 than in previous years; but, as we shall see later, this is only what we should anticipate from sun-spot considerations. The value for 1893 is certainly somewhat conspicuously low compared to the values in 1892 and 1894, while the value for 1890 appears somewhat large. On the whole, however, I think we may conclude that the phenomenon is sufficiently definite to form a satisfactory basis for intercomparison of stations and years. There is a well-marked annual variation proceeding with very fair regularity. There are two minima, near midwinter and midsummer, with maxima near the beginning and end of winter. This is similar to the phenomena observed in declination disturbances,* more

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* See MASCART'S 'Magnétisme Terrestre,' Art. 108.

especially at Greenwich. When expressed in a FOURIER series the annual variation shown in Table XXXII. takes the form

$$3''{\cdot}91 + 0''{\cdot}377 \sin (t + 88^\circ) + 0''{\cdot}496 \sin (2t + 292^\circ),$$

where t is measured from the beginning of January exactly as in Table XXX. The semi-annual term is here the larger of the two. Its phase angle differs by only 1° from that obtained in Table XXX. for the corresponding term in the case of the sum of the 24 hourly differences in D. It indicates March 20 as the approximate time for the first maximum.

The annual term has its first maximum about January 2, and its minimum of course six months later; it is thus nearly opposite in phase to the annual term in the expressions for the range in the sum of the 24 hourly differences in D.

Sun-Spot Relations. Introduction.

§ 41. General mention has already been made in § 2, and incidently in other parts of the paper, of relations between magnetic phenomena and sun-spot frequency, and the numerical results obtained by WOLF and WOLFER for sun-spot frequency have been already recorded in Table I. There are other methods of estimating solar disturbance, and it would be of interest to consider likewise data based on these, and to investigate the question as to apparent variations in magnetic phenomena with variation in the position of the spotted areas in the sun's surface. I have thought it better, however, to confine myself wholly on the present occasion to WOLF and WOLFER's numbers, and to cover a limited portion of the ground in a comparatively thorough way, rather than to wander at large over the whole field. My own opinion is that the true inter-relationships of the several phenomena are hardly likely to be reached, and they certainly cannot be *demonstrated*, without a really minute and careful study of the facts.

In treating of sun-spot relations, I shall not adhere strictly to the order followed in the first part of the paper, but shall take first the case of the diurnal periodic changes.

§ 42. It has been established, largely through the work of BALFOUR STEWART and ELLIS, that there is a close connection between epochs of maximum and minimum in sun-spot frequency and in amplitude of diurnal inequality of magnetic elements. In investigating this matter, Mr. ELLIS eliminated the annual variation in the amplitude of magnetic ranges by assigning to any individual month the mean amplitude deduced from twelve consecutive months, of which it was the central month. I have pursued a different method. This consists in expressing the range for any given month as a percentage of the arithmetic mean of the ranges for this particular month of the year throughout the series of years dealt with. This method is obviously less satisfactory when applied to a short number of years than when applied to a period including many sun-spot cycles, a defect from which Mr. ELLIS' method is largely free.

It has, however, the advantage of being equally satisfactory whether the sun-spot and magnetic relationship is or is not variable throughout the year. Mr. ELLIS' method tends to smooth down the magnetic results, and he very properly employs correspondingly smoothed sun-spot numbers, so that the results he obtains are certain *a priori* to present fewer irregularities than those obtained by me. The results I have obtained for D and H appear in Tables XXXIII. and XXXIV. In both cases "range" means the excess of the greatest over the least hourly value in the diurnal inequality derived by combining the five quiet days of each month, the non-cyclic increment being eliminated. The absolute mean value of the range is given for each month of the year, so that the absolute values for individual months can be at once deduced if required.

TABLE XXXIII.—Variation of Declination Range.

(100 × mean for month ÷ mean for that month for 11 years.)

	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.	Absolute range. Mean for month.
January	92	96	151	140	144	59	126	84	64	59	85	4′·39
February	104	77	131	134	146	113	103	82	79	63	68	5·18
March	84	97	108	135	118	113	106	102	77	84	77	9·00
April	93	86	104	125	128	116	101	95	78	96	78	10·68
May	76	103	120	130	118	102	93	87	107	88	77	11·07
June	82	97	126	116	109	138	93	77	82	94	86	10·74
July	89	104	121	125	106	118	96	89	90	79	84	10·48
August	89	93	128	122	124	111	89	89	86	85	84	11·02
September	75	103	116	128	116	102	115	69	90	97	88	9·81
October	89	121	128	120	101	101	98	82	92	79	89	7·63
November	100	138	97	149	124	91	88	74	89	75	75	4·90
December	101	117	160	124	113	109	84	68	78	72	74	3·56
Means for years	89	103	124	129	121	106	99	83	84	81	81	

TABLE XXXIV.—Variation of Horizontal Force Range.

(100 × mean for month ÷ mean of that month for 11 years.)

	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.	Absolute range. Mean for month.
January	84	102	152	136	122	93	100	100	71	52	88	$16 \cdot 3\gamma$
February	86	90	134	156	140	120	129	68	52	54	72	$17 \cdot 9$
March	66	85	138	148	114	115	109	82	76	73	94	$27 \cdot 8$
April	83	80	104	142	127	142	95	98	74	82	73	$37 \cdot 5$
May	74	95	110	124	135	124	81	85	103	99	70	$39 \cdot 0_5$
June	86	106	103	119	143	134	83	76	83	83	84	$39 \cdot 0$
July	81	107	122	133	131	118	81	99	79	68	81	$39 \cdot 3$
August	81	115	130	123	119	109	99	74	88	87	75	$38 \cdot 8$
September	68	114	108	125	120	89	123	74	96	102	81	$35 \cdot 7$
October	83	127	116	133	114	97	99	85	86	71	90	$29 \cdot 3$
November	58	139	98	151	162	92	86	70	89	92	62	$20 \cdot 9$
December	106	124	126	162	140	148	61	86	38	58	52	$11 \cdot 9_5$
Means for years	80	107	120	138	131	115	95	83	78	77	77	

§ 43. Before passing to the immediate question of the sun-spot connection, I would call attention to the fact that the values assigned to the ranges in Tables XXXIII. and XXXIV. are without exception greater than those already given in Tables XI. and XIII., and that the differences between the two sets of results are more conspicuous in winter than in summer. This is an exceedingly good illustration of the principle already discussed in § 21. A range in Table XXXIII. is the arithmetic mean of 11 ranges, each based on a combination of only 5 days' results; whereas in Table XI. a range is based on the combination of 55 days' results. The range in Table XXXIII. thus exceeds that in Table XI., the excess being most noticeable at those seasons of the year when the hours of occurrence of maxima and minima are most variable, or when irregular disturbances are largest and most numerous.

§ 44. Referring to Table I. we see that August, 1893, was the month in which sun-spot frequency was greatest. The largest percentage in Table XXXIII. appears in December, 1892, while in Table XXXIV. the largest percentage answers to December, 1893, and November, 1894. The 12 consecutive months for which the sun-spot frequency was largest extended from August, 1893, to July, 1894. The 12 months for which the sum of the percentages is largest run from December, 1892, to November, 1893, in the case of D, and from January to December, 1893, in the case of H. Of calendar years 1893 is that having the largest mean value in all three tables.

The years 1892 to 1895 stand out as years of largest magnetic ranges, but their superiority is not quite so prominent as in the case of sun-spot frequencies; 1890 shows a distinctly smaller sun-spot frequency than any of the 10 following years, but the mean magnetic ranges in 1890 appear slightly greater than in 1899 and 1900. In these two latter years, somewhat curiously, the mean percentages are alike in the case of both D and H. The rise to the maximum is more sudden for magnetic ranges, as well as for sun-spot frequency, than the subsequent decline. This phenomenon has been remarked on by Mr. ELLIS and others.

It will be observed that the percentages in Table XXXIV. show a wider range than in Table XXXIII. The full significance of this will appear presently.

Curves illustrative of Sun-Spot Relations.

§ 45. In the tables devoted to the diurnal inequalities of D, H, N and W the mean inequality for the year is shown not merely for the combined 11 years, but also for two groups of years, viz., 1890, 1899 and 1900, representing small sun-spot frequency, and 1892 to 1895 representing large sun-spot frequency. The great excess of the ranges and the sums of the 24 hourly differences in the second group as compared to the first is conspicuous, but at first sight there is no appreciable difference in the nature of the inequalities shown in the two cases. Fairly definite though minor differences do however exist. If the amplitude of the diurnal inequality alone varied, then curves representing the inequalities for the two groups of years in the ordinary way should transform into one another by merely changing the scale of ordinates, and the same should be true of the difference curve, whose ordinates represent the excess of the ordinates of the sun-spot maximum curve over those of the sun-spot minimum curve. A glance at the curves for D and H, in figs. 18 and 19, shows that this is not the case. The difference curves, due allowance being made for their smaller amplitude, are very decidedly flatter topped than the curves for either group of years. The same phenomenon would be equally shown by N or W curves.

§ 46. Perhaps an even better way of showing the difference in the diurnal inequalities to the eye is to employ vector diagrams. This has been done in figs. 20 and 21. In fig. 20 the mean vector diagram for the whole year has been drawn from the same origin for the two groups of years, while fig. 21 represents a difference vector diagram whose radius vector is the difference between corresponding radii vectors in the two curves of fig. 20. The scale in fig. 21, it should be noticed, is double that in fig. 20. The mean magnetic meridians for the two groups of years are not absolutely identical, but could hardly be shown apart on the scale of the figures.

§ 47. If the sole difference between the inequalities in years of sun-spot maximum and sun-spot minimum were one of amplitude, then the points answering to the same hour

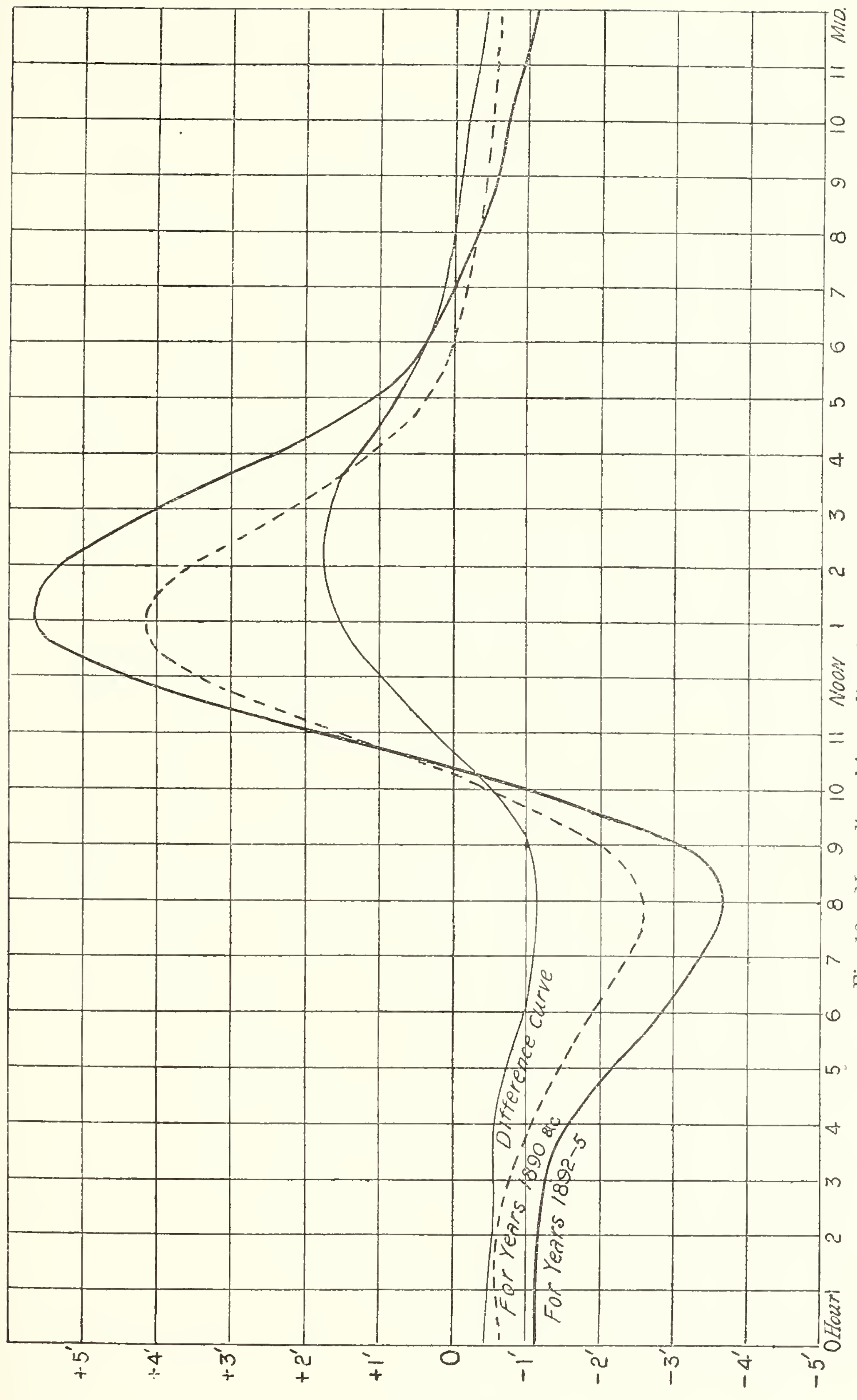


Fig. 18. Mean diurnal inequality of declination for the year.

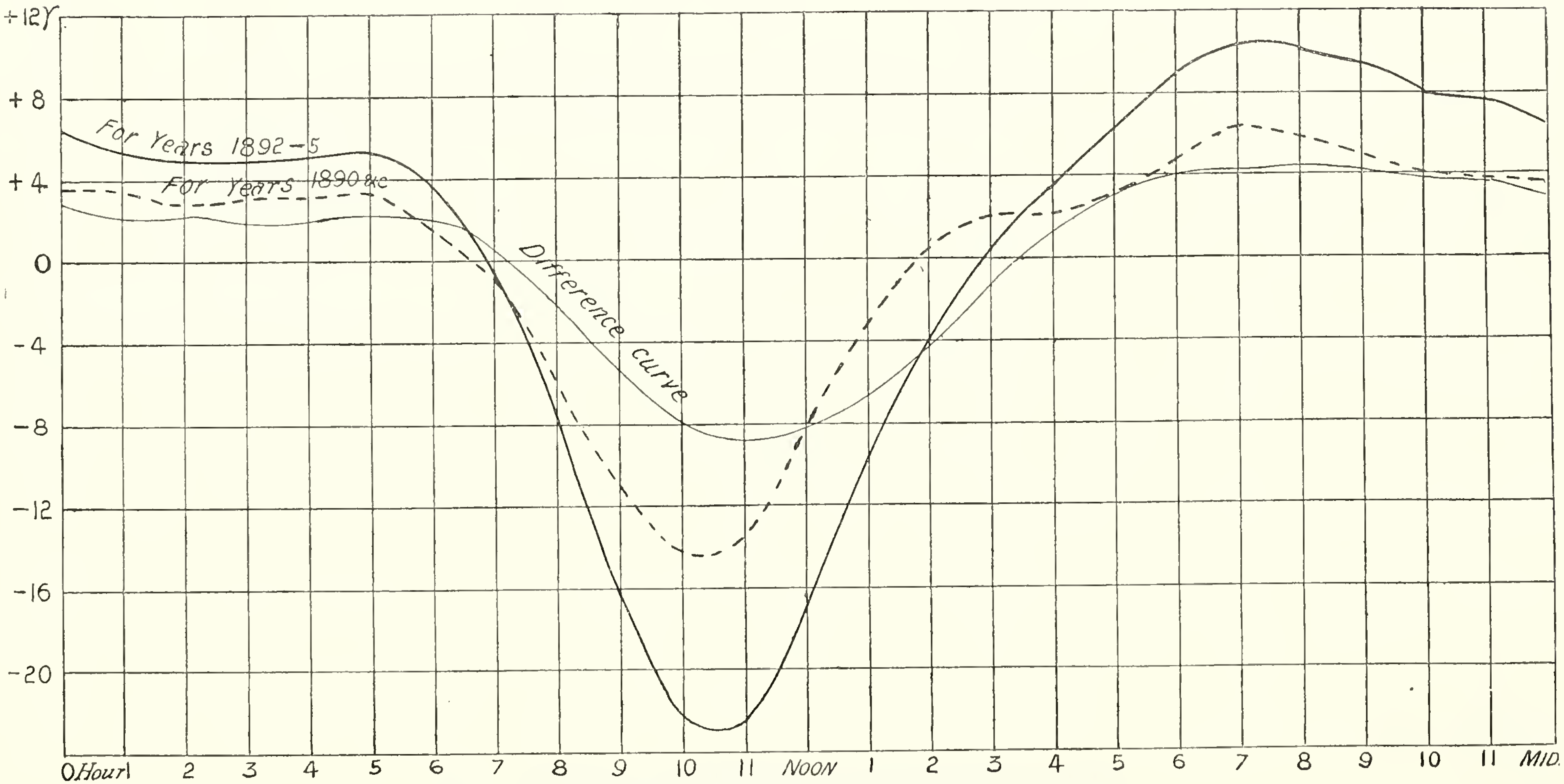
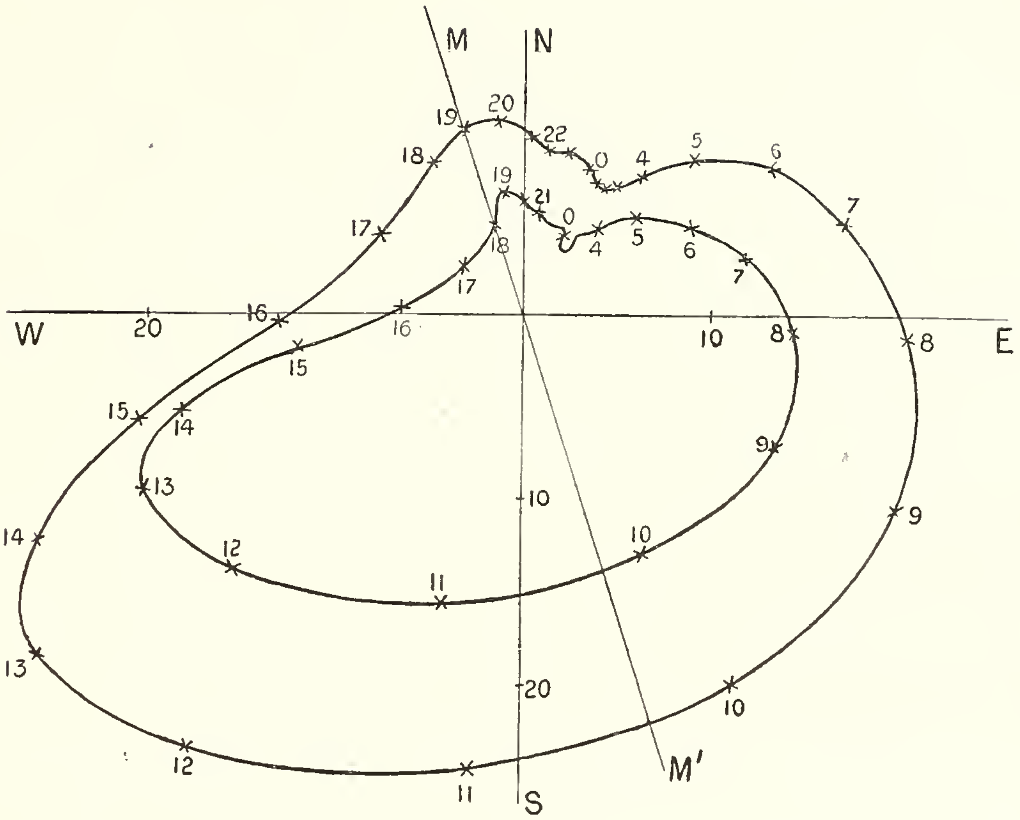


Fig. 19. Mean diurnal inequality of horizontal force for the year.



Inner curve 1890, 1899, 1900. Fig. 20. Outer curve 1892 to 1895.

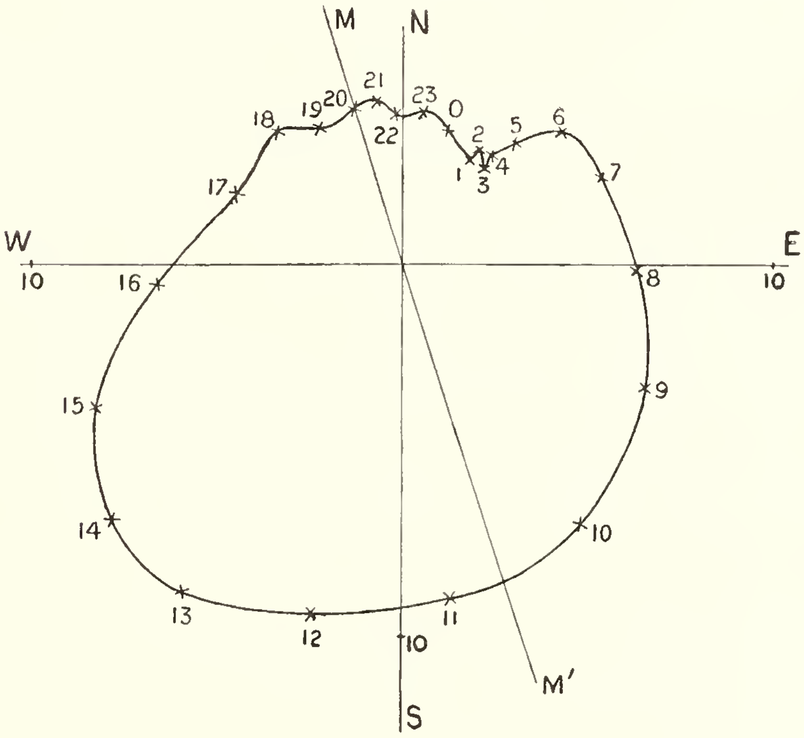


Fig. 21. Difference curve.

in the two curves of fig. 20 should lie on the same radius vector, and the curves should be similar and similarly situated; also the curve in fig. 21 should be similar and similarly situated to the curves in fig. 20. This is obviously not the case. At 9 A.M. corresponding points in the two curves in fig. 20 lie very nearly on the same radius vector, but thereafter the radius vector of the inner curve (sun-spot minimum) forges ahead, and continues ahead until the early morning. The points answering to 1 P.M. and 6 P.M. on the sun-spot minimum curve lie almost exactly on the same radii as the points answering to 2 P.M. and 7 P.M. on the sun-spot maximum curve.

The difference between the shape of the curves in figs. 20 and 21 is conspicuous; the latter curve is much more nearly symmetrical with respect to the geographical meridian than the former.

Sun-Spot Relations apparent in Fourier Coefficients.

§ 48. To push the comparison further, I had Fourier coefficients calculated for the monthly inequalities of D and H from the two groups of years 1890, 1899, 1900 and 1892 to 1895. Corresponding results for the last group of years were also calculated for Greenwich, making use of the values of the "a" and "b" coefficients in the Greenwich annual publications. This gave results more strictly parallel to the Kew results than if one had employed the annual Greenwich values for the "c" coefficients. To facilitate intercomparison of the different cases, I have expressed the monthly values of the c's as percentages of their mean. It is these percentage values that form the main part of Tables XXXV. and XXXVI. The absolute values for each month can however be obtained at once by combining the percentage with the absolute mean value given at the foot of the tables. The data for the 11 years have already appeared in Table XXIV., but it was desirable to show them in juxtaposition to the others. Besides the monthly data, the tables give the values of the c's for the three seasonal inequalities, expressed in percentages of their mean, and likewise the absolute values of the c's in the mean inequalities for the year.—(See pp. 408–411.)

There are of course irregularities in the monthly values, but there is an unmistakable general tendency for the percentage values to rise in winter and fall in summer as we pass from sun-spot minimum years through average years to sun-spot maximum years at Kew.

In the case of D the Greenwich data stand on the far side, so to speak, of the Kew sun-spot maximum data. The same is true for c_3 in H, but in the case of the other three coefficients in H the Greenwich data approach most closely to the average year results for Kew. It would be of interest to know how much of the differences between Kew and Greenwich is due to difference in geographical position, and how much is due to the fact that the Kew data are from quiet days only, while the Greenwich data are from all days.

Tables XXXVII. and XXXVIII. are derived from the same data as Tables XXXV. and XXXVI., but they are intended to show the influence of sun-spot frequency on the relative importance of the *different* Fourier terms.

Table XXXVII. deals only with the mean diurnal inequality for the whole year but gives data for W and N as well as for D and H.

Table XXXVIII. gives seasonal values of the ratios, but for D and H only.—(See p. 412.)

TABLE XXXV.—Annual Variation of Fourier Coefficients in

	c_1.				c_2.			
	Kew.			Greenwich.	Kew.			Greenwich.
	Sun-spot minimum.	11 years.	Sun-spot maximum.	Sun-spot maximum.	Sun-spot minimum.	11 years.	Sun-spot maximum.	Sun-spot maximum.
January . .	53	56	62	63	43	46	47	51
February . .	64	75	84	92	49	56	59	64
March . . .	97	99	96	104	105	110	112	114
April . . .	126	116	115	111	140	131	128	144
May . . .	127	130	129	124	141	144	139	131
June . . .	152	144	144	131	144	135	136	133
July . . .	143	136	131	128	129	132	130	127
August . .	136	133	128	114	143	141	144	127
September .	118	118	113	109	118	119	117	108
October . .	87	89	90	94	88	88	84	91
November .	53	61	58	68	58	56	58	65
December .	44	44	49	62	42	42	44	47
Winter . .	54	59	63	72	48	50	52	57
Equinox . .	107	105	103	104	112	111	110	113
Summer . .	139	135	133	124	139	138	138	130
Absolute values of coefficients in mean diurnal inequality for the year	1·801	2·322	2·858	3·204	1·541	1·789	2·106	2·007
Mean of 12 monthly values	1·859	2·371	2·905	3·313	1·567	1·818	2·146	2·063

the Diurnal Inequalities for Different Groups of Years in D.

c_3.				c_4.				
Kew.			Greenwich.	Kew.			Greenwich.	
Sun-spot minimum.	11 years.	Sun-spot maximum.	Sun-spot maximum.	Sun-spot minimum.	11 years.	Sun-spot maximum.	Sun-spot maximum.	
43	52	50	43	79	90	91	99	January
57	66	72	85	80	92	117	113	February
135	136	137	142	169	175	191	155	March
148	150	156	157	128	128	139	145	April
116	122	117	109	78	56	49	49	May
91	95	94	92	23	17	11	19	June
103	101	100	99	93	66	45	40	July
141	130	134	138	64	64	77	66	August
140	131	128	117	139	175	114	102	September
106	111	106	110	161	165	168	179	October
79	68	67	62	116	112	127	153	November
41	38	39	46	68	59	70	81	December
55	56	57	59	89	92	105	119	Winter
132	131	131	131	158	166	157	153	Equinox
113	113	112	110	53	42	38	28	Summer
0·752	0·889	1·013	0·867	0·281	0·278	0·287	0·260	Absolute values of coefficients in mean diurnal inequality for the year
0·809	0·902	1·026	0·878	0·303	0·296	0·300	0·286	Mean of 12 monthly values

TABLE XXXVI.—Annual Variation of Fourier Coefficients in

	c_1.				c_2.			
	Kew.			Greenwich.	Kew.			Greenwich.
	Sun-spot minimum.	11 years.	Sun-spot maximum.	Sun-spot maximum.	Sun-spot minimum.	11 years.	Sun-spot maximum.	Sun-spot maximum.
January . .	20	29	37	34	59	69	61	63
February . .	40	48	58	44	61	63	73	69
March . . .	81	89	95	85	102	100	102	102
April . . .	124	131	136	136	139	138	139	132
May . . .	162	153	145	141	85	111	124	117
June . . .	165	150	147	164	121	114	116	133
July . .	154	151	148	160	112	123	124	126
August . .	154	148	140	151	118	113	116	113
September .	137	128	114	106	128	106	85	92
October . .	110	101	89	98	132	107	93	113
November .	41	55	64	53	96	98	99	79
December . .	13	16	29	28	48	56	67	61
Winter . .	24	37	47	39	67	73	76	69
Equinox . .	114	112	108	106	124	110	103	108
Summer . .	162	151	145	155	109	117	121	123
	γ.	γ.	γ.	γ.	γ.	γ.	γ.	γ.
Absolute values of coefficients in mean diurnal inequality for the year	6·95	9·44	12·25	13·72	4·02	5·14	6·62	6·91
Mean of 12 monthly values	7·40	9·88	12·82	14·45	4·32	5·43	6·98	7·19

the Diurnal Inequalities for Different Groups of Years in H.

c_3.				c_4.				
Kew.			Greenwich.	Kew.			Greenwich.	
Sun-spot minimum.	11 years.	Sun-spot maximum.	Sun-spot maximum.	Sun-spot minimum.	11 years.	Sun-spot maximum.	Sun-spot maximum.	
84	70	56	81	95	102	111	107	January.
72	91	88	115	78	105	136	76	February.
132	133	137	148	132	133	125	128	March.
125	135	151	130	118	122	127	148	April.
101	74	83	49	144	95	100	106	May.
76	88	96	70	96	50	47	78	June.
115	85	70	70	51	41	40	62	July.
150	123	115	121	111	110	99	67	August.
128	153	151	125	148	169	158	158	September.
108	126	124	137	117	134	133	146	October.
71	81	81	85	83	92	86	73	November.
37	40	48	71	27	47	39	50	December.
67	73	71	90	72	87	97	78	Winter.
121	133	137	132	129	141	139	145	Equinox.
111	94	92	78	99	73	64	77	Summer.
γ.	γ.	γ.	γ.	γ.	γ.	γ.	γ.	
2·14	2·38	2·81	2·93	1·31	1·28	1·35	1·36	Absolute values of coefficients in mean diurnal inequality for the year.
2·43	2·58	3·04	3·21	1·38	1·35	1·47	1·47	Mean of 12 monthly values.

TABLE XXXVII.—Ratios of Fourier Coefficients in Mean Diurnal Inequality for the Year.

	c_2/c_1.				c_3/c_1.				c_4/c_1.			
	D.	W.	H.	N.	D.	W.	H.	N.	D.	W.	H.	N.
Kew sun-spot minimum . .	·86	·88	·58	·61	·44	·49	·31	·23	·16	·20	·19	·12
,, 11 years	·77	·78	·54	·58	·38	·43	·25	·19	·12	·15	·14	·09
,, sun-spot maximum . .	·74	·74	·54	·58	·35	·40	·23	·19	·10	·13	·11	·07
Greenwich sun-spot maximum	·63	—	·50	—	·27	—	·21	—	·08	—	·10	—

TABLE XXXVIII.—Ratios of Fourier Coefficients in Mean Diurnal Inequalities for the Three Seasons.

	c_2/c_1.			c_3/c_1.			c_4/c_1.		
	Winter.	Equinox.	Summer.	Winter.	Equinox.	Summer.	Winter.	Equinox.	Summer.
Declination—									
Kew sun-spot minimum . . .	·76	·88	·84	·44	·53	·35	·25	·23	·06
,, 11 years	·65	·82	·78	·36	·47	·32	·18	·19	·04
,, sun-spot maximum . . .	·61	·78	·76	·32	·45	·30	·17	·15	·03
Greenwich sun-spot maximum .	·49	·68	·65	·22	·33	·23	·13	·12	·02
Horizontal force—									
Kew sun-spot minimum . . .	1·58	·63	·38	·89	·34	·22	·54	·21	·11
,, 11 years	1·07	·54	·42	·50	·30	·16	·31	·17	·06
,, sun-spot maximum . . .	·88	·51	·45	·34	·29	·14	·23	·14	·05
Greenwich sun-spot maximum .	·87	·51	·39	·50	·27	·11	·20	·14	·05

Table XXXVII. shows a steady decline in the relative importance of the higher terms of the Fourier series as the sun-spot frequency increases, and this decline is accentuated in the Greenwich data. Table XXXVIII. shows that the decline apparent in the case of the mean inequality for the year is shared in general by the seasonal inequalities.

§ 49. The angles in the Fourier series were also calculated for each month for the several groups of years. It will suffice, however, to record the results obtained in the case of the inequalities for the three seasons and the year in D and H, adding the values for the year in W and N. These appear in Table XXXIX. The angles all refer to G.M.T., but the differences between the values at the same season of the year would, of course, be the same if local solar time were used.

In the case of the mean inequalities for the year, with the exception of the 6-hour term in H and N, we see a decided decrease of the angle in passing from years of sun-spot minimum, through average years, to years of sun-spot maximum. This means, as already explained, a later hour of occurrence of the maximum in the Fourier series' term. In the case of α_1 the excess of the angle for the sun-spot minimum over the sun-spot maximum years varies from 2° 47′—answering to about 11 minutes in time—in N, to 4° 46′—or about 19 minutes in time—in H; the average difference in time for the four elements, D, W, H, and N, is about $15\frac{1}{2}$ minutes. The corresponding average differences in time in α_2 and α_3 are about 18 minutes and 14 minutes respectively. In α_4 the algebraic mean of the differences for the four elements almost exactly vanishes.

In D in α_1, α_2, and α_3, the difference in angle between sun-spot minimum and sun-spot maximum is conspicuously greatest in winter, and is least in summer. In H the difference in α_1 in winter is opposite in sign to what it is at the other seasons. With the exceptions of α_4 in D, and α_3 in H, the differences between the angles for sun-spot minimum and sun-spot maximum are much the same for the equinox as for the whole year.

TABLE XXXIX.—Angles in Fourier Series for Diurnal Inequalities.

		Declination.				W.	Horizontal Force.				N.
		Winter.	Equinox.	Summer.	Year.	Year.	Winter.	Equinox.	Summer.	Year.	Year.
α_1	Sun-spot minimum	248° 49′	224° 51′	214° 30′	224° 14′	211° 10′	73° 50′	111° 14′	130° 50′	119° 7′	98° 42′
	11 years	240 55	223 24	214 49	222 57	209 9	82 33	109 16	129 58	116 37	97 18
	Sun-spot maximum	235 36	221 27	213 47	221 1	206 28	85 14	106 52	128 57	114 21	95 55
	Sun-spot minimum less sun-spot maximum	+ **13 13**	+ **3 24**	+ **0 43**	+ **3 13**	+ **4 42**	− **11 24**	+ **4 22**	+ **1 53**	+ **4 46**	+ **2 47**
α_2	Sun-spot minimum	40 25	46 24	55 13	49 33	40 45	289 35	309 59	326 59	311 37	281 37
	11 years	30 18	42 25	52 27	45 3	35 22	276 39	302 49	315 55	301 44	275 24
	Sun-spot maximum	26 3	40 59	50 50	42 57	32 20	272 56	298 37	312 2	297 40	273 39
	Sun-spot minimum less sun-spot maximum	+ **14 22**	+ **5 25**	+ **4 23**	+ **6 36**	+ **8 25**	+ **16 39**	+ **11 22**	+ **14 57**	+ **13 57**	+ **7 58**
α_3	Sun-spot minimum	255 10	233 51	244 29	241 45	234 23	158 25	165 18	211 15	180 27	143 13
	11 years	243 14	231 11	241 26	237 16	229 43	152 51	166 23	198 4	172 56	135 32
	Sun-spot maximum	236 7	229 5	240 29	234 41	226 32	145 12	164 21	184 8	165 58	130 36
	Sun-spot minimum less sun-spot maximum	+ **19 3**	+ **4 46**	+ **4 0**	+ **7 4**	+ **7 51**	+ **13 13**	+ **0 57**	+ **27 7**	+ **14 29**	+ **12 37**
α_4	Sun-spot minimum	64 22	59 25	51 45	59 25	50 27	7 14	13 24	24 14	15 29	− 2 54
	11 years	55 19	60 45	39 52	56 8	48 16	4 30	14 40	39 22	17 37	0 14
	Sun-spot maximum	49 25	57 17	37 55	52 13	45 25	5 46	17 58	46 37	20 1	5 3
	Sun-spot minimum less sun-spot maximum	+ **14 57**	+ **2 8**	+ **13 50**	+ **7 12**	+ **5 2**	+ **1 28**	− **4 34**	− **22 23**	− **4 32**	− **7 57**

Sun-Spot Formula; Numerical Relationships.

§ 50. The previous methods of investigation all point to the conclusion that the relationship between sun-spot frequency and magnetic phenomena varies considerably with the season of the year. To give greater definiteness to the results, I have assumed provisionally a linear relationship*

$$R = a + bS \equiv a\{1 + (b/a)S\}$$

between the range R of a magnetic element and the sun-spot frequency S, with "a" and "b" constants for any one month of the year. I have applied the formula to quantities other than ranges, *e.g.*, to the sum of the 24 hourly differences in the diurnal inequalities, and to the Fourier coefficients of type c. Various methods have also been adopted for calculating a and b.

The first application was to the range data already employed in calculating Tables XXXIII. and XXXIV., and to the corresponding data for I and V. In this case the constants were determined from the 11 values of the range answering to the same month of the year, in the different years, by least squares. The results thus found for a and b and the corresponding values of b/a are given in Table XL.

The values of b and b/a are multiplied by 10^4 so as to avoid decimals. The unit in a is $1'$ in the case of D and I, and 1γ in the case of H and V.

In addition to the values for the individual months of the year, means are also given for the whole year and for the three seasons. It should be noticed, however, that in this case the "a" or "b" assigned to a season (or to the year) is not itself deduced from a seasonal diurnal inequality, but is simply the arithmetic mean of the a's or b's for the individual months of the season (or year); also the value of b/a assigned to a season (or year) is derived from the mean "b" and the mean "a" for the season (or year).

The value of "a" represents of course the value of the range—or other quantity dealt with—which corresponds to a total absence of sun-spots. b is measured in the same units as a. S is simply a number, its values for individual months of the period dealt with being given in Table I.; consequently b/a is also a number, and so independent of the particular units employed in the measurement of force or of angles.

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* See "Preliminary Note" for historical references.

TABLE XL.—Values of Constants in Sun-Spot Formula Calculated by Least Squares.

Ranges.

	Declination.			Inclination.			Horizontal force.			Vertical force.		
	a.	$b \times 10^4$.	$(b/a) \times 10^4$.	a.	$b \times 10^4$.	$(b/a) \times 10^4$.	a.	$b \times 10^3$.	$(b/a) \times 10^4$.	a.	$b \times 10^3$.	$(b/a) \times 10^4$.
January	3·16	307	97	0·81	64	80	11·6	118	101	5·3	72	137
February	3·55	383	108	0·62	116	186	10·5	172	164	8·1	75	93
March	7·13	526	74	1·05	145	138	19·3	238	124	18·8	43	23
April	8·56	508	59	1·23	201	164	25·7	284	111	24·5	28	11
May	9·34	401	43	1·58	139	88	29·6	219	74	24·6	153	62
June	8·45	504	60	1·47	161	110	32·6	142	44	23·6	83	35
July	8·75	387	44	1·52	150	98	28·6	238	83	24·7	94	38
August	9·11	421	46	1·89	101	53	31·6	160	51	21·2	44	21
September . . .	7·48	517	69	1·48	137	92	27·0	192	71	14·3	125	88
October	6·13	361	59	1·28	106	83	22·2	171	77	12·3	91	74
November . . .	3·60	369	102	0·80	144	180	13·0	225	173	8·5	38	44
December . . .	2·62	234	89	0·30	95	316	6·7	131	193	6·1	15	24
Mean of monthly values for—												
Year. . . .	6·49	410	63	1·17	130	111	21·5	191	89	16·0	72	45
Winter . . .	3·23	323	100	0·63	105	166	10·5	161	145	7·0	50	71
Equinox . .	7·32	478	65	1·26	147	117	23·5	221	94	17·5	72	41
Summer . .	8·91	428	48	1·61	137	85	30·6	190	62	23·5	94	39

§ 51. The variation of "a" throughout the year in Table XL. is fairly similar to what we have already observed in the case of the ranges from 11 year means. There is a conspicuous minimum in winter, usually in December, and at least a trace of a second minimum near midsummer. The fluctuations of b and of b/a from month to month are somewhat irregular, and are doubtless in part purely accidental. It would probably require a long series of years, including several sun-spot cycles, to give a smooth annual variation. The general features are however clear enough, and may be easily grasped from a comparison of the mean values assigned to the three seasons. In all four elements b is decidedly least, but b/a decidedly greatest, in winter. A smaller value of b implies a smaller absolute increase to the value of an element for a given increase of sun-spot frequency. A larger value of b/a means a larger percentage change in the element for a given change in sun-spot frequency.

The value of b/a appears less in summer than at the equinox in all four elements, and this is even true, though much less conspicuously, of the value of b itself in all the elements except V.

For such practical purposes as navigation and survey work the value of b is probably the most important thing, but for theoretical work, especially when dealing with data from a single station, the value of b/a will probably prove to possess more significance. If we divide the yearly and seasonal values of $(b/a) \times 10^4$, in Table XL., by 5, 4, 3 and 2 respectively, we get the following results, going to the nearest integer :—

	Year.	Winter.	Equinox.	Summer.
$\frac{1}{5}(b/a)\,10^4$ in I	22	33	23	17
$\frac{1}{4}(b/a)\,10^4$ in II	22	36	23	16
$\frac{1}{3}(b/a)\,10^4$ in D	21	33	22	16
$\frac{1}{2}(b/a)\,10^4$ in V	22	35	21	19
Mean	22	34	22	17

This brings out the remarkable similarity in the seasonal changes of b/a in the different elements, and the closeness between the values of b/a for the equinox and for the year as a whole.

Whilst the sun-spot influence as given by Table XL. is decidedly least for V, the difference from the other elements is less than would appear from the "Preliminary Note." The results given there for V were appreciably influenced by the neglect of the temperature correction in years prior to 1897, already explained in § 19. The omission of the correction diminished the range in V, and brought its values in years prior to 1897—mostly years of large sun-spot frequency—closer to the values in the later years than they ought to have been.

§ 52. Ranges based on only five quiet days are somewhat uncertain, and calculations by least squares are somewhat laborious, I thus investigated a second method of finding values of a and b, which seems to work satisfactorily. It makes use of values deduced from the three groups of years 1892 to 1895, 1890, 1899, 1900, and 1890 to 1900. The method will be most easily grasped by considering a concrete case. For this purpose, let us consider the declination range for January. We have the following data :—

Inequality from 1892 to 1895 . .	Range 4′·97	Sun-spot frequency . .	72·65
,, ,, 1890, 1899, 1900 .	,, 3′·26	,, ,, . .	11·40
Differences	1·71		61·25

Consequent value for $b = 1{\cdot}71 \div 61{\cdot}25 = 279 \times 10^{-4}$.

Inequality from 1890 to 1900 . .	Range 4′·07	Sun-spot frequency . .	39·8.

Hence value for $a = 4'{\cdot}07 - 39{\cdot}8 \times 279 \times 10^{-4} = 2'{\cdot}96$.

And value for $b/a = {\cdot}0279 \div 2{\cdot}96 = 94 \times 10^{-4}$.

The values obtained in this way for the ranges and for the sums of the 24 hourly differences in the diurnal inequalities of D and H are given in Tables XLI.

Table XLI.—Values of Constants in Sun-Spot Formula, Calculated from Groups of Years.

	Declination.						Horizontal force.					
	Ranges.			Sum of 24 differences.			Ranges.			Sum of 24 differences.		
	a.	$b \times 10^4$.	$(b/a) \times 10^4$.	a.	$b \times 10^3$.	$(b/a) \times 10^4$.	a.	$b \times 10^3$.	$(b/a) \times 10^4$.	a.	$b \times 10^2$.	$(b/a) \times 10^4$.
January	2·96	279	94	15·07	216	144	10·4	123	118	33·2	82	246
February	3·06	398	130	17·43	313	179	9·2	177	192	41·1	113	274
March	6·35	695	109	30·70	378	123	15·5	283	183	75·6	211	279
April	8·84	416	47	41·30	208	50	23·4	295	126	137·0	191	139
May	8·63	530	61	39·82	312	78	28·5	222	78	168·2	154	92
June	8·28	515	62	45·15	258	57	28·8	217	75	164·8	145	88
July	7·90	509	64	40·84	277	68	28·2	256	91	154·5	184	119
August	9·00	443	49	45·52	206	45	30·2	165	55	172·8	120	70
September	7·41	520	70	34·04	330	97	26·4	186	71	147·8	110	75
October	6·05	351	58	28·26	266	94	21·9	128	58	134·1	82	61
November	3·71	296	80	18·58	228	123	12·2	221	181	52·2	158	302
December	2·63	177	67	12·28	153	124	5·2	134	257	21·0	67	320
Mean of monthly values for—												
Year	6·24	427	68	30·75	262	85	20·0	200	100	108·5	135	124
Winter	3·09	287	93	15·84	228	144	9·3	164	177	36·8	105	285
Equinox	7·16	496	69	33·58	296	88	21·8	223	102	123·6	149	120
Summer	8·45	499	59	42·83	263	62	28·9	215	74	165·1	151	91

§ 53. As in Table XL., the yearly and seasonal values of a and b given in Table XLI. represent simply arithmetic means of the values for the individual months, and the values assigned to b/a are obtained by combining the b for the season with the mean a. The units employed are, as in Table XL., $1'$ for D, and 1γ for H.

In comparing Tables XL. and XLI., it should be remembered that the ranges in the former are derived from five days in one year, while in the latter they are derived from a group of years supplying at least 15 days. This implies, as already pointed out, that the average range dealt with in Table XL. is larger than the average range dealt with in Table XLI.

It will be observed that the yearly and seasonal values of "a," given in Table XL., are invariably larger than those given in Table XLI., and the same is true of the great majority of individual months. On the other hand the yearly and seasonal values of b, given for D and H, in Table XL., are, with one exception, less than the corresponding values given in Table XLI. A third point of difference is, that the equinoctial values of b for the ranges in Table XLI. have not the pre-eminence compared to the summer values that they show in the corresponding cases in Table XL.

Whilst minor differences exist, the main features in Tables XL. and XLI. are alike. Both show, in winter, a conspicuous minimum in b, but a conspicuous maximum in b/a. Both make the equinoctial values of b/a nearly equal to the mean values for the year. The values found for b and b/a, in individual months, are evidently affected by considerable uncertainties, but the modes of annual variation in the two tables resemble one another more closely than I had anticipated.

It will be noticed that the values found for b/a for the sum of the 24 hourly differences in Table XLI. exceed the corresponding values for the ranges in every single case in H, and in all but two individual months in D. This difference between the two sets of values of b/a is very decidedly larger in winter than in summer. The inference is that sun-spot influence on Terrestrial Magnetism is really underestimated if we confine our attention to the *range* of the diurnal inequalities, and this is especially true of winter.

The phenomena, one need hardly say, absolutely bear out the remarks made in § 45 as to the flat-topped character of the difference curves in figs. 18 and 19.

§ 54. The method on which Table XLI. is based, has also been applied to the "c" Fourier coefficients in the diurnal inequalities. The results thus obtained from the mean annual and seasonal inequalities for the three groups of years are given in Table XLII. Yearly data are given for N and W, as well as for D and H.

For comparison, yearly results are also given for Wilhelmshaven, based on tables of values of the c coefficients for individual years, from 1889 to 1895, published by Dr. BÖRGEN.* I have employed 1892 to 1895 for the group of sun-spot maximum

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* 'Beob. aus dem Magn. Obs. zu Wilhelmshaven,' Fünfter Theil, pp. 46 *et seq.*

years, and 1889, 1890 as the group of sun-spot minimum years in dealing with the Wilhelmshaven data. The latter group, it will be noticed, differs from that used for Kew.

The Wilhelmshaven data also differ in being from all days in the year, and in their case one had to employ arithmetic means of the *c*'s from individual years instead of employing values answering to the inequality from the group of years combined. This last difference would inevitably tend to increase the size of the Wilhelmshaven coefficients as compared to the Kew, though probably to but a trifling extent.

As the declination at Wilhelmshaven is some $4\frac{1}{2}°$ less westerly than at Kew, the results for N and W at the two places are presumably less directly comparable than the results for H.

TABLE XLII.—Values of Constants in Sun-Spot Formula, Calculated from Groups of Years. Fourier Coefficients in Expressions for Diurnal Inequality.

		c_1.			c_2.			c_3.			c_4.		
		a.	$b \times 10^4$.	$(b/a) \times 10^4$.	a.	$b \times 10^4$.	$(b/a) \times 10^4$.	a.	$b \times 10^4$.	$(b/a) \times 10^4$.	a.	$b \times 10^4$.	$(b/a) \times 10^4$.
Declination, unit = 1′	Kew winter	0·87	134	155	0·68	59	87	0·41	23	56	0·22	8	38
	,, equinox	1·77	174	99	1·59	103	65	0·98	48	49	0·46	2	3
	,, summer	2·43	170	70	2·03	104	51	0·86	32	37	0·14	− 5	− 38
	,, year	1·65	162	98	1·43	86	61	0·75	34	46	0·27	1	3
Horizontal force, unit = 1γ	Kew winter	1·00	663	660	2·34	386	165	1·52	76	50	0·88	64	72
	,, equinox	7·04	959	136	4·50	334	74	2·51	198	79	1·67	42	25
	,, summer	10·81	903	84	3·96	506	128	2·30	11	5	1·19	− 53	− 44
	,, year	6·06	811	134	3·48	398	115	1·95	103	53	1·25	7	5
	Wilhelmshaven year	7·39	876	119	4·18	527	126	2·47	114	46	1·24	31	25
Northerly component, unit = 1γ	Kew year	7·02	877	125	4·29	461	107	1·57	116	74	0·94	− 6	− 6
	Wilhelmshaven year	9·30	886	95	4·99	518	104	2·41	111	46	1·01	29	28
Westerly component, unit = 1γ	Kew year	8·16	766	94	7·24	392	54	4·15	173	42	1·67	13	8
	Wilhelmshaven year	9·73	785	81	7·25	480	66	3·43	223	65	1·55	31	20

§ 55. Considering first the Kew data in Table XLII. by themselves, we see that the phenomena presented in D and H by c_1—*i.e.*, the 24-hour term—are very similar to those already described in the case of the ranges. Absolutely considered, b is least in winter, and is, if anything, slightly greater at the equinoxes than at midsummer; the value of b/a is conspicuously greatest in winter, and least in summer. The value of b/a for c_2 is also largest in winter, but in the case of H the summer value appears also in excess of the equinoctial. At Kew, the values of b/a for c_2 are with one exception decidedly smaller than the corresponding value for c_1; in like manner the values for c_3 are generally less than those for c_2, and the values for c_4 less than those of c_3. In fact, in summer we have negative values for b/a in c_4 for D, H and N. This may be accidental, as the numerical values appear very small, but we may at least conclude that sun-spot frequency exerts but a trifling influence on the value of c_4 at Kew.

The reduction in the value of b/a as we pass from c_2 to c_3, and from c_3 to c_4, is also well shown at Wilhelmshaven, though not quite so prominently as at Kew. Where the Wilhelmshaven data differ most notably from those at Kew, is in giving a larger value of b/a for c_2 than for c_1, in both H and N.

The values of b/a found for c_1 at Kew appear decidedly larger than those found in Table XLI. for the range, or even as a rule than those found for the sum of the 24 hourly differences.

Comparing the different elements at Kew, we see that in c_1 and c_2 the mean values of b/a for the year are pretty much alike in H and N, and again in D and W, the values appearing slightly larger in H than in N, and very slightly smaller in W than in D. The quantities c_3 and c_4 are themselves so small that conclusions based on the apparent differences in their case in the different elements, would possess an uncertain value.

Comparing Wilhelmshaven with Kew, we see that in the case of c_1 the Wilhelmshaven values are in excess of the Kew for both a and b; but the differences between the corresponding values for b are so small that the Kew values for b/a are decidedly the larger. In the case of c_2 all the figures for Wilhelmshaven are in excess of the corresponding figures for Kew, except the value of b/a in N. In c_3 the Wilhelmshaven values of b/a are the larger in W, but the smaller in H and N. In c_4 the Wilhelmshaven values for b and b/a are decidedly larger than the Kew, but still very small. Whilst differences exist, there is a sufficiently close resemblance between the results at the two places to prove that the phenomena observed at Kew are by no means of an exceptional character.

§ 56. The method of employing three groups of years has also been applied to the ranges and the sums of the 24 hourly differences in the mean diurnal inequalities for the year. The object was partly to obtain a comparison with Parc St. Maur through the intermediary of data published by MOUREAUX.* These data are the values of

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* 'Ann. du Bureau Central Météorologique de France,' 1899, "Mémoires," p. B.9.

the ranges in the mean diurnal inequalities for the individual years of the period 1889 to 1899. For sun-spot maximum at Parc St. Maur I took the years 1892 to 1895, and for sun-spot minimum 1889, 1890 and 1899. The value assigned to a group of years was in this case the arithmetic mean of the values for its individual years.

In the case of Kew, the results for I and V were obtained exactly like those for Parc St. Maur, except that 1900 took the place of 1889 and 1890; but in D, H, N and W, I took the values given by the inequalities for the group of years combined, as given in Tables XI., XIII., XV., XVI. The reason for doing this was that individual years' results for N and W did not exist, and it was desirable that these two elements and D and H should be treated exactly alike. The difference in the method of treatment would tend slightly to reduce the values of the ranges in D, H, N and W at Kew as compared to Parc St. Maur.

For facility of comparison, the results for the ranges at the two places are juxtaposed. The angular and force units are respectively 1′ and 1 γ.

TABLE XLIII.—Values of Constants in Sun-Spot Formula, from mean Diurnal Inequalities for Individual Years or for Combinations of Years (Years Grouped).

	Kew.						Parc St. Maur.		
	24 differences.			Ranges.			Ranges.		
	a.	$b \times 10^3$.	$(b/a) \times 10^4$.	a.	$b \times 10^4$.	$(b/a) \times 10^4$.	a.	$b \times 10^4$.	$(b/a) \times 10^4$.
D . . .	30·5	261	86	6·20	407	66	7·27	429	59
W . . .	150·1	1234	82	32·4	1850	57	38·3	2358	62
H . . .	99·2	1304	131	18·3	1896	104	20·4	2170	106
N . . .	117·9	1491	126	19·4	1942	100	22·2	2257	102
I . . .	4·91	75	153	0·89	120	135	1·14	132	116
V . . .	77·8	422	54	14·5	779	54	16·7	1003	60

§ 57. Comparing the Kew results in Table XLIII. with the corresponding results in Table XLI., we find an excellent agreement, especially in the case of D. Comparing the Kew data for the ranges in Table XLIII. with the corresponding data in Table XL., we see that the values found for "a" in Table XLIII. are always slightly the smaller. This is also true of the values of "b" except in the case of V. On the other hand, the values found for b/a in Table XLIII. are larger than those given in Table XL. The differences between the two tables are by no means large, but they emphasise the necessity of bearing in mind the principle explained in § 21. Still confining our attention to the Kew data, we see that, as in the case of c_1 in Table XLII., the values of b/a for D and W come close together, the former being slightly the larger, while the values of b/a for H and N also differ but slightly, and in the same direction in the two cases.

Coming now to the results for Parc St. Maur, we see that the values for "a" are all in excess of the corresponding values for Kew, but the values of b/a at the two places are in general closely alike, the difference being sometimes in one direction, sometimes in the other. The agreement in the values of b/a at the two places is closest in H and N, and least close in I. The fact that at Parc St. Maur V shows a slightly larger value of b/a than D is noteworthy.

On the whole, the similarity in the phenomena shown at Kew and Parc St. Maur is exceedingly satisfactory. The resemblance appears decidedly closer than between Kew and Wilhelmshaven. This is probably partly due to the fact that the declinations at Parc St. Maur and Kew differ only about 2°.

§ 58. Table XLIV. gives a final set of results from the mean diurnal inequalities for the year. They were obtained from the individual inequalities for 11 or 10 years by least squares. The agreement with the results in Table XLIII. is good. This is satisfactory, if only because it shows that it is possible to obtain by means of the much simpler method of Table XLIII. results giving a good approximation to those found by least squares.

TABLE XLIV.—Values of Constants in Sun-Spot Formula from Mean Diurnal Inequalities in Individual Years by Least Squares.

	24 differences.			Ranges.		
	a.	$b \times 10^3$.	$(b/a) \times 10^4$.	a.	$b \times 10^4$.	$(b/a) \times 10^4$.
Declination . . . (unit 1′)	30·5	264	87	6·10	433	71
Inclination . . . " "	4·63	81	175	0·87	125	145
Horizontal force (unit 1γ)	97·8	1358	139	18·1	1942	107
Vertical force . . " "	77·0	439	57	14·3	806	56

§ 59. I have also applied the sun-spot formula to the results for non-cyclic effect in I and H given in Tables VI. and VII., and to the monthly results obtained for the variability of D as explained in § 39. The years were grouped after the fashion explained in § 52.

The results are given in Table XLV. for the whole year, and for the three seasons. Owing to the extreme smallness of the observational quantities, it would require a very long series of years to eliminate accidental sources of error. Thus the seasonal results, more particularly for the non-cyclic effect, are probably affected by considerable uncertainties, especially as regards the values of b/a. In fact, my object in recording the seasonal values was largely to enable the reader to judge for himself what attitude he should adopt towards the mean results for the year.

TABLE XLV.—Values of Constants in Sun-Spot Formula.

	Non-cyclic effect.						Variability of declination in seconds of arc per minute.		
	Horizontal force (unit 1γ).			Inclination (unit $1'$).					
	a.	$b \times 10^4$.	$(b/a) \times 10^4$.	a.	$b \times 10^5$.	$(b/a) \times 10^4$.	a.	$b \times 10^4$.	$(b/a) \times 10^4$.
Winter	1·50	507	338	0·07	470	702	3·00	289	96
Equinox . . .	2·77	217	78	0·22	90	42	3·32	240	72
Summer . . .	2·10	171	81	0·17	124	71	2·49	188	76
Year	2·12	292	138	0·14	251	179	2·93	239	81

§ 60. The conclusions I myself draw from Table XLV. are that non-cyclic effect and variability of declination are both strongly influenced by sun-spot frequency, and that this influence is decidedly most prominent in winter, though hardly I should imagine to the extent indicated by the values found for b/a in the non-cyclic effects.

One exceptional feature in Table XLV. is that "a" appears greatest, and b/a least, at the equinox. This might arise from an over-estimate of "a."

It will be noticed that the mean values for the year of b/a in non-cyclic effect in H and I, and in the variability in D, are remarkably close to the corresponding values found in Table XLIV. for the case of the 24 hourly differences in these respective elements.

When we find two phenomena presenting similar laws of variation, whilst the conditions are artificially varied in a definite manner, we infer at least an intimate relationship between their causes. One is thus tempted to deduce that the source, or sources, of the non-cyclic effect is not absolutely distinct from that of the regular diurnal inequality. If, for instance, the inequality is due to electric currents in the upper atmosphere, one would be disposed to infer that the source of the non-cyclic effect is there also. It seems improbable that two absolutely distinct loci would be so similarly influenced by the changes, whatever they are, that proceed *pari passu* with sun-spot variations.

It is unsafe to base theories on a few numerical coincidences, which after all may be accidental, but I hope it will at least be allowed that non-cyclic effect and declination variability are true manifestations of terrestrial magnetism, and that the phenomena they exhibit at different stations and over different periods of time form rather a promising field of investigation.

Relations with Meteorological Phenomena.

§ 61. Evidence has been adduced by many physicists, including Dr. BALFOUR STEWART and Sir NORMAN LOCKYER, suggestive of connection between sun-spots and various meteorological phenomena, such as rainfall, barometric pressure, &c. It is thus desirable to see what was happening meteorologically at Kew from 1890 to 1900, and, more especially, whether there was or was not any appreciable difference between the meteorological data for the two groups of years 1892 to 1895 and 1890, 1899 and 1900.

Table XLVI. gives particulars of the mean values of the chief meteorological elements at Kew for the whole period, and for the two shorter groups of years. In the case of vapour pressure, 1891 was omitted, as reliable data were wanting for two or three months of the year. The mean daily range of temperature in the table is the mean excess of the maximum over the minimum on individual days.

What impresses one chiefly on studying the table, is the remarkably close agreement between the means for such comparatively short periods of years. When the means for the two shorter periods differ, they are as often as not on the same side of the mean for the 11-year period.

TABLE XLVI.—Mean Values of Meteorological Elements at Kew.

Period.	Mean temperature for the day.	Mean daily range of temperature.	Mean hours of sunshine for year.	Mean vapour pressure.	Mean amount of cloud (Total = 10).	Mean total annual rainfall.	Mean height of barometer.	Average wind velocity, miles per hour.
	° F.	° F.		inch		inches	inches	
1890 to 1900 . .	49·71	13·68	1521	0·287	6·5	22·360	29·978	10·21
1892 to 1895 . .	49·48	13·90	1536	0·283	6·2	23·538	29·964	10·20
1890, 1899, 1900 .	49·87	13·83	1584	0·288	6·5	21·310	29·970	10·20

§ 62. As results from the diurnal inequalities are more strictly parallel to most of the Kew magnetic data, mean diurnal inequalities of temperature and barometric pressure—the two most important meteorological elements—were calculated from the data published by the Meteorological Office in their "Hourly Observations." This was done for groups of sun-spot maximum and sun-spot minimum years. Data for 1900 being not yet available, 1889 was substituted in the sun-spot minimum group. The following were the results :—

RANGES in Mean Diurnal Inequalities for the Year.

Group of years.	Temperature.	Barometric pressure.
	° F.	inch.
1892 to 1895	10·00	·0265
1889, 1890, 1899	9·70	·0267

DIURNAL Inequalities Expressed in Fourier Series.

Group of years.	Temperature, in degrees Fahrenheit.
1892 to 1895	$4^\circ\cdot91 \sin (t+224^\circ\cdot6)+0^\circ\cdot79 \sin (2t+43^\circ\cdot7)+0^\circ\cdot14 \sin (3t+17^\circ\cdot7)+0^\circ\cdot06 \sin (4t+180^\circ\cdot9)$
1889, 1890, 1899	$4^\circ\cdot73 \sin (t+224^\circ\cdot8)+0^\circ\cdot79 \sin (2t+42^\circ\cdot0)+0^\circ\cdot13 \sin (3t+16^\circ\cdot1)+0^\circ\cdot05 \sin (4t+197^\circ\cdot8)$

Group of years.	Barometric pressure (unit = 0·001 inch).
1892 to 1895	$5\cdot11 \sin (t+27^\circ\cdot1)+10\cdot37 \sin (2t+150^\circ\cdot9)+0\cdot57 \sin (3t+3^\circ\cdot5)+0\cdot34 \sin (4t+270^\circ\cdot0)$
1889, 1890, 1899	$3\cdot99 \sin (t+21^\circ\cdot7)+10\cdot78 \sin (2t+148^\circ\cdot9)+0\cdot97 \sin (3t+9^\circ\cdot7)+0\cdot32 \sin (4t+261^\circ\cdot4)$

Here again, what strikes one principally is the closeness of agreement between results from periods containing so few years.

§ 63. As supplementing the results for barometric pressure, attention may be drawn to the following important results obtained at the Dutch Colonial Observatory at Batavia* for Fourier series expansions of the diurnal inequality. The unit in all cases is 1 millim. of mercury.

Group of years.	Mean pressure, 758+.	24-hour term.		12-hour term.		8-hour term.	
		Amplitude.	Phase angle.	Amplitude.	Phase angle.	Amplitude.	Phase angle.
			°		°		°
1866–70 . . .	0·81	0·61	23·1	0·94	158·0	0·04	7·3
1871–75 . . .	0·43	0·63	25·4	0·95	158·1	0·04	16·6
1876–80 . . .	0·81	0·62	26·4	1·00	160·6	0·04	13·4
1881–85 . . .	0·91	0·66	26·1	1·03	160·5	0·04	20·0
1886–90 . . .	0·71	0·62	28·0	1·03	160·1	0·04	23·4
1891–95 . . .	0·70	0·63	25·7	1·03	161·0	0·04	27·0
1896–1900 . . .	0·82	0·63	25·3	1·01	160·6	0·04	29·6

I would specially call attention to the extreme smallness of the variation in the amplitudes of the several terms, and to the fact that 1891 to 1895 represents, as compared to the two adjacent groups of years, large sun-spot frequency.

We know from the important researches of M. ANGOT, referred to in the "Preliminary Note," that the connection between magnetic variations and sun-spot frequency is unmistakable at Batavia as in Europe.

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* 'Observations made at the Mag. and Met. Observatory at Batavia,' vol. 23, 1900, p. 143.

§ 64. In considering results such as those in Table XLVI., allowance must be made for the fact that in the case of such an element as rainfall the results from any single station for a single year, or even occasionally for a group of three years, may not be fairly representative for more than a very limited area of country. But most of the other elements are much more representative in character, and it seems safe to conclude that, as between the two groups of years of sun-spot maximum and minimum, there was not in the south of England generally any difference of meteorological character at all of the same order as that manifested in the magnetic elements. From this generalization I would however exclude atmospheric electric potential.

There seem, unfortunately, no data whence one can derive trustworthy information as to changes from year to year in the mean potential gradient in the open. An attempt is at present being made at Kew to fill this gap, but with what success remains to be seen. I think information on the point, both at high and low levels, is much to be desired.

§ 65. We shall now consider certain resemblances between magnetic and meteorological phenomena in the average year, which merit consideration in connection with theories as to the source of the magnetic diurnal variations.

If we take the mean monthly values of temperature range and vapour pressure at Kew, used in obtaining Table XLVI., and represent each monthly value as a percentage of the mean of the 12 monthly values, we get the results in Table XLVII. For comparison, this also gives the corresponding monthly percentages which are the means found for the ranges of D and H employed in the calculation of Tables XXXIII. and XXXIV.

TABLE XLVII.

	Jan.	Feb.	March.	April.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.
D and H ranges . . .	54	62	102	128	134	132	131	133	120	96	66	42
Temperature ranges . .	62	75	98	117	125	128	124	116	119	95	76	67
Vapour pressure . . .	72	70	74	85	99	126	139	142	127	102	90	74

In the case of vapour pressure, we are dealing not with a diurnal range, but with the mean value for the 24 hours. I have introduced it principally to show that the seasons of maximum and minimum vapour pressure are conspicuously later in the year than the seasons of maximum and minimum magnetic range, and that the values of vapour pressure in March and December are much alike, whereas magnetic ranges in the former month are double those in the latter.

It will be noticed that the annual range in temperature percentages in Table XLVII., viz., from 62 to 128, is less than that for D and H, and that the winter minimum for temperature occurs unmistakably in January, and so is *later* than the magnetic minimum.

§ 66. The points of agreement and difference between temperature and magnetic phenomena are brought out more fully by a consideration of the Fourier series for the diurnal inequalities of temperature. Such series have been given by General STRACHEY* for first order stations of the Meteorological Office employing an 11-year period, and for Greenwich employing a 20-year period. Taking General STRACHEY'S figures, I have calculated the annual variation of the "c" coefficients—*i.e.*, the amplitudes of the periodic terms—expressing the value for each month as a percentage of the mean of the 12 monthly values. The results are given in Table XLVIII., along with corresponding magnetic data representing the mean results for D, I, H, and V, as given in Tables XXIV. and XXV. In the case of c_1 and c_2, I give a mean result for Valencia, Falmouth, and Stonyhurst, in addition to values for Greenwich and Kew. General STRACHEY'S notation is P for my c.

TABLE XLVIII.—Variation of Fourier Coefficients in the Diurnal Inequality, throughout the Year.

	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.
c_1.												
Temperature (Valencia, Falmouth, Stonyhurst) . . .	40	57	97	130	161	149	144	135	115	81	52	40
Temperature, Greenwich . .	37	62	92	127	145	151	152	141	127	82	55	32
,, Kew	39	52	102	126	147	144	146	139	123	91	54	37
Magnetics, Kew	42	58	91	126	150	147	148	138	122	94	57	27
c_2.												
Temperature (Valencia, Falmouth, Stonyhurst) . .	91	109	126	114	70	48	58	99	137	137	113	94
Temperature, Greenwich . .	87	117	125	112	66	52	61	103	158	143	108	70
,, Kew	100	113	157	111	40	33	23	87	154	167	124	90
Magnetics, Kew	56	57	102	134	134	127	130	126	113	94	78	49
c_3.												
Temperature, Greenwich . .	85	71	43	114	149	144	153	130	69	69	95	78
,, Kew	73	50	37	120	178	134	157	149	102	45	87	68
Magnetics, Kew	54	79	133	140	110	91	94	133	145	119	68	35

§ 67. Before discussing Table XLVIII. I wish to explain my position.

General STRACHEY† has pointed out that the fact that a diurnal inequality can be

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* 'Phil. Trans.' for 1893, p. 617.

† *Loc. cit.*, p. 636.

analysed into Fourier terms is no proof of the existence of "distinct physical influences operating in recurring cycles of 24, 12 . . . (hours)." He has in fact shown that the simple hypothesis that the heating effect of the sun varies as the sine of his altitude, being nil when the sun is below the horizon, gives rise to Fourier series which constitute not at all a bad first approximation to the results actually found at certain stations.

Accepting this contention, we may however get much useful information from the FOURIER'S analysis. For instance, we know that the consequences of surface heating on underground temperature can be most easily arrived at by an analysis which treats the Fourier terms as independent entities. Also the examination of differences between the relative values of c coefficients at different seasons of the year, or in different years at the same season, is perhaps the most hopeful way of ascertaining community of origin in different phenomena.

§ 68. Returning to Table XLVIII. we see that in the case of c_1 there is a very close resemblance between the annual variations in temperature and magnetics. The agreement is just about as good as that between the temperature results for Kew and Greenwich, and decidedly better than that between some of the individual magnetic elements at Kew. The difference between December and January is certainly less conspicuous in temperature than in magnetics, but still at both Kew and Greenwich the December temperature mean is the lower.

In the case of c_2 and c_3 the temperature results at the different stations differ more widely than in the case of c_1, but clearly the law of annual variation is here altogether different from that appearing in magnetics. The temperature data for c_4 seemed too small and uncertain to be worth detailed consideration.

As regards the relative importance of the different Fourier terms in temperature and magnetics, the following are the ratios for the yearly means :—

	c_2/c_1.	c_3/c_1.	c_4/c_1.
Temperature (after STRACHEY) mean from Greenwich . . .	·21	·08	·03
" " " 7 British stations .	·23	·10	—
Magnetics (at Kew) mean from D, I, H and V	·64	·32	·13

This shows the much greater relative importance of the 24-hour term in temperature than in magnetics. The difference is probably even greater than the figures suggest. The magnetic values of c_1, &c., refer to mean inequalities for the year; whereas General STRACHEY'S corresponding values represent arithmetic means of 12 monthly values, and his phase angles are most variable in the shorter period terms. It will be seen in fact that the values obtained for c_2/c_1, &c., from the mean temperature inequalities for 1892 to 1895, or 1889, 1890 and 1899, in § 62, are less than the values we have just derived from General STRACHEY'S figures.

§ 69. A rather striking illustration of the points of agreement and difference just discussed, was afforded by the case of V at Kew. As already stated, all the tables had to be re-calculated, making allowance for the non-application of a temperature correction in earlier years of the period. I was puzzled for a time by the. at first sight, remarkable fact that whilst the new values of c_1 differed very appreciably from the old, there was exceedingly little difference between the new and old values of the other c coefficients, or of any of the phase angles. The explanation simply was that the external diurnal temperature inequality was pretty exactly represented in the magnetograph room—of course, on a very much reduced scale—with the hours of maximum and minimum so retarded as to bring them much closer to the corresponding times for the diurnal variation of V.

§ 70. There are other important conclusions to be drawn from the comparison of temperature and magnetics. The source of the solar diurnal inequality in magnetism is, of course, the sun, acting in some way or other; the only question is how. The researches of GAUSS, SCHMIDT, ADAMS, and others all point to the conclusion that magnetic force at the Earth's surface is derived, if not exclusively, at least in a wholly preponderating degree, from centres of force within that surface. Accepting this conclusion, one would most naturally perhaps look for the action of the sun on the Earth itself as the cause of the diurnal inequality. MAXWELL and others have pointed out that the tidal effect of the sun by modifying internal strains must exert *some* influence on magnetic strata; but the trifling size of the lunar magnetic inequality indicates that any such effect must be very small.

The only other obvious direct solar effect on the Earth itself is the diurnal heating and cooling of the surface. It has been pointed out, however, by Principal RÜCKER that, owing to the great preponderance of ocean, the portion of the Earth's surface exposed to appreciable temperature variation is comparatively small. What I wish to point out in addition to this is that any diurnal variation of temperature in the Earth diminishes very rapidly as the depth increases, and the rate of decrease is more rapid for the part of the surface heating represented by the 12-hour and 8-hour Fourier terms than for the part answering to the 24-hour term. Also any seasonal underground change of temperature lags behind the surface change. Now we have seen that the ratios borne by the amplitudes of the higher order Fourier terms to the amplitude of the 24-hour term are not smaller, but much larger, in the magnetic elements than in temperature; whilst magnetic seasonal changes seem earlier than those of surface temperature, and much earlier than those presented by an element such as vapour pressure known to be directly dependent on temperature. There is, of course, the further obvious point that surface temperature shows no large difference from years of sun-spot maximum to years of minimum, and still less will underground temperature.

This reasoning may appear quite unnecessary to those who accept Professor SCHUSTER's able paper in the 'Phil. Trans.' for 1889, p. 467, as *proving* the chief if not exclusive source of the magnetic diurnal inequality to be external to the Earth. I must confess, however, that whilst I consider the conclusion, which has been arrived at by other physicists from other points of view, to be probably in the main correct, I think that the investigation ought to be repeated when practicable for at least two different groups of years, one representing numerous, the other few sun-spots; and trustworthy *simultaneous* data from at least ten or twelve well distributed observatories would be highly desirable, if not absolutely necessary. Meantime, I suspect, the vertical force is likely to prove a stumbling block.

Nature of the Relationship between Sun-Spots and Terrestrial Magnetism.

§ 71. It was pointed out in the "Preliminary Note" that WOLFER'S table of sun-spot frequencies is based on *all* days for which solar observations exist, whereas the Kew magnetic data refer to five days a month only. If one divided the days of a month for which sun-spot data exist into two equal groups, the one containing the days of the lowest frequency, and if from this group one selected five days at random, the mean frequency for these days would often be but a small fraction of WOLFER'S own mean for the month. Thus if, as has frequently been suggested, sun-spots were the immediate cause of magnetic disturbances, the disturbance being synchronous with the spot, the presumption would be that the sun-spot frequency for *all* and for *quiet* days would be altogether different, the latter being much the smaller. As explained in the "Note," data which WOLFER does publish for individual days were not used for the following reasons; (1) being only *provisional* they are presumably less trustworthy than the finally accepted monthly values appearing in Table I.; (2) not infrequently data were wanting for several of the selected quiet days.

I have, however, looked carefully into the matter, to see whether the results here arrived at would have been materially modified if sun-spot frequencies had been taken from *quiet* days only. For this purpose, frequencies were calculated for each month, using WOLFER'S *provisional* values for the selected *quiet* days. These are compared in Table XLIX. with the corresponding data derived by WOLFER from his provisional values for *all* days. In forming the means I have left out of account three months when there were less than two quiet days.

TABLE XLIX.—WOLFER'S *Provisional* Sun-Spot Frequencies.

	All days.	*Quiet* days.		*All* days.	*Quiet* days.		*All* days.	*Quiet* days.
January . .	40·1	47·6	May . . .	43·5	42·2	September .	45·6	45·7
February. .	40·4	42·0	June . . .	45·3	43·3	October . .	41·6	41·1
March . .	35·6	30·0	July . . .	45·4	42·3	November .	32·4	35·1
April . . .	41·2	39·8	August . .	45·7	47·4	December .	35·6	37·3

I also show side by side in Table L. the mean seasonal and yearly values obtained for sun-spot frequencies from Table I. and from the two sets of provisional data made use of in Table XLIX. Results are given for the groups of sun-spot maximum and minimum years, as well as for the whole period.

TABLE L.—Mean Seasonal and Yearly Values of WOLFER's Sun-Spot Frequencies.

	Winter.			Equinox.			Summer.			Year.		
	11 years.	1892–5.	1890, &c.	11 years.	1892–5.	1890, &c.	11 years.	1892–5.	1890, &c.	11 years.	1892–5.	1890, &c.
Final values Table I.	39·4	71·1	8·2	41·0	68·9	11·2	44·7	84·8	9·2	41·72	75·0	9·5
Provisional *all* days	37·4	67·1	6·9	41·0	69·2	11·3	45·0	85·6	9·2	41·22	74·1	9·1
Provisional *quiet* days	40·8	72·7	8·7	39·2	69·0	10·6	43·8	81·8	10·4	41·28	74·5	9·9

§ 72. The smallness of the differences between the means from *all* and from *quiet* days seems to dispose absolutely of any theory which regards sun-spot frequency on a given day as any guide whatsoever to the quiet or disturbed character of Terrestrial Magnetism on that particular day. For our immediate purpose, however, the important thing is the evidence afforded by the above Tables, that the results we have obtained for the a and b constants in the sun-spot formula, would be but little affected if we took frequencies answering to magnetically quiet days only.

In the methods in which we have employed groups of years, the sun-spot data required for calculating seasonal or mean yearly values of b and a are those given in Table L. It is thus obvious, so far at least as mean annual values are concerned, that the result of substituting *quiet* day frequencies would be as nearly as possible nil. Summer values of b and b/a would be slightly raised by the substitution, winter and equinoctial values very slightly diminished.

§ 73. I next investigated whether rises and falls in WOLFER's frequencies, as given in Table I., and as deduced from provisional values for quiet days proceeded on parallel lines. Table I. presents a rather singular feature. If we attach the signs + or − according as there is a rise or fall in the frequency in passing from one month to the next, we find that there are no fewer than 90 changes of sign out of a total possible of 130. We have long sequences of + and − occurring alternately, *e.g.*, from January, 1895, to March, 1896. It looks as if the monthly changes generally went beyond the temporary equilibrium position, or else as if the estimate of them generally overshot the mark. The quiet day provisional frequencies present the same feature, though the monthly changes they show differ appreciably in general from those deduced from Table I. Omitting the three months already referred to, we have 125 monthly changes common to the two sets of frequencies. Of these 97 agree, and 28 differ in sign. If, however, we take only those cases in which the monthly change amounted to at least 10 in one or other of the two sets of data, we find an agreement in sign in no less than 60 cases out of 72.

Passing to the monthly changes in the percentage values of the D and H ranges, given in Tables XXXIII. and XXXIV., we find there also frequent alternations of rises and falls. For instance, in Table XXXIII., rises and falls alternate without a break from January, 1893, to January, 1894. On the whole, however, there are appreciably fewer transitions of sign in the D and H Tables than in Table I. When the monthly changes in the two sets of sun-spot frequencies differ in sign, the changes in Tables XXXIII. and XXXIV. agree sometimes with the one set, sometimes with the other, there being in both tables a very slight preponderance of agreements with WOLFER'S *all* day frequencies. This may be purely accidental, but at all events the magnetic changes agree at least as well with the sun-spot data from all days as with those from quiet days only.

§ 74. There still remains the question whether there is a distinct connection between the mean values for individual *months* of sun-spot frequencies and magnetic ranges. In the case of H there does seem fairly definite evidence of such a connection. If we take the changes of sign we have just been considering in Tables I. and XXXIV., we find an agreement in sign in 74 cases, as against disagreement in 55 cases; and if we confine ourselves to cases where the changes between successive months' values, in Table I., is at least 10, we find agreement in 34 cases out of 50. This amount of agreement is more than would be at all likely to happen by pure chance. In the case of D, however, the agreements and disagreements in sign are almost equally numerous, and even when we confine ourselves to cases where the sun-spot change was at least 10 the balance of agreements is too small to be relied on.

In the case of H a diurnal range of 50γ is exceptionally large; the curve is read only to 1γ; the average non-cyclic effect is 3γ, and there may be a small uncertainty through temperature. Thus the uncertainty in individual figures in Table XXXIV. cannot well be less than 2 or 3 per cent. even at midsummer. In the case of D, the range often exceeds $10'$, and seldom falls below $5'$; the curve is read to $0'\cdot1$; the non-cyclic effect is very small, and there is no temperature correction. Thus the uncertainty in individual figures in Table XXXIII. should be considerably less than in Table XXXIV. Thus the absence of an unmistakable connection between D ranges and sun-spot frequencies in individual months has stronger evidence in its favour than has the apparent connection between H ranges and monthly sun-spot frequencies.

If instead of individual months we take years the connection is clear, and it is manifest enough, even in D, for considerably shorter periods than years at times when sun-spot frequency has a rapid general drift in one direction.

§ 75. Some light on the degree of intimacy of the connection is derivable from the amount of agreement between the individual monthly ranges observed in D, H and I and those calculated from the values of a and b in Table XL. The probable errors calculated from the differences between the eleven observed and calculated values for four months representing different seasons of the year were as follows:—

	D.	I.	H.
Greatest	0′·9	0′·23	3·2γ
Least	0·5	0·13	2·2γ
Mean	0·65	0·18	2·8γ

These probable errors are by no means large, considering that the range for any individual month depends on only five days' results, and that the non-cyclic effects in I and H are so considerable. Still the results tend to confirm the conclusion to which other considerations point, that the departures from the mean shown by magnetic phenomena on quiet days cannot be solely determined by the simultaneously existing sun-spot frequency, unless we are prepared to hold that either WOLFER's sun-spot data or Kew magnetic data are habitually affected by considerable errors.

§ 76. There are a variety of ways of explaining the phenomena, some of which may be indicated briefly. The whole solar system may be under the action of some external agency, whose effect on the sun is made manifest by the occurrence of sun-spots. As the influence simultaneously existent would naturally vary from part to part of the solar system, this hypothesis would not be inconsistent with the view that the influence on the sun itself is measured by the sun-spot frequency. The influence might be of the nature of a radiation making the Earth's atmosphere offer a lessened resistance to the electric currents due to solar action to which various physicists ascribe the diurnal magnetic inequality.

Or the sun itself might be the sole agent, if we suppose that sun-spot frequency is a qualitative rather than a quantitative measure of its activity. The sun-spot might stand to the really active cause somewhat as the smoke from a locomotive to the heat of its furnace. When smoke issues we know the fire is alight, but we cannot deduce the actual heat.

There is a third obvious alternative, viz., that the sun-spot frequency is a direct measure of the sun's contemporaneous activity, but that the effect at the earth depends appreciably on what has been happening at the sun for some time previously. This is what we might expect to happen if the sun were the origin of a radiation which took a considerable time to part with all its ionising power, or which travelled so much slower than light that emanations leaving different parts of the sun simultaneously reached the earth at appreciably different times. If however this third alternative were true, we should expect magnetic phenomena to show a general tendency to lag behind sun-spot frequency. Mr. ELLIS has made investigations on this point, but has detected no certain lag. It is, however, open to doubt whether a short lag—a month or two for instance—would with certainty be shown by the method he employed.

Before concluding, I wish to acknowledge the valuable assistance given me by several members of the staff of the Observatory Department of the National Physical Laboratory.

Mr. T. W. Baker, the Chief Assistant, gave much useful help in the interpretation of the earlier magnetic records.

To Mr. G. Badderly and Mr. B. Francis I am indebted for much careful arithmetical work, especially in connection with the calculation of Fourier coefficients.

The calculation work has been exceedingly heavy, and some errors have doubtless escaped me, but every reasonable precaution has been taken to secure accuracy.

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ON THE PHOTO-ELECTRIC DISCHARGE FROM METALLIC SURFACES IN DIFFERENT GASES

BY

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X. *On the Photo-Electric Discharge from Metallic Surfaces in Different Gases.*

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Communicated by Professor J. J. Thomson, *F.R.S.*

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The experiments described in this paper were designed with a view to studying as systematically as possible the dependence of the magnitude of the photo-electric current from a metal surface illuminated by ultra-violet light—or Hallwachs effect, as it is called, after the name of its discoverer, by continental physicists—on the pressure and nature of the gas in which the illuminated surface is enclosed.

Very few experiments appear to have been made on the comparison of photo-electric currents in different gases, and the experiments hitherto carried out on the photo-electric effect in gases at pressures other than atmospheric have been made principally to test special points in theory; such as those made by Townsend ('Phil. Mag.,' 6th series, vol. 3, p. 557, 1902) in support of the theory of the genesis of ions by collision.

The researches of Stoletow and of von Schweidler are, however, exceptions, though their results do not enable comparisons of the photo-electric currents at different pressures to be made, except under certain very special conditions. The deductions drawn by Stoletow from his observations—which are summarized in the 'Comptes Rendus,' vol. 108, p. 1241, 1889—will be dealt with more fully later, but it will be advantageous to refer at the present stage to von Schweidler's experiments ('Sitz.-Ber. d. k. Akad. Wien,' Abth. IIa, vol. 107, p. 881, 1898, and vol. 108, p. 273, 1899).

E. von Schweidler examined more especially the effect of varying the potential difference between the electrodes on the photo-electric current, giving curves connecting these quantities at a few different pressures between 1 and 760 millims. mercury. The curves at the different pressures were independently obtained, and no data are given which enable a comparison of the curves with one another to be made. They show, however, that at each pressure examined the current increases rapidly with the potential difference up to a certain value, after which the increase is much more gradual until another critical value is reached, when a further increase in the potential again causes a rapid increase in the current. The experiments were conducted solely in air and the results obtained are purely qualitative.

Owing to the complicated nature of the connection between the photo-electric current and the potential difference between the electrodes, it is not possible to compare the currents for different pressures or gases under any simple definite conditions, as would have been the case if a saturation current had existed for ionisation produced by the photo-electric effect as it does for that produced by Röntgen rays. Under the circumstances the only satisfactory method of comparing, for example, the currents in a gas at two different pressures appeared to be to draw the complete curve connecting the current and the potential difference for each pressure, keeping the intensity of the illumination constant throughout the whole series of observations at both pressures.

Source of Ultra-Violet Light.

The greatest difficulty encountered during the course of the research was that of obtaining a source of ultra-violet light which could be relied upon to remain approximately constant, at least, in intensity throughout the whole course of long ranges of observations, often extending over many hours. An arc light or the spark between zinc terminals in the secondary of an induction coil worked from accumulators, with some form of interrupter in the primary circuit, which are the sources of ultra-violet light ordinarily used, proved utterly unsuitable, as did also arrangements suggested by KREUSLER ('Verh. der Phys. Gesel. Berlin,' Jahrg. 17, p. 898) and WULF ('Ann. der Phys.,' vol. 9, p. 948, 1902).

The source ultimately adopted and used in the majority of the experiments described below was an arc between iron wire terminals. The wires were tapped into the ends of long brass screws working in corresponding threads in brass pieces attached to the sides of a wooden frame, this arrangement rendering it easy to adjust the sparking distance without displacing its position.

The terminals of the arc were connected to the secondary terminals of an induction coil, in parallel with which were also three large Leyden jars. An alternating current of about 4 ampères passed through the primary of the coil when a key in the primary circuit was closed.

In order to obtain an arc which will work constantly for a sufficiently long time it is necessary to use iron wires of such a diameter, and regulate the current through the primary, so that although the terminals become white hot, yet the heat developed is just not sufficient to cause particles of the iron to be melted off. Under favourable conditions, when the ends of the terminals had once become properly rounded, the intensity of the arc would remain quite constant, without any need for adjusting the spark length, when run for as many as fifty or a hundred 10-second periods with intervals of a few minutes between each.

An arc between aluminium terminals was also tried, but proved unsatisfactory owing to the rapid volatilization of the aluminium and consequent lengthening of the arc, thus causing an alteration in the intensity of the light emitted.

The arrangement described above, although proving satisfactory as a rule, required much attention at times, and a modified form has recently been adopted which, though not so simple in construction, affords a much more reliable source of ultra-violet light. The improvement consists in having the iron terminals in an atmosphere of pure hydrogen, the spark apparatus being shown diagrammatically in fig. 1. A brass tube B, 12 centims. in length and 3 centims. in diameter, was closed at one end by a quartz window Q. The iron terminals TT were admitted through the side tubes SS, and were surrounded by glass tubes GG, as shown in the figure. This was necessary in order to prevent short-circuiting across the brass vessel, and long side tubes were necessary, as it was found that a metallic film was deposited on surfaces near the spark, which was also liable to cause short circuits unless some such precaution was taken. All joints were made airtight by sealing wax. A continuous slow stream of hydrogen was passed through the apparatus, entering at A and leaving at E. The hydrogen was prepared in a KIPP's apparatus from pure zinc and hydrochloric acid, and was dried by bubbling slowly through concentrated sulphuric acid and passing through long tubes packed with calcium chloride. It was necessary to ensure that the hydrogen was perfectly free from oxygen, or water vapour was formed when the discharge passed, and this being opaque to ultra-violet rays would quickly rob the light passing out through the quartz window of these rays. The length of spark used was about 6 millims.

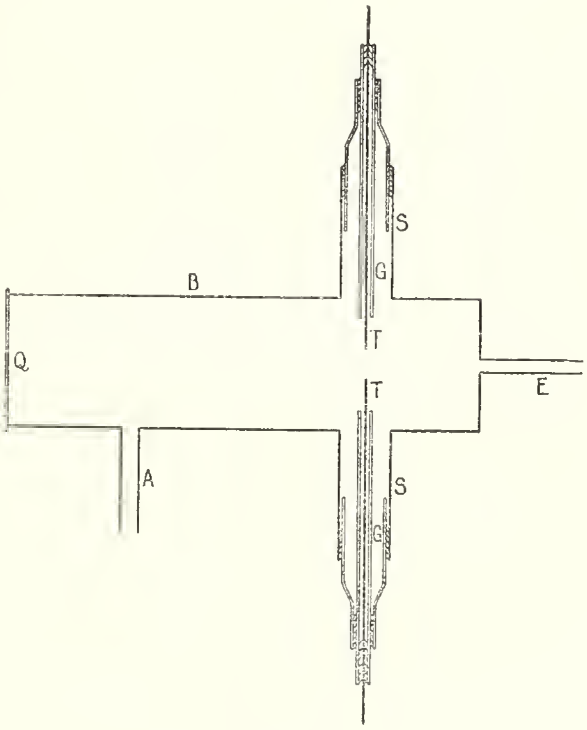

Fig. 1.

The ultra-violet light obtained by this method remained practically unaltered in intensity for hours or even days, the spark being usually run for 10-second periods every few minutes.

The later series of experiments were made using this source of light, though the simpler arc in air is quite satisfactory unless very long series of observations are needed or great accuracy is required.

Apparatus and Method Employed.

In order to be able to test the constancy of the ultra-violet light employed, two separate pieces of apparatus were used, in one of which the conditions under which the photo-electric currents were measured remained invariable, whilst in the other the conditions were altered as required. The first apparatus served as a means of testing the regularity of the intensity of the light, and, on the assumption that the photo-electric effect is proportional to the intensity, of correcting for any small irregularities which might occur in the strength of the light, though this was rarely necessary, while in the second apparatus the experiments proper were carried out.

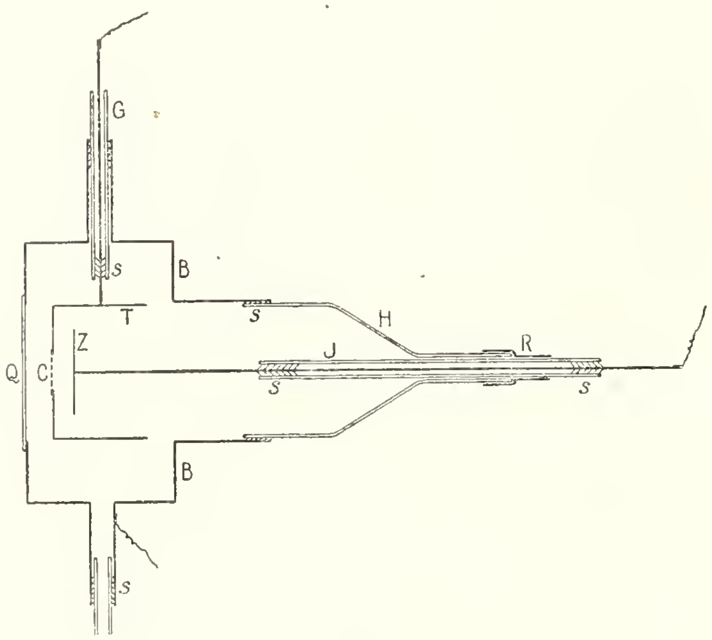

Fig. 2.

The apparatus with which most of the series of observations were made is shown diagrammatically in fig. 2.

The brass vessel, BB, consisted of two cylinders of different diameters arranged end-on as shown. An opening 4·5 centims. in diameter, cut in the front face of the larger cylinder, was closed by a quartz window Q, attached by sealing wax. Two brass side tubes were soldered on to this cylinder, through one of which passed a glass tube G. Through this was fixed a stout brass rod which supported a thin copper tube T, one end of which was covered by a very fine copper grating C, the wires of which were 0·25 millim. in diameter, placed 0·25 millim. apart, and which formed one electrode. The other side tube served to connect to a pump and gauge. Into the back of the smaller cylinder fitted a wide glass tube H, drawn down narrower at the other end, into which a second glass tube, J, would just slide easily. A brass rod supporting the other electrode, F, passed through this inner tube, and by this arrangement the electrode could be changed or removed to be polished by breaking the one joint between the wide glass tube H and the brass cylinder. All the joints SS were of sealing wax and perfectly air-tight. They were arranged as far as possible so as to ensure the insulation of the electrodes remaining permanently good.

The joint between the two glass tubes carrying the rod connecting to the electrode F (that at R) was made by slipping rubber compression tubing over the two tubes, after lubricating well with glycerine. This made a perfectly air-tight joint and enabled the distance between the two electrodes to be altered by any desired amount, when the apparatus was exhausted, without admitting any air and thereby altering the pressure.

The front of the tube T, covered by the gauze, or rather grating, formed of similar wires to those described above, only allowed the light to fall on the central portion of the electrode F, and the apparatus had the further advantage that the light only traversed a small thickness of the gas in the vessel before reaching the electrode.

The second apparatus, used principally for testing the ultra-violet light, is shown diagrammatically in fig. 3. It was of much smaller volume than the other one, and in this apparatus the electrode, Z, was always of zinc. The apparatus was only used at low pressures and it was seldom necessary to repolish the zinc, it being found that at pressures below, say, a tenth of an atmosphere, zinc showed little or no signs of fatigue when illuminated by ultra-violet light. Further description of this apparatus is unnecessary, the lettering of fig. 2 applying also to this diagram.

Each leak apparatus (as they may be termed for brevity) was connected to a Töpler pump and to a barometer column. The pressures were read by noting the differences in height between these and true barometer columns placed beside them. The main apparatus was also connected to a McLeod gauge which enabled pressures down to 0·001 millim. to be accurately read. Suitable drying bulbs containing phosphorous pentoxide were included between the pump, McLeod gauge, and leak apparatus. A side tube closed by a good stop-cock was attached to the tube connecting the pump and leak apparatus, by means of which any desired gas could be admitted into the apparatus or the whole exhausted down to any pressure above about 20 millims. by connecting to a water pump.

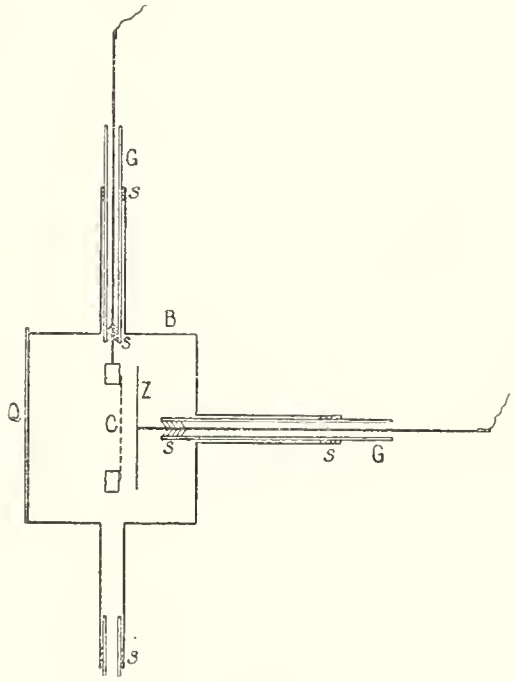

Fig. 3.

The apparatus was so arranged that the spark gap was in the focus of a quartz convex lens of about 30 centims. focal length, and by turning the lens slightly a parallel beam of rays could be thrown on to the sensitive electrode of either leak apparatus. Each of these electrodes was connected to the negative terminal of a battery of small secondary cells, the number of which could be varied up to 180. The other electrodes, the gauzes, were connected through a three-way key to one pair of quadrants of an electrometer and to earth, except when a key, which we will term the electrometer key, was raised. The other pair of quadrants of the electrometer, the positive terminal of the battery, and the metal case of each leak apparatus, were all permanently earthed. All wires leading to the electrometer were run through earthed brass tubes, and when additional capacity was introduced into the electrometer circuit, a parallel plate condenser enclosed in a metal-lined box was used, the casing of the box being also connected to earth.

The electrometer was of the ordinary type, and was used with electric lamp filament and scale. The needle was usually charged to a potential of 400 volts, and, as tested with a standard cell, gave a deflection of about 70 divisions for a volt on a scale 3 metres away.

In taking an observation, the electrometer key was first raised so as to insulate the one pair of electrometer quadrants and the zero position of the filament image on the scale noted. The key in the primary circuit of the induction coil was now closed and the spark allowed to run for usually 10 seconds, when the primary circuit was again broken, and the deflection of the electrometer needle noted. The spark was run and the observations taken at regular intervals as far as possible.

Variation of the Photo-Electric Current with the Pressure of the Gas.

The following series of experiments on the variation of the photo-electric current from an illuminated zinc surface with the pressure of the surrounding gas, were carried out in hydrogen, so as to avoid errors arising from the tiring of the zinc surface which occurs in air at ordinary pressures when it is illuminated by ultra-violet light. In hydrogen, the zinc showed no signs of this fatigue effect under the influence of the light, and after taking a complete series of observations it was always possible to repeat any one of them and obtain the same values for the currents as before; the same holds true in air also at pressures below about one-tenth of an atmosphere.

The results obtained for a whole series of pressures, ranging from 760 millims. down to 0·008 millim., are given in Table I. The zinc electrode was situated 3·5 millims. behind the gauze electrode, and a difference of potential of 1 volt between the electrometer quadrant-pairs corresponded to a deflection of 60·6 divisions on the scale. The currents are measured in electrometer scale divisions per 10 seconds. The total capacity of the leak apparatus, electrometer, and connecting wires was about 90 centims., so that a deflection of 60 divisions per 10 seconds corresponds to a current of 10^{-10} ampère (very nearly).

The intensity of the ultra-violet light, as measured by the second leak apparatus, showed no appreciable change throughout the course of the observations, the deflections obtained for 10 seconds' illumination being, at the beginning, 212, 208 divisions; at intervals during the experiments, 204, 209, 212, 215 divisions; and at the end, 214 and 209 divisions. As a further precaution, the first set of observations taken (that at 760 millims.) was repeated at the close, and almost identical values for the currents obtained, as the numbers given show.

TABLE I.

Potential to which zinc is charged in cells. (1 cell = 2·1 volts.)	Current from zinc surface in hydrogen in electrometer scale divisions in 10 seconds, the pressure being—											
	760 millims.	351 millims.	101 millims.	49·5 millims.	20 millims.	8 millims.	3·3 millims.	0·70 millim.	0·27 millim.	0·13 millim.	0·008 millim.	760 millims.
4	—	—	21	29	48	71	108	118	92	89	67	—
20	16	26	40	51	80	111	158	213	149	131	—	16
40	—	—	—	—	—	—	280	412	240	—	—	—
60	—	—	64	77	116	204	—	—	—	140	—	—
80	—	—	—	—	—	338	—	—	—	—	—	—
100	34	44	76	100	167	—	—	—	—	142	—	33
140	—	—	—	—	303	—	—	—	—	144	—	—
180	43	61	98	145	—	—	—	—	—	158	67	45

These results can be seen more clearly from fig. 4, where the curves connecting the currents and potential difference at the different pressures are plotted. The curves corresponding to the three lowest pressures are shown by dotted lines to avoid confusion.

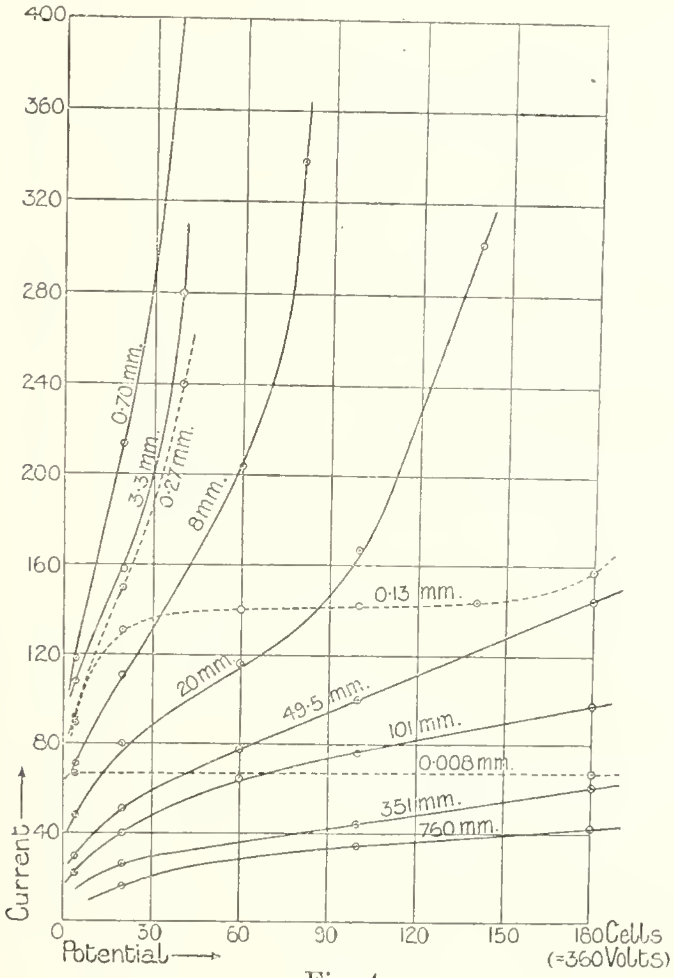

Fig. 4.

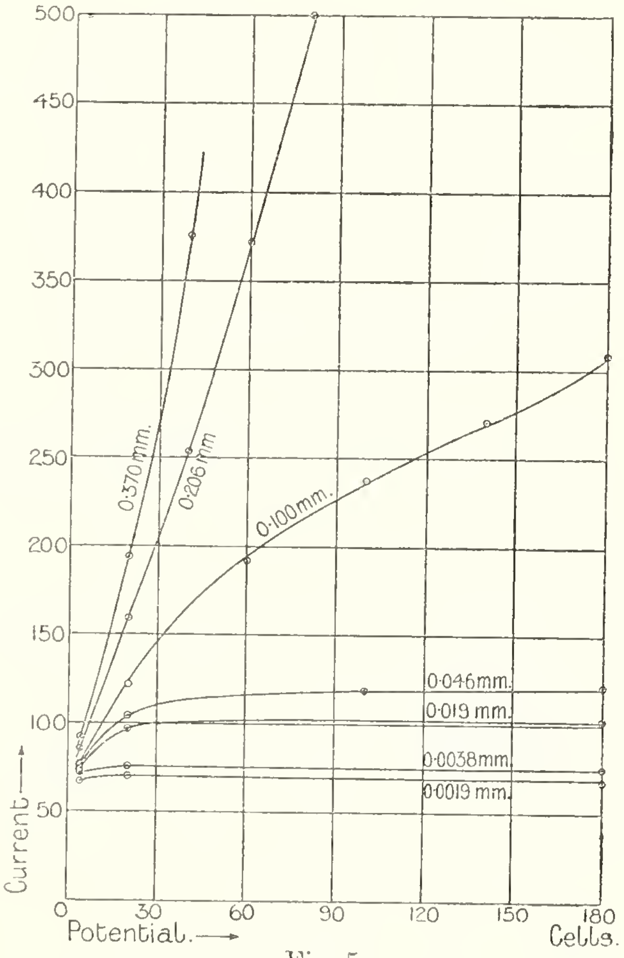

Fig. 5.

The results of a further set of observations, showing more fully than the above the variation of the photo-electric current at very low pressures, are given in Table II. The distance between the electrodes was again 3·5 millims., and 1 volt on the electrometer corresponded to a deflection of 76 divisions. The illuminated electrode was, as before, of zinc, but the experiments were carried out in air. The intensity of the light remained perfectly constant throughout the series. These experiments were carried out in the smaller leak apparatus (the larger being used as the standard) to avoid loss of time in pumping between successive sets of observations. The current-P.D. curves derived from these results are plotted in fig. 5.

TABLE II.

Potential to which zinc is charged in cells. (1 cell = 2·1 volts.)	Current from zinc surface in air in electrometer scale divisions in 10 seconds, the pressure being—						
	0·370 millim.	0·206 millim.	0·100 millim.	0·046 millim.	0·019 millim.	0·0038 millim.	0·0014 millim.
4	92	85	76	75	73	71	66
20	194	159	122	104	96	75	70
40	375	254	—	—	—	—	—
60	630	371	193	—	—	—	—
80	—	501	—	—	—	—	—
100	—	—	237	119	—	—	—
140	—	—	270	—	—	—	—
180	—	—	309	122	102	75	68

A further set of observations was made on the relation between the currents and pressure, using a platinum electrode instead of zinc. The larger leak apparatus was used, and the platinum electrode situated 2 millims. behind the gauze. 1 volt P.D. on the electrometer gave a deflection of 65·6 scale divisions. The series of observations was taken in the order given in Table III., and it was found that between the first and last experiments the light increased nearly 10 per cent. in intensity. This increase was gradual, and has been disregarded.

TABLE III.

Potential to which platinum is charged in cells. (1 cell = 2·1 volts.)	Current from platinum surface in air in electrometer scale divisions in 15 seconds, the pressure being—					
	25 millims.	7 millims.	2 millims.	0·24 millim.	0·061 millim.	0·026 millim.
4	—	—	26	42	36	35
20	29	40	65	65	41	36
40	—	—	117	97	—	—
60	42	62	200	125	—	—
80	—	105	357	—	—	—
100	50	198	—	162	44	—
120	—	406	—	—	—	—
140	67	—	—	209	—	—
160	—	—	—	330	—	—
180	103	—	—	—	46	35

The photo-electric currents from the platinum electrode were found to be from 15 to 20 times less than those from a zinc electrode under the same conditions in air at a pressure of 25 millims.

The results given in Table III. are plotted in fig. 6, the ordinates, as before, representing the currents, and the abscissæ the potentials to which the platinum is charged.

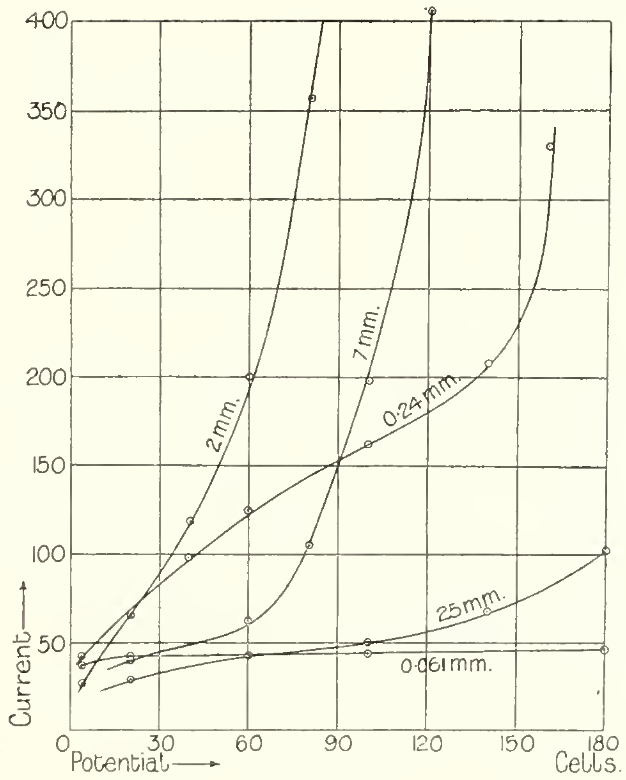

Fig. 6.

Comparison of Photo-Electric Currents in Different Gases.

The results of a number of series of observations on the photo-electric currents from an illuminated zinc surface in the three gases, air, hydrogen, and carbon dioxide are given in the following Tables IV. to VII. The hydrogen was prepared in a Kipp's apparatus from pure zinc and hydrochloric acid, and was dried by keeping it for some time in a long tube filled with lumps of calcium chloride before permitting it to enter the leak apparatus. The hydrochloric acid was removed by passing the gas through a tube containing solid caustic potash in most of the experiments at low pressures; but this was found to be an unnecessary precaution, the hydrogen gas being given off so very slowly that no appreciable amount of the acid was carried over with it. The carbon dioxide was prepared from marble and hydrochloric acid, and was similarly dried. Before allowing a fresh gas to enter the leak apparatus, the latter was exhausted until the pressure of the gas remaining in it was less than $\frac{1}{100}$ millim. mercury. The new gas was then admitted, the stop-cock closed, and the apparatus again exhausted and refilled, so that no trace of the original gas might remain. Other details are given as Notes at the foot of each table.

TABLE IV.

Potential to which zinc is charged in cells. (1 cell = 2·1 volts.)	Current from zinc surface in electrometer scale divisions in 10 seconds in—				
	H_2.		CO_2.		Air.
	760 millims.	76 millims.	760 millims.	76 millims.	760 millims.
4	—	36	—	81	—
20	32	96	45	192	39
100	73	176	128	323	89
180	92	261	176	455	112

Notes.—The experiments were carried out in the small leak apparatus, the zinc electrode being situated 3·5 millims. behind the gauze. A P.D. of 1 volt between the electrometer quadrants corresponded to a deflection of 72 divisions.

The standard apparatus indicated a sudden change in the intensity of the light of 22 per cent. during the course of the last set of readings (CO_2 at 76 millims. pressure), which has been corrected for in the table.

The curves plotted from these observations are given in fig. 7.

TABLE V.

Potential to which zinc is charged in cells. (1 cell = 2·1 volts.)	Current from zinc surface in electrometer scale divisions in 10 seconds in—		
	Air.	H_2.	CO_2.
	30 millims.	30 millims.	30 millims.
4	80	67	133
20	182	144	225
60	253	213	295
80	—	277	—
100	339	407	396
120	406	665	537
140	502	—	825

Notes.—The experiments were carried out in the large leak apparatus, the zinc electrode being situated 2 millims. behind the gauze. A P.D. of 1 volt between the electrometer quadrants corresponded to a deflection of 66·4 divisions. A capacity of 240 centims. was placed in parallel with the electrometer. A very intense spark was used which kept constant to within 3 or 4 per cent., the various sets of observations being repeated a second time after the whole had been once taken.

The results given in this table are plotted in fig. 8.

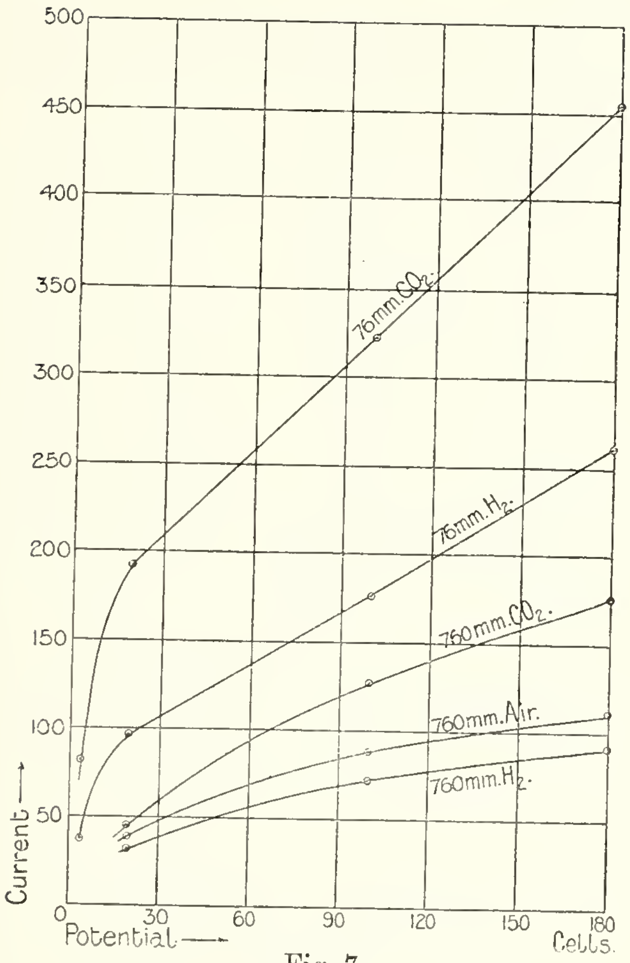

Fig. 7.

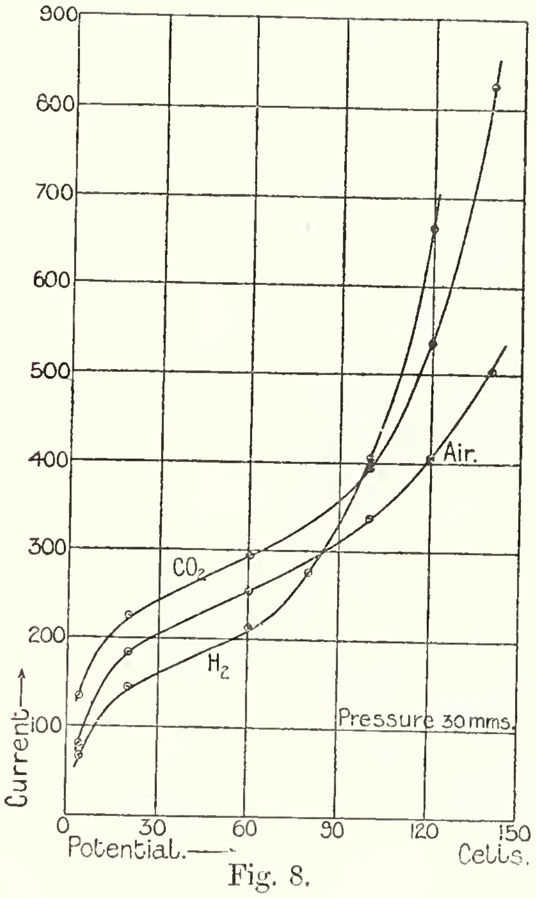

Fig. 8.

TABLE VI.

Potential to which zinc is charged in cells. (1 cell = 2·1 volts.)	Current from zinc surface in electrometer scale divisions in 10 seconds in—					
	Air.		H_2.		CO_2.	
	18 millims.	6 millims.	18 millims.	6 millims.	18 millims.	6 millims.
4	36	49	32	47	65	84
20	78	118	60	93	104	130
40	—	143	—	140	—	158
60	116	166	96	253	139	225
80	132	243	111	459	—	335
100	149	450	142	—	165	—
120	164	—	205	—	—	—
140	178	—	358	—	215	—
160	216	—	—	—	282	—
180	282	—	—	—	375	—

Notes.—The experiments were carried out in the small leak apparatus, the zinc electrode being situated 3·5 millims. behind the gauze. A P.D. of 1 volt between the electrometer quadrants corresponded to a deflection of 77 divisions.

This set of observations was one of the last taken and the spark used was so constant as to render the use of a second apparatus as a check quite unnecessary, the first set of readings taken being repeated at the end and in every case identical values obtained.

The results given in this table are plotted in fig 9.

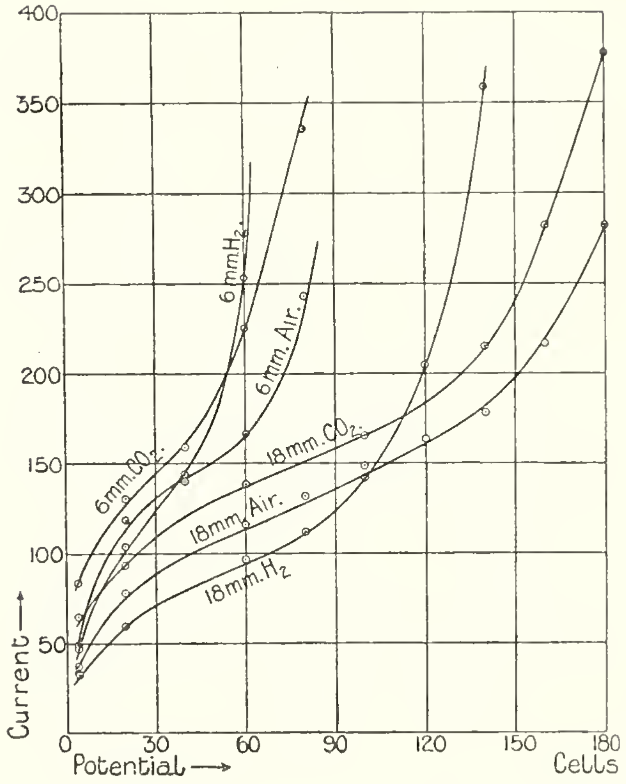

Fig. 9.

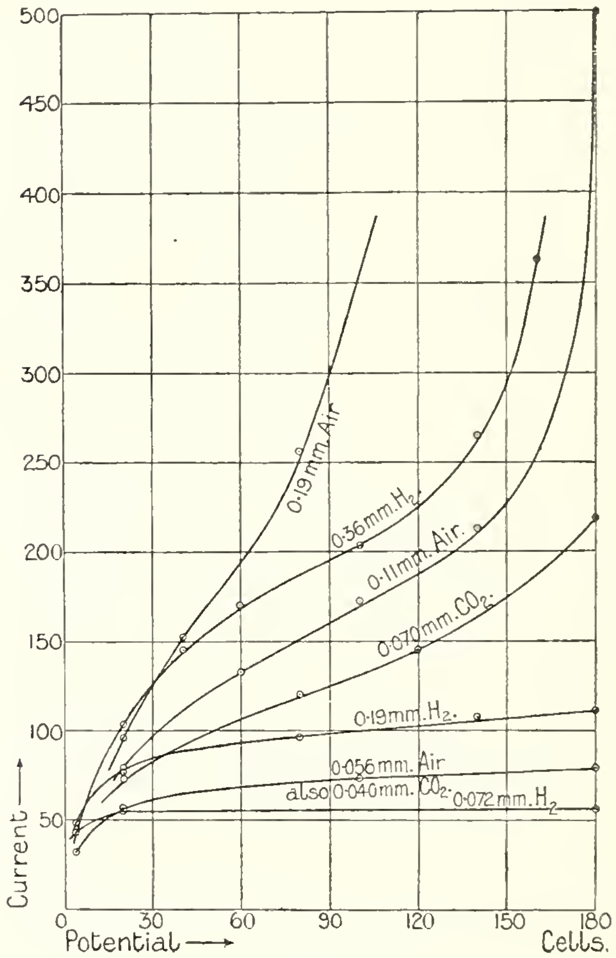

Fig 10.

TABLE VII.

Potential to which zinc is charged in cells. (1 cell = 2·1 volts.)	Current from zinc surface in electrometer scale divisions in 10 seconds in—											
	H_2.				Air.					CO_2.		
	0·36 millim.	0·25 millim.	0·19 millim.	0·072 millim.	0·44 millim.	0·19 millim.	0·11 millim.	0·056 millim.	0·016 millim.	0·21 millim.	0·070 millim.	0·050 millim.
4	43	49	48	42	58	50	45	32	29	47	—	—
20	104	90	80	55	116	96	78	56	34	93	74	61
40	145	—	—	—	200	153	—	—	—	155	—	—
60	170	—	—	—	387	—	133	—	—	234	—	—
80	—	—	96	—	—	256	—	—	—	330	120	—
100	203	124	—	—	—	354	172	74	—	—	—	73
120	—	—	—	—	—	—	—	—	—	—	140	—
140	265	147	107	—	—	—	213	—	—	—	—	—
160	362	—	—	—	—	—	—	—	—	—	—	—
180	700	191	111	57	—	—	508	80	34	—	217	78

Notes.—The experiments were carried out in the small leak apparatus, the zinc electrode being situated 3·5 millims. behind the gauze. A P.D. of 1 volt. between the electrometer quadrants corresponded to a deflection of 68·4 divisions. A capacity of 240 centims. was placed in parallel with the electrometer. The standard showed that no appreciable alteration occurred in the intensity of the light during the course of the observations. The results given in this table are plotted in fig. 10.

The results of two sets of observations taken after substituting a platinum electrode for the zinc are given in Tables VIII. and IX., and the corresponding curves in figs. 11 and 12. The large leak apparatus was used, and the distance separating the platinum and gauze was 2 millims. in each case.

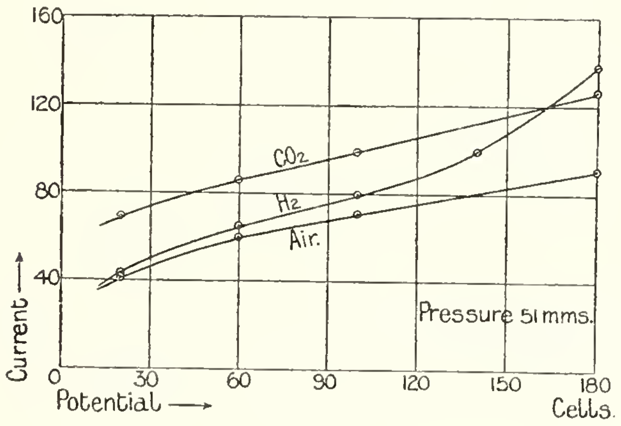

Fig. 11.

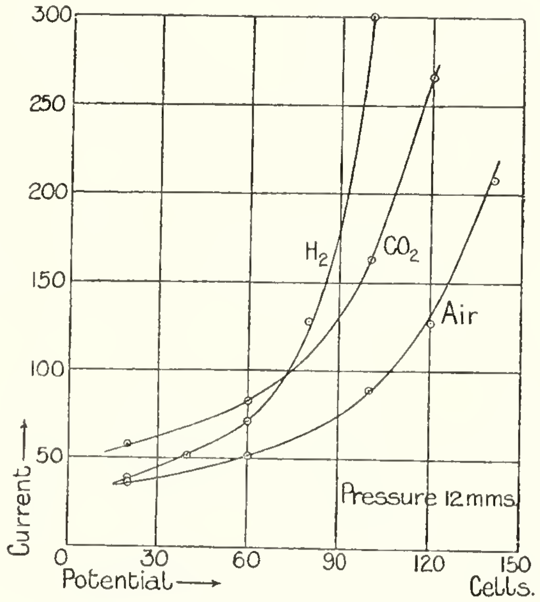

Fig 12.

TABLE VIII.

Potential to which platinum is charged in cells. (1 cell = 2·1 volts.)	Current from platinum surface in electrometer scale divisions in 15 seconds in—		
	Air.	H_2.	CO_2.
	51 millims.	51 millims.	51 millims.
20	41	43	69
60	60	65	86
100	71	80	99
140	—	100	—
180	91	138	127

Note.—1 volt P.D. between the electrometer quadrants corresponded to a deflection of 68 divisions.

TABLE IX.

Potential to which platinum is charged in cells. (1 cell = 2·1 volts.)	Current from platinum surface in electrometer scale divisions in 15 seconds in—		
	Air.	H_2.	CO_2.
	12 millims.	12 millims.	12 millims.
20	36	39	58
40	—	51	—
60	51	72	83
80	—	128	—
100	90	301	163
120	128	—	266
140	208	—	—

Note.—1 volt P.D. between the electrometer quadrants corresponded to a deflection of 67 divisions.

The photo-electric currents in carbon monoxide were also compared with those in air, the results at two typical pressures, viz., 20 millims. and 0·045 millim., being given in the following Table X. The zinc electrode was situated 3 millims. behind the gauze, and 1 volt P.D. between the electrometer quadrants corresponded to a deflection of 72 divisions. The carbon monoxide was prepared from sodium formate and strong sulphuric acid, and was washed and dried before allowing it to enter the leak apparatus.

TABLE X.

Potential to which the zinc is charged in cells. (1 cell = 2·1 volts.)	Current from zinc surface in electrometer scale divisions in 10 seconds in—			
	Air.	CO.	Air.	CO.
	20 millims.	20 millims.	0·045 millim.	0·045 millim.
4	92	73	144	111
20	144	124	182	154
60	212	170	218	173
100	263	203	216	169
140	351	258	—	—
160	475	—	—	—
180	—	394	214	170

These results are plotted in fig. 13.

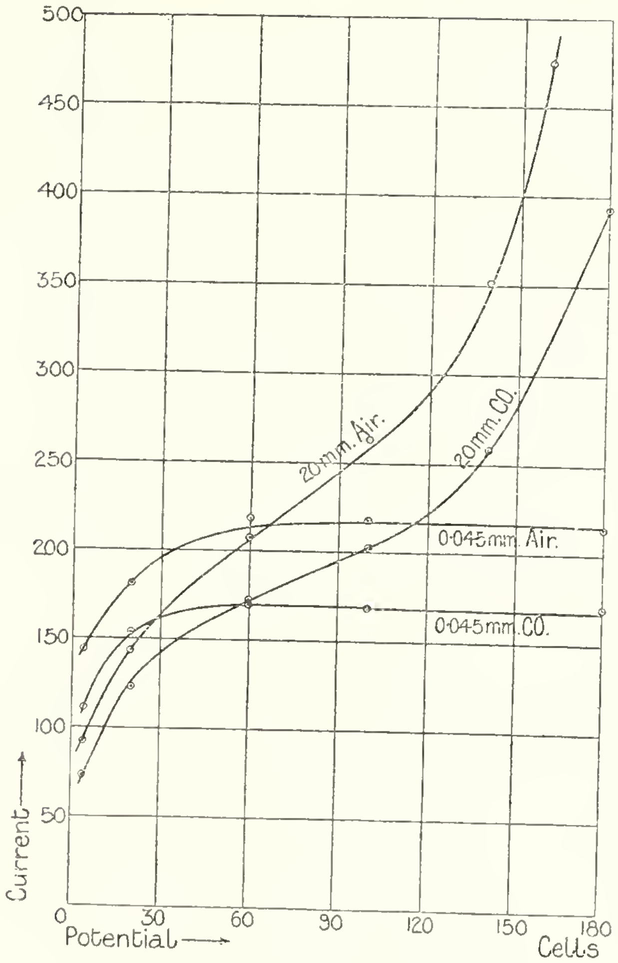

Fig. 13.

Discussion of Observations.

From the series of curves given in figs. 4 and 5 certain of STOLETOW'S results can be verified at a glance. Thus the first result given by STOLETOW—that when the potential is kept constant and the pressure gradually decreased, the current first increases, reaches a maximum, and then decreases towards a finite limit which is independent of the potential within very wide limits—can be seen at once from fig. 4. The second result given by STOLETOW—that at ordinary pressures the current increases slowly with the potential difference, approaching a kind of saturation which is more marked at low pressures—needs modification. As the pressure is lowered the flatter part of the current-E.M.F. curve, corresponding to approximate saturation, becomes steeper and steeper until at a few millimetres pressure there does not appear to be any approach to saturation, a small change in the potential difference producing a big alteration in the current, whatever the potential difference may be. It is only when the pressure is much lower than this that a further decrease in pressure produces a closer approach to saturation, until at a pressure of about a tenth of a millimetre, depending on the distance between the electrodes, we actually get a true saturation current which decreases with the pressure, approaching a finite value as the pressure is indefinitely decreased.

Except for the fact that at the higher pressures no true saturation current exists, the sets of curves obtained can be simply explained by the ionic theory of conduction. We regard the metal surface illuminated by ultra-violet light in a similar manner to a hot surface, and suppose that negative corpuscles escape from the surface under the influence of light, and, in the absence of any force tending to drag them further, simply diffuse back into the metal. If now the illuminated surface is negatively charged, a field is set up and the corpuscles are enabled to escape, and a state of equilibrium will be established when the total number of corpuscles given out by the metal is equal to the sum of the number finding their way to the positive electrode and the number diffusing back into the metal; and, as the field is increased, the latter number will become small compared to the former and we shall get a saturation current—neglecting, of course, any complications introduced by the presence of the surrounding gas.

The curves of fig. 4 show that although we never get a saturation current at the higher pressures, yet at all pressures the current-E.M.F. curve is less steep as soon as a certain potential gradient has been reached. As the potential difference is further increased the current increases more slowly, but uniformly, with the potential difference until another critical potential gradient has been reached, beyond which the current increases much more rapidly than the potential difference, and this rapid increase goes on until an actual spark discharge takes place between the electrodes. From fig. 4 we see that in hydrogen at 20 millims. pressure this latter stage begins when the potential gradient is about 80 cells per 3·5 millims., or nearly 500 volts per centimetre. This second rise in the curve has been shown by Professor TOWNSEND ('Phil. Mag.,' 6th series, vol. 1, p. 198, 1901) to be due to the ionisation of the molecules of the gas by the corpuscles themselves, and the potential gradient at which it begins is inversely proportional to the pressure.

The fact that the current-E.M.F. curves are not horizontal even when we should expect saturation, and that they become steeper and steeper at their flattest parts as the pressure is decreased, seems to indicate that there is ionisation by collision to some extent at gradients much below those at which the second rise in the curve leading up to the spark discharge commences. We have not as yet, however, succeeded in obtaining a thoroughly satisfactory explanation of this phenomenon.

According to PASCHEN'S tables, quoted in Professor J. J. THOMSON'S 'Recent Researches,' the potential gradient necessary for a spark to pass between plates 0·35 centim. apart in air is 116 electrostatic units per centimetre, or 34,800 volts per centimetre at 750 millims. pressure, and in hydrogen 0·55 of this, or 19,200 volts per centimetre. On the supposition, therefore, that ionisation by collision begins at potential gradients slightly lower than those necessary for the discharge to occur—which appeared to be the case at these moderately low pressures, the current-potential difference curve becoming rapidly steeper and steeper until the actual discharge passed—and that the sparking potential is inversely proportional to the pressure, ionisation by collision should commence in hydrogen at 20 millims. pressure at a potential gradient somewhat less than 520 volts per centimetre, which is in close agreement with the value taken from the corresponding curve in fig. 4, and given above, viz., 500 volts per centimetre.

When the pressure is decreased below a few tenths of a millimetre, the character of the curves alters completely, and we now begin to get perfect saturation currents. This critical pressure corresponds to that at which the mean free path of the ions becomes comparable with the distance separating the electrodes. As soon as this is the case, the number of molecules which can be struck by the corpuscles shot off from the illuminated electrode becomes very limited and a small potential gradient will be sufficient to cause saturation. Further decreasing the pressure will decrease this saturation current, until at very low pressures the whole current will be practically due to the corpuscles shot off from the cathode, as only a very small fraction of these will strike a molecule in the course of their journey from one electrode to the other. The curves in fig. 5 show most clearly the variation of the currents at these low pressures. We see that there is a sudden change in the curves between pressures of 0·2 and 0·05 millim., and we know from other considerations that the mean free path of the corpuscle in air is of the same order as the distance between the electrodes (0·35 centim.) at about these pressures.*

The curves at the very lowest pressures agree with LENARD's result ('Ann. der Physik,' vol. 2, p. 359, 1900) for cathode rays produced by ultra-violet light, that in a vacuum a very large change in the potential difference produces no change in the current.

The curves of fig. 6, obtained with a platinum cathode in air, present no peculiar features, being similar to those obtained with the zinc cathode. The fact that the electrodes in this case were only 2 millims. apart introduces slight modifications, the sudden change in the curves which occurs when the mean free path of the ion and the distance apart of the electrode become comparable, appearing at a higher pressure than before when the electrodes were 3·5 centims. apart, as we should naturally expect.

The curves given in figs. 7 to 10, showing the relations between the photo-electric currents in the three gases air, hydrogen, and carbon dioxide, all show that at the higher pressures the current is greater in carbon dioxide than in air, and greater again in air than in hydrogen for all potential gradients up to those at which the genesis of ions by collision begins. They also show that this stage begins in hydrogen at a much lower potential gradient than in air or carbon dioxide, the potential gradient required to cause ionisation by collision in these two gases being approximately the same. This is what we should expect, on the supposition

---

* TOWNSEND, in 'Phil. Mag.,' February, 1901, p. 224, gives the mean free path of an ion in air as $4 \cdot 3 \times 10^{-5}$ centim. at 760 millims. pressure, corresponding to a mean free path of 0·34 centim. at 0·10 millim. pressure.

previously made as to the connection between the potential at which ionisation by collision commences and that necessary for a discharge to pass, from a consideration of the sparking potentials in these gases at atmospheric pressures, the potential gradient necessary for a discharge to pass in hydrogen being only 0·55 times that required in air.

A comparison of the curves for hydrogen in figs. 4 and 9 will show the consistent character of the results obtained.

For pressures down to a tenth of an atmosphere the currents in carbon dioxide are approximately 1·75 times as great as those in hydrogen for all potential gradients for which the current lies on the more horizontal part of the current-E.M.F. curve, that is for those currents nearest approaching to saturation. The currents in air are greater than those in hydrogen, though not nearly so great as those in carbon dioxide. At lower pressures (see figs. 7 and 8) the ratio becomes much less, at 18 millims. pressures the current in carbon dioxide being less than 1·5 times that in hydrogen, as before, for points lying on the less steep portion of the curve.

At still lower pressures the ionisation by collision introduces complications even with small potential differences, and soon becomes the dominant factor in determining the currents until the very lowest pressures are reached. At pressures below about 0·005 millim. the method employed ceases to be satisfactory, as the corpuscles given off by the cathode are shot right through the meshes of the gauze. Some observations which were made, using a gauze of rather wide mesh, are given in the following table as showing some apparently remarkable results which were traced to this cause :—

TABLE XI.

Potential difference between the electrodes in volts.	Current in arbitrary units.
2	52
8	109
40	124
120	148
200	138
280	126
360	112

The experiments were made in air at a pressure of 0·024 millim., the distance separating the electrodes being 2 millims. They show that beyond a certain potential an increase in the potential difference between the electrodes produced a decrease in the current. That this was due to the corpuscles being shot through the meshes of the gauze as soon as the potential gradient was big enough to give them a sufficiently great velocity was shown by substituting a much finer gauze, when, under otherwise identical conditions, no such decrease in the current was obtained.

The curves given in fig. 10, showing the relation between current and potential at various low pressures in air, hydrogen, and carbon dioxide, are all readily understood if we remember that the mean free path of the corpuscles in hydrogen is, from the kinetic theory of the gases, about twice that in air or carbon dioxide, and that a lower potential difference is required to start ionisation by collision in hydrogen than in the other gases.

The curves of figs. 11 and 12 obtained after substitution for the zinc of a platinum electrode are similar to those obtained using the zinc electrode, except that at the lower potential differences the currents in hydrogen are slightly greater than those in air, whereas the opposite was the case with the zinc.

The currents in air, hydrogen and carbon dioxide were also compared using an aluminium electrode. The results obtained were identical in their general character with those obtained using zinc, though the sensitiveness of the aluminium was much smaller than that of the zinc.

From the curves of fig. 13 we see that the currents in carbon monoxide, using a zinc electrode, are some 20 per cent. less than in air, being in fact almost the same as those in hydrogen until the potentials used are great enough to cause ionisation by collision, which sets in in air and carbon monoxide at about the same potential gradient.

Experiments have been carried out on the photo-electric effect in certain less simple gases, such as marsh gas and benzene vapour. The results obtained are complicated by the very large absorption of the ultra-violet light in its passage through the gas, and are being further investigated.

My best thanks are due to Professor J. J. Thomson, in whose laboratory the above investigation was carried out, for his advice and encouragement throughout the whole course of the research.

[*Note added October 18th*, 1903.—During the past Long Vacation Term experiments have been made on the photo-electric currents in gases at very low pressures with a new form of apparatus, in which the use of the gauze electrode was discontinued as not being suitable for work at pressures below about 0·02 millim. Two parallel plates, separated by a distance of 12 millims., were employed as electrodes, the ultra-violet light falling obliquely on to the sensitive electrode, and a guard ring arrangement being used to procure a perfectly uniform field between the electrodes. With this apparatus experiments have been made on the magnitude of the photo-electric currents in the various gases down to pressures of less than 0·002 millim. Below a pressure of 0·01 to 0·005 millim. the currents seem to be quite independent of either the nature or pressure of the gas. No precautions were taken to free the gas from mercury vapour; but it is hoped at an early date to further investigate the currents at these low pressures, taking precautions to absorb all the mercury vapour in the leak apparatus.

The results indicate that the whole of the differences observed in the magnitude of the currents in the various gases depend only upon secondary ionisation occurring at the surface of the metal and on ionisation by collision in the gas itself.]

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[PLATE 13.]

AN ENQUIRY INTO THE VARIATION OF ANGLES OBSERVED IN CRYSTALS; ESPECIALLY OF POTASSIUM-ALUM AND AMMONIUM-ALUM.

BY

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XI. *An Enquiry into the Variation of Angles observed in Crystals; especially of Potassium-alum and Ammonium-alum.*

By HENRY A. MIERS, *D.Sc., M.A., F.R.S., V.P.G.S., V.P.C.S., Waynflete Professor of Mineralogy in the University of Oxford.*

Received March 10,—Read March 26, 1903.

[PLATE 13.]

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PART I.

(1.) THE VARIATIONS OF ANGLE PREVIOUSLY OBSERVED.

ALL who have been practically engaged in goniometric measurements are well aware that in crystals of one and the same substance small variations of angle are usually encountered even when the crystals are taken at the same time from the same solution. The differences are sometimes so small that they are only appreciable by a goniometer which will read accurately to 1 minute or less, and very often the crystal faces themselves are too irregular or too imperfect to yield sharp images of the collimator slit such that they can be adjusted within, say, half a minute.

But even if account be taken only of those faces which are truly plane and yield a perfectly sharp reflection of the collimator slit, the individual variations may amount to 5 or 10 minutes, and the measurements of the same angle made upon, say, 20 good crystals of the same substance, may differ to this extent. I have studied* an example from the mineral kingdom in the case of the very beautifully crystallised Proustite, where the angle between perfectly smooth and plane rhombohedron faces varied between 42° 39′ 50″ and 42° 48′ 27″, *even upon the same crystal.*

It is customary to eliminate these variations, as well as errors of reading due to the imperfection of the faces, by measuring a considerable number of crystals and taking the mean of corresponding measurements. This process appears to lead to very satisfactory results, for angles may sometimes be obtained which are consistent even within half a minute of arc; that is to say, the lengths and mutual inclinations of the crystal axes having been calculated from some of these angles, the remaining angles are calculated on the assumption that they belong to planes whose intercepts are certain rational sub-multiples of the axes, and they are then found to agree very closely with the means of the observations.

Two assumptions are here made: (1) that the individual variations are just as likely to give angles which are too large as angles which are too small, and (2) that the faces do obey the law of *simple* rational indices.

Even when the calculations are made by the method of least squares, these assumptions still underlie the process.

The small individual variations are, in fact, regarded as irregular and of secondary importance, and are practically ignored; if they be thus left out of account, it cannot be denied that within narrow limits the angles of most crystals do approximate very closely to those required by the law of simple rational indices. Occasionally, however, the deviation is too great to be treated in this way, and the direction of the face can

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* 'Mineralogical Magazine,' vol. 8, 1888, p. 49.

no longer be expressed by simple rational indices, but only by very high numbers. Cubes of fluor, for example, will often yield no reflections corresponding to the true faces of a cube, and, therefore, do not possess angles of 90°; but each apparent cube face really consists of a very flat pyramid whose adjacent planes are inclined to each other at the angle 2° $31\frac{3}{4}'$. These faces would intersect the axes of the cube in the ratio 1 : 32, and belong to the form (32.1.0).

Such "vicinal faces" are encountered upon crystals of most substances; sometimes they are produced by the solvent action of the mother-liquor; but they may certainly also appear during the growth of the crystal when it is not being redissolved. The vicinal faces themselves are sometimes as perfectly plane and smooth as any on the crystals.

In the case of fluor, the presence of the group of four such planes in place of the cube face shows that they are not merely due to the distortion of a cube face, but belong to a different form. But even when a face with high indices occurs upon a crystal as a single isolated plane, it is generally regarded as a vicinal face and either as due to the etching action of a solvent, or as replacing a face with simpler indices owing to the operation of some unknown cause.

Whether the vicinal faces really obey the law of rational indices at all is not certain. Planes to which it is necessary to attribute high indices are usually called "vicinal," and are regarded as something different from ordinary faces; many careful measurements of individual vicinal planes have been made in order to determine their indices, whereas it is the custom to eliminate variations in the angle between what appear to be faces of simple forms. Sometimes, however, these variations are so large, even in the case of what appear to be quite simple forms, that they can scarcely be ignored in this manner.

In most of the crystalline systems the theoretical angles of the crystal are not known, but have to be calculated from some of the observed angles, which may be themselves liable to these variations, so that it is difficult to say whether the variations are really irregular. But in the cubic system, by virtue of its symmetry, the angles are known absolutely, and it is possible to compare the measured angles with the theoretical values. Crystals belonging to the cubic system appear, however, to be liable to the same variations of angle with those of other systems, and also exhibit vicinal faces.

Now the whole value of the law of rational indices, which is the foundation-stone of crystallography, rests upon the permanence of angle. The faces of an octahedron belonging to the cubic system are inclined to each other at 70° 31′ 44″; and, similarly, the angle of the form (112), of which any face cuts two of the axes of the octahedron at their extremities and bisects the third, is 38° 56′ 33″. If the octahedron and icositetrahedron faces do not make these angles, respectively, then the law of rational indices is only a first approximation, and there is some disturbing influence which has yet to be investigated.

It must be observed that two interpretations are possible :—

(1) That the faces really have simple indices, but are liable to irregular variations ;

(2) That they have not really simple indices, but are vicinal faces.

Thus an octahedron whose angle is found to be, not 70° 31′ 44″, but 69° 41′, would on the first interpretation be an octahedron of which one or more faces are distorted from their true position by some unexplained cause ; on the second interpretation they would not be faces of the octahedron at all, but a vicinal form having the indices (65.65.64), of which each face is inclined at 25 minutes to the octahedron face with which it nearly coincides.

In the simple case here contemplated it ought to be quite easy to distinguish between the two interpretations, for the form (65.65.64) consists of, not 8, but 24 faces, and each face of the apparent octahedron should yield, when measured on the goniometer, not one image of the collimator slit, but three images, due to three facets, each deviating by 25 minutes from the true octahedron face.

Very careful observations upon the angles of cubic crystals have been made by several investigators. PFAFF published in 1878* an investigation on the variations of crystal angles, in which he found that angles which were known from the symmetry of the system might differ by 30 minutes from the theoretical value, or might agree with it to within 1 minute. He came to the conclusion that the variations of angle are related to the existence of optical anomalies, and that in the cubic system those crystals which are birefringent exhibit these variations, whereas those which are isotropic do not. A natural deduction would be that the observed variations are the result of strain.

Some years later this problem was proposed for a prize essay by the Philosophical Faculty of the University of Marburg, and the inquiry was limited to crystals belonging to the cubic system ; candidates were directed to measure isotropic and birefringent crystals of the same substance with the view of ascertaining whether any such relationship exists.

The prize essay, by R. BRAUNS, was published in 1887.† He carefully measured octahedra of lead nitrate, of spinel, and of ammonia-alumina-alum, choosing both isotropic and birefringent crystals, and came to the conclusion that there is no difference between the angles of isotropic and birefringent cubic crystals. Of 120 measured angles (on 15 crystals) 86 gave a deviation of 5 minutes or less, and 63 a deviation of more than 10 minutes. The largest deviation from the theoretical value was 19′ 20″ ; the largest deviation for the angle as measured between faces which gave very perfect images was 13′ 20″, in the case of a crystal of lead nitrate.

BRAUNS further made an interesting suggestion regarding the cause of these

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* 'Sitzungsber. d. Physik. Med. Soc. zu Erlangen,' Heft 10, p. 59.

† 'Neues Jahrbuch,' 1887, (1), p. 138.

deviations; the crystals of lead nitrate showed a certain regularity in the angles; they had all grown lying on an octahedron face $(\overline{1}\overline{1}\overline{1})$; now if the obtuse angles made by the upper face (111) with the three adjacent faces be compared with the acute angle which it makes with the three other faces, it is found that the average value of the former is less than 70° 31′ 44″, and that of the latter is greater than 109° 28′ 16″. **Brauns** drew the conclusion that the action of gravity is the disturbing cause; this is not perceptible in spinel and alum, but does come into evidence in the denser substance, lead nitrate.

The investigations of **Brauns** are the only precise and direct attempts to determine and explain the angular variations of cubic crystals. They lead to the conclusion that the planes of the crystal are octahedron faces, distorted by some cause which in the case of lead nitrate appears to be the action of gravity. The faces were all sufficiently good to yield measurements reliable to 1 minute, and the author makes no mention of multiple images, so that they were all presumably single plane surfaces, and were, therefore, regarded as not vicinal forms but true octahedron faces.

(2.) OBJECT OF THE PRESENT INVESTIGATION.

One serious difficulty underlies all attempts to study the problem by the ordinary methods of crystal measurement. Where several octahedron crystals, for example, are taken from a solution and found to give angles which are not the theoretical angles of the octahedron, it is impossible to ascertain whether any face of the one crystal corresponds exactly to any face of another. It occurred to me that the only way of studying changes in angle, and of investigating kindred problems, is to ascertain how far the variations are constant for one and the same crystal *during its growth.* For this purpose it will not suffice to take a crystal out of the solution and measure it, and then to re-immerse the crystal, allow it to grow, and measure it again; for one is ignorant whether any faces of the nucleus are parallel to those of the shell by which it becomes enveloped; it is necessary to devise a plan by which one and the same crystal can be measured at different times during its growth in the solution.

This would further render it possible to trace the changes in the position of any given face as the crystal grows, and, if the changes are due to variations in the conditions of equilibrium between crystal and solution, might conceivably afford means for studying these conditions. Much has been written concerning internal structure of crystalline media, but it must not be forgotten that every point within a crystal has at some period been a point on its surface, and that our knowledge of the structure is very incomplete until the life-history of the crystal has been studied by observing the changes that take place at its surface and determining the conditions of equilibrium which obtain there.

In measuring crystals in the ordinary way it is very difficult to know whether the faces are plane and smooth until the crystal has been taken from the solution and dried, and then one cannot feel sure that their surface has not been altered by the evaporating solution during the process. By measuring crystals while still immersed in the solution this difficulty also would be obviated. I feared at first that when immersed in a medium of so high a refractive index as the saturated solution, the faces of a growing crystal would not yield sufficiently brilliant images of the collimator signal. This, however, is not the case; and having convinced myself by preliminary experiments that very good images can be obtained with the ordinary telescope and collimator, I had an instrument constructed which is really nothing more than a telescope-goniometer, inverted so that the crystal is suspended in the solution. Another advantage of this method is that the zone which is being measured has all its faces vertical, so that the possible distorting action of gravity is eliminated. The liquid is contained in a glass vessel with plane-parallel sides, through one of which the light enters normally from the collimator, while through another the reflected light emerges normally to enter the telescope.

A grant for the purpose having been obtained from the Royal Society in 1892, the goniometer was constructed according to my design by Messrs. TROUGHTON and SIMMS.

(3.) THE GONIOMETER.

The graduated circle of the goniometer, fig. 1 (Plate 13), rests upon a horizontal disc which is carried by two vertical metal columns about 20 centims. in height; these spring from the base plate of the instrument; and in an aperture in one of them is fixed the collimator. The vernier is engraved upon the rim of the fixed disc. The telescope is fitted to the lower end of a solid counterpoised arm, which can be rotated about the goniometer axis and clamped in any desired position. The crystal holder, which may consist of the usual centring and adjusting movements, is at the lower end of a vertical axle which passes through the centre of the goniometer disc, and may be raised or lowered by a screw with milled head, so as to bring the crystal into the horizontal plane of the telescope and collimator.* The axle of the crystal holder is clamped by a split ring grip above the holder. The glass trough which contains the solution is a square vessel 6 centims. square, with plane-parallel sides mounted in a brass frame; it stands upon a brass table, which can be raised or lowered by rack and pinion fitted below the base-plate, so as to bring the crystal into the solution or out of it. A brass guide upon the table receives one side of the frame,

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* For economy of space, the centring movements in this instrument were not effected by the usual slides travelling between straight guides, but by two plane discs, which swing about pivots and move in contact with one another, as described for another instrument in 'Mineralogical Magazine,' vol. 10, 1887, p. 215.

and ensures that the trough shall be so placed as to have one of its faces perpendicular to the collimator tube.

The collimator being fixed, it may be desired to rotate either the crystal holder or the telescope while keeping the other parts fixed, or to rotate either of them together with the scale. For this purpose the usual clamping screws which bear upon the axle are dispensed with, and a circular metal disc, 15 centims. in diameter and 1 millim. thick, is provided, which may be clamped to the goniometer stand by one screw, to the telescope by a second screw, or to the crystal holder by a third screw. The disc is itself in rigid connection with the divided circle. Thus any two parts of the instrument may be coupled together, and it may be used either as a goniometer or a spectrometer. The telescope is clamped to the stand by a fourth screw with lever head.

Both telescope and collimator, as well as the eye-pieces, are mounted in collars provided with three screws, by which they may be fully adjusted. The telescope is also provided with a rack and pinion, so that it may, when used as a microscope, be moved towards or from the axis, and thus be focussed upon crystals immersed in liquids of different refractive indices. For the measurement of crystals growing in their solutions the crystal is fixed in a small clip made of stout platinum wire or ribbon; as the crystal grows the clip becomes enveloped by it and affords an absolutely rigid holder.

In addition to the ordinary eye-pieces, it was found necessary at an early stage of the research to provide a special eye-piece (fig. 2) for measuring the displacement of an image in any required direction within the field of view of the telescope. During the growth of a crystal the measurements can only be conveniently made in a single zone, and it is inadvisable to alter the adjustment of this zone during a series of observations. But, clearly, variations of angle may be due to the displacement of a face not only in the direction of a zone but out of it.

If a face has been adjusted so that the image O (fig. 2) of the square collimator signal is on the intersection of the cross wires, and if during the growth of the crystal the face alters its position slightly so that the image moves to P out of the horizontal zone CC, it will be sufficient to measure the distance OP, and the angle which the line OP makes with the horizontal cross wire, without moving the crystal at all. For this

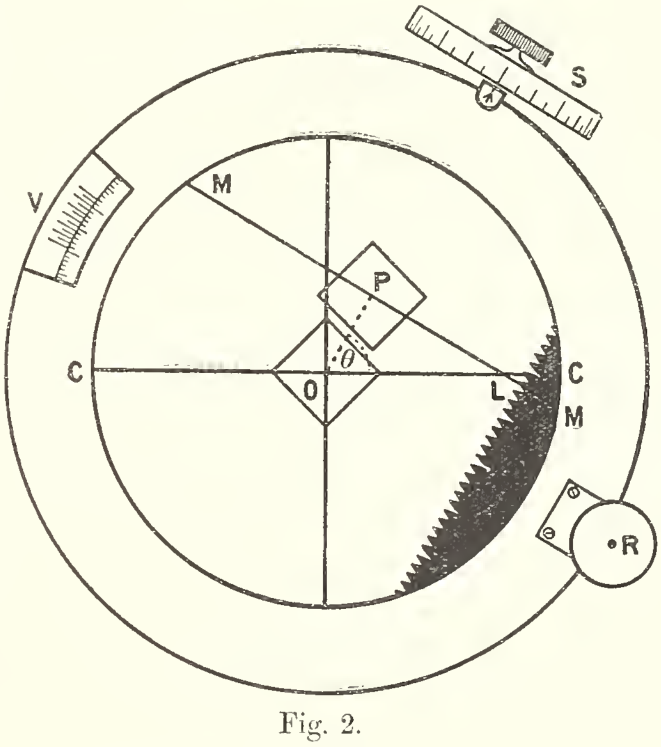

Fig. 2.

purpose the eye-piece is provided with an additional cross-wire MM, which can be moved across the field of view by a micrometer screw S, so that the angular value of any displacement along a diameter can be measured in terms of divisions upon the head of the drum at S. The movable wire, with its micrometer adjustment, is attached to a circular frame, C, which has a milled edge, and can be rotated about the centre O through any required angle; this frame is in the form of a case enveloping a circular disc which is graduated, and the angle through which it is turned is read by means of a vernier, V, engraved upon the side of an aperture cut in the case C, through which the scale is viewed. A toothed scale at L registers the number of complete turns which have been imparted to the micrometer screw, each interval corresponding to one turn. In this way the distance OP and the angle POC can be accurately measured. R is a screw by which the circle is clamped.

This eye-piece was subsequently described by Mr. TUTTON ('Phil. Trans.,' A, vol. 192, 1899, p. 463), who added it to his crystal-grinding apparatus; it would be a useful adjunct to any telescope goniometer.*

For the purpose of measuring crystals immersed in the mother-liquid, one face of the glass trough having been set perpendicular to the collimator, the telescope is set perpendicular to the adjacent face of the trough by the so-called Gauss method, *i.e.*, by viewing the image of the cross-wires reflected at its surface by means of the light derived from a lamp placed beside the telescope and sent down the telescope by a glass plate held obliquely in front of the eye-piece.

It was found advisable for the experiments described on pp. 493–515 to fix the trough on a table which can be adjusted by means of three screws, so that a side of the trough can be accurately set perpendicular to the telescope (see fig. 16, Plate 13).

The temperature of the solution is recorded by a thermometer immersed in it and clamped to the frame of the instrument, as shown in fig. 1, Plate 13.

(4.) PURPOSES FOR WHICH THE GONIOMETER CAN BE USED.

The goniometer here described can clearly be used for any work which the ordinary goniometer is required to perform. In can further serve several other purposes. Crystals can be measured, as in the present research, while immersed in a concentrated solution of their own material, and the changes of form which they experience during growth may thus be studied; deliquescent crystals, or such as are liable to alteration under ordinary conditions, can be measured while immersed in oil or in some other appropriate liquid; the action of solvents on crystals can be studied by measuring them while immersed in acids or other solvents, and this method affords the only safe means of ascertaining the angles made by the prerosion faces due to the

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* Another telescopic adjunct, described in the same memoir by Mr. TUTTON, as devised by myself (p. 464), namely, the swinging lens before the eye-piece, was not, as might appear from his description, used with this instrument, but with another goniometer.

action of the solvent, with the original faces, when the latter have been removed by the solvent; the refractive indices of solid plates, prisms, or crystals can be measured by total reflection or minimum deviation by immersing them in appropriate liquids; and the refractive index of a liquid can similarly be measured by means of a plate or prism immersed in it.

Again, the angles of isomorphous mixtures may be ascertained as the composition changes, by measuring a crystal while in a solution of different composition; or measurements may be made of a crystal enveloping a similar crystal of a substance isomorphous with it by immersing the latter in a solution of the isomorphous material; this would render it possible to ascertain the angles between the faces of the shell and the corresponding faces of the kernel. Examples of some of these uses will be found in the following pages.

With the object of testing the goniometer, some observations were made upon the etching of calcite by dilute HCl, and upon the parallel growth of sodium nitrate with calcite. Since these are either new, or were new at the time when they were made (1893), and were certainly made by a new method, and since they bear upon the subject of vicinal faces, a few of the results of these measurements may be here mentioned.

(A.) *Etching of Calcite with* HCl.

A cleavage rhomb of calcite immersed in about 50 cub. centims. of water gave the following readings for two faces Rr:—

$$\left[\begin{array}{l} \mathrm{R}\ 211^\circ\ 52\tfrac{3}{4}' \\ r\ \ 136^\circ\ 57\tfrac{1}{4}' \end{array}\right. \qquad \mathrm{R}r = 74^\circ\ 55\tfrac{1}{2}'.$$

One drop of dilute HCl was added and after the lapse of 1½ hours distinct pits were etched on both faces, having at first the form of linear channels parallel to the edge Rr, and subsequently assuming a more triangular outline, and faint images begin to make their appearance close to those from R and r. After 9 hours the following well-defined images were obtained in the zone [Rr]:—

$$\left[\begin{array}{l} \mathrm{R}\ 211^\circ\ 51' \\ r\ \ 136^\circ\ 57' \\ r_1\ 136^\circ\ 49' \end{array}\right. \qquad rr_1 = 0^\circ\ 8'.$$

Another rhomb gave readings:—

$$\left[\begin{array}{l} \mathrm{R}\ \ 42^\circ\ 37\tfrac{1}{2}' \\ r\ 327^\circ\ 41' \end{array}\right. \qquad \mathrm{R}r = 74^\circ\ 56\tfrac{1}{2}' \text{ before etching.}$$

$$\left[\begin{array}{l} R' \ 42^\circ\ 49' \\ r' \ 327^\circ\ 47\tfrac{1}{2}' \end{array}\right. \qquad R'r' = 75^\circ\ 1\tfrac{1}{2}' \text{ after etching.}$$

$$RR' = 0^\circ\ 11\tfrac{1}{2}',$$

$$rr' = 0^\circ\ \ 6\tfrac{1}{2}'.$$

In another series of experiments good readings were obtained from etched facets upon a cleavage rhomb immersed in very dilute acid; these were inclined to the cleavage faces at 0° 13¾′ after 2 hours,

,, 0° 15¾′ ,, 4 ,,

,, 0° 17¾′ ,, 8 ,,

These images belong to facets lying in the zone R*r* and are accompanied by other images not lying in this zone and belonging to facets on the other side of the triangular etched figures.

These and other experiments indicate that well-defined facets may be developed by the action of very dilute acid, but that they are inclined at different angles to the original face, and that the inclination of the etched facets changes as the etching proceeds, the value in general increasing.

(B.) *Parallel Growth of* $NaNO_3$ *with Calcite.*

A cleavage rhomb of calcite was adjusted and immersed in a concentrated solution of $NaNO_3$. The crystals of sodium nitrate which grew upon the surface of the calcite could not, of course, have all their faces parallel to those of the calcite, for the rhombohedron angle of calcite is 74° 55′, whereas that of sodium nitrate is 73° 30′.

It was found that the sodium nitrate always lies on the calcite in such a way that the two rhombohedra have one edge parallel, and generally also one face containing that edge in the sodium nitrate is parallel, or nearly parallel, to the corresponding face of the calcite. This result is in accordance with that arrived at in another way by O. MÜGGE, 'Neues Jahrbuch,' 1896 (2), p. 74.

It is also analogous to the union of twin crystals, in which the two individuals are not always exactly in the position demanded by the law of twinning but may deviate therefrom by several minutes or even by a degree or more. In these cases the deviation takes place in such a way that the crystals retain the parallelism of at least one face or one edge, as I have shown for Proustite and Bournonite.*

* 'Mineralogical Magazine,' vol. 6, 1884, p. 77; vol. 8, 1888, p. 75.

(5.) The Octahedron Angle of Potash-alum.

A large number of observations were next made upon potash-alum with the object of discovering whether the octahedron angle of a crystal of this substance changes during the growth of the crystal, and if so, in what manner and to what extent.

The observations were carried out in the following way: a brilliant and uniform crystal having been selected, it was mounted in the platinum clip and adjusted on the instrument. The glass trough, filled with concentrated solution, and having a few small crystals in the bottom of the vessel, was then raised until the mounted crystal was completely immersed. Generally, the crystal would become slightly re-dissolved immediately after immersion, but it was constantly watched through the telescope until its faces began to grow in a uniform manner, and yielded brilliant reflections. It was then measured again and again at short intervals during many hours or at longer intervals during several days and nights.

The best sets of measurements were those obtained by immersing the crystal in slightly warmed and supersaturated solution and then observing it while the temperature was falling for several consecutive hours near an open window during a winter night. With a rise of temperature on the following day the crystal would become slightly etched and re-dissolved; but this made it possible to trace the changes of angle produced by incipient re-solution, and then the phenomena of growth could be watched a second time upon the same crystal during the following night.

After once the crystal has grown sufficiently to envelope the platinum clip completely, there is no danger of its moving even to the smallest extent during any number of subsequent observations; it may be etched, partly re-dissolved, and allowed to grow again many times in succession without any change in its orientation.

When a crystal of potash-alum was watched in this way it was found :—

(1) That the images from the various faces continually altered their positions;

(2) That the angle between the adjacent faces was never the theoretical angle of the regular octahedron;

(3) That the faces usually yielded multiple images lying very close together.

Thus, in the very first crystal measured, the following readings were obtained from two very good faces, A being a cube face and o an octahedron face.

$$\left[\begin{array}{l} o\ \ 181^\circ\ 10\tfrac{1}{4}', \\ A\ \ 126^\circ\ 25\tfrac{1}{2}'. \end{array}\right. \qquad oA = 54^\circ\ 44\tfrac{3}{4}'\ \text{(theoretical angle, } 54^\circ\ 44'\ 8''\text{),}$$

Next day

o $181^\circ\ 20\frac{1}{2}'$ two images, one vertically above the other,
A_1 $126^\circ\ 42\frac{1}{2}'$,
,, ,, ,, beside the other,
A_2 $126^\circ\ 39\frac{1}{2}'$.

$$oA_1 = 54^\circ\ 38', \qquad oA_2 = 54^\circ\ 41',$$

two hours later A yielded a single image, and $oA = 54^\circ\ 38\frac{1}{4}'$.

Another crystal yielded the following from a pair of adjacent brilliant octahedron faces, o and ω.

o_1 $96^\circ\ 49\frac{1}{2}'$ two images, one vertically above the other,
o_2 $96^\circ\ 40'$ single image, $o_1\omega_1 = 70^\circ\ 37'$,
ω_2 $26^\circ\ 21'$,, ,, $o_2\omega_2 = 70^\circ\ 19'$,
ω_1 $26^\circ\ 12\frac{1}{2}'$ two images, one vertically above the other.

Two days later the readings had become

o_1 $96^\circ\ 49'$ not quite in the zone,
o_2 $96^\circ\ 38'$ in the zone,
$o_1\omega_1 = 70^\circ\ 39'$,
ω_2 $26^\circ\ 24'$ not quite in the zone,
$o_2\omega_2 = 70^\circ\ 14'$,
ω_1 $26^\circ\ 10'$,, ,, ,,

On the following day the readings were

o_1 $96^\circ\ 49'$ below the horizontal wire $o_1\omega_2 = 70^\circ\ 27'$,
o_2 $96^\circ\ 46\frac{1}{2}'$ above ,, ,, ,, $o_2\omega_2 = 70^\circ\ 24\frac{1}{2}'$,
o_3 $96^\circ\ 37\frac{1}{2}'$ on the horizontal wire $o_3\omega_2 = 70^\circ\ 15\frac{1}{2}'$,
ω_2 $26^\circ\ 22'$,, ,, ,,

A day later, in the morning

o_1 $96^\circ\ 49'$,
$o_1\omega_1 = 70^\circ\ 39'$,
o_2 $96^\circ\ 47'$ three overlapping images,
$o_3\omega_2 = 70^\circ\ 18'$,
o_3 $96^\circ\ 39'$,
ω_2 $26^\circ\ 21'$,, ,, ,,
ω_1 $26^\circ\ 10'$ two overlapping images.

In the afternoon

$$\left[\begin{array}{ll} o_1 & 96^\circ\ 44', \\ o_2 & 96^\circ\ 42' \\ \omega_2 & 26^\circ\ 17' \\ \omega_1 & 26^\circ\ 14'. \end{array}\right. \qquad \begin{array}{l} \\ o_1\omega_1 = 70^\circ\ 30', \\ o_2\omega_2 = 70^\circ\ 25', \\ \\ \end{array}$$

On the following day

$$\left[\begin{array}{lll} o_1 & 96^\circ\ 48' & \text{two overlapping images,} \\ o_2 & 96^\circ\ 46' & \\ o_3 & 96^\circ\ 38' & \\ \omega_2 & 26^\circ\ 22' & \text{,, ,, ,,} \\ \omega_1 & 26^\circ\ 10', & \end{array}\right. \qquad \begin{array}{l} \\ o_1\omega_1 = 70^\circ\ 38', \\ o_3\omega_2 = 70^\circ\ 16', \\ \\ \\ \end{array}$$

and so on.

This example will serve to illustrate the difficulty of adjusting and measuring one of these crystals, for images which lie on the horizontal wire at one time are subsequently replaced by images slightly out of the zone. This difficulty necessitated the introduction of the micrometer eye-piece described above, but the observations were enough to show that each octahedron face of potash-alum is replaced by two, three, or more vicinal faces which continually change during growth.

I may now pass over a number of intermediate experiments, which ultimately suggested the correct interpretation of these multiple images, in order to state at once the explanation to which I was led, and will give one or two sets of experiments by which it is illustrated.

When an eye-piece of sufficient strength is employed, it is seen that many apparently simple images are in reality overlapping images lying very close together. These are usually three in number; one may be brighter than the others, and one or two of them may be so faint as to be almost invisible. Similarly, when the surface of the growing crystal is minutely examined,* and with a sufficient magnification, it is seen that corresponding to these three images are three reflecting surfaces; when the images are equally bright the octahedron face is seen to be replaced by three equal-sized facets of a very flat triakis-octahedron, as in fig. 3; when two are bright and the third is almost invisible, two of the faces are large and the third small (fig. 4); when the octahedron face apparently yields a single image, one facet is much larger than the other two, and gives an image in the zone if the arrangement is as in fig. 5, but an image situated below the zone if the arrangement is as in fig. 6.

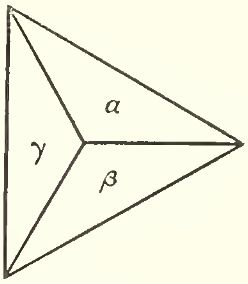

Fig. 3.

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* This may very conveniently be done by a lens held in front of the eye-piece.

If figs. 5 and 6 represent two adjacent octahedron faces, they will appear to be single planes, and may give only single visible reflections, but they will not be inclined to each other at the theoretical angle of the regular octahedron. This will doubtless explain the deviations observed by Brauns and others. The octahedron angle of the second crystal, described on p. 470, would appear to possess various values ranging between 70° 14′ and 70° 39′, according to the time when the crystal was taken out of the solution if it were measured in the ordinary way, and these are angles of precisely the sort observed by Brauns.

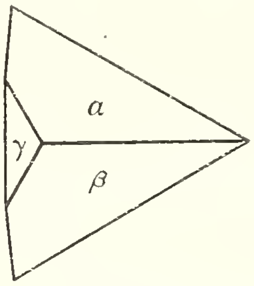

Fig. 4.

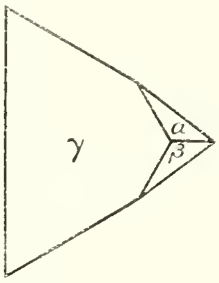

Fig. 5.

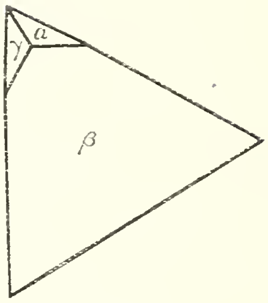

Fig. 6.

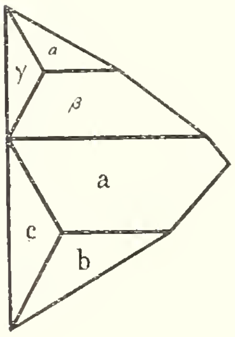

Fig. 7.

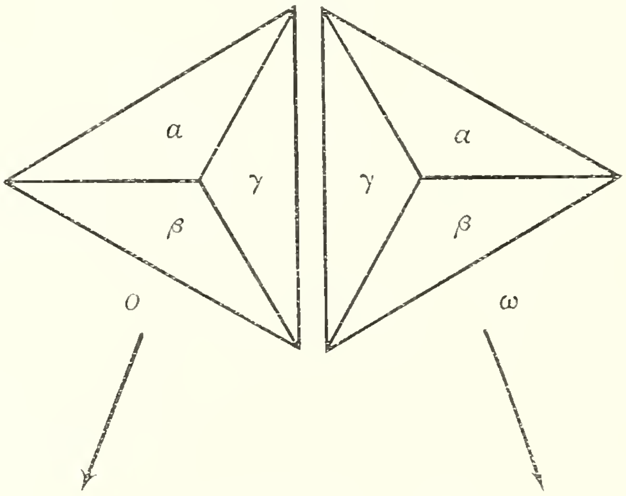

Fig. 8.

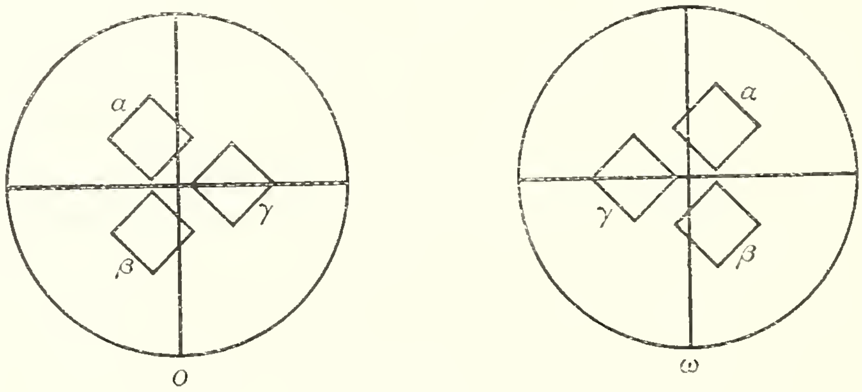

Fig. 9.

When more than three images were yielded by an apparent octahedron face, they were found to be due to the fact that there were two or more triakis-octahedra;

these are generally two in number, one flatter than the other, and replacing the upper and lower portions of the large apparent octahedron face (fig. 7).

An apparent octahedron face of alum gives, therefore, in general, not one but three images. For the purpose of correct adjustment, and in order to distinguish easily between the various images, I have generally used a small square aperture as collimator signal in place of the customary Websky slit.

Two apparent faces, o, ω, of the octahedron (fig. 8), consisting in reality of the flat triakis-octahedron α, β, γ, will then give the reflections represented in fig. 9. The three images α, β, γ belonging to the face o are not necessarily separated from each other by the same intervals as those belonging to the face ω; but the zone can be correctly adjusted by means of the images o_γ and ω_γ.

Example.

A very perfect octahedron, after 10 days' immersion in solution and various changes of temperature, was found on November 27, 1893, at 10 A.M., to yield three very well-defined images from each of the four octahedron faces in the adjusted zone (fig. 10).

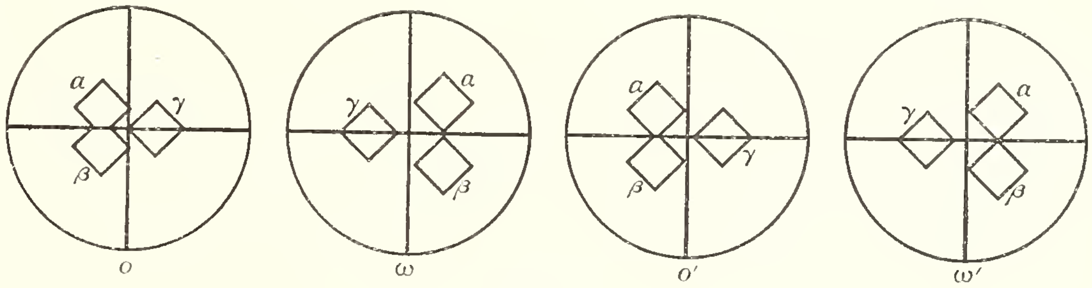

Fig. 10.

Calling these faces o, ω, o', ω' respectively, the readings and images were as follows :—

$$\left.\begin{aligned} o_\alpha = o_\beta &= 328^\circ\ \ 5', \\ o_\gamma &= 327^\circ\ 57\tfrac{1}{4}', \\ \omega_\gamma &= 257^\circ\ 40\tfrac{1}{4}', \\ \omega_\alpha = \omega_\beta &= 257^\circ\ 26\tfrac{1}{2}', \\ o'_\alpha = o'_\beta &= 148^\circ\ \ 6\tfrac{1}{4}', \\ o'_\gamma &= 147^\circ\ 56\tfrac{3}{4}', \\ \omega'_\gamma &= \ \ 77^\circ\ 39\tfrac{1}{4}', \\ \omega'_\alpha = \omega'_\beta &= \ \ 77^\circ\ 26\tfrac{1}{2}'. \end{aligned}\right.$$

(Here and in the following pages o_α denotes the reading for which the image from α is on the vertical wire.)

Here none of the measured angles is the true octahedron angle, but if we assume that the three faces α, β, γ of the triakis-octahedron replacing any one octahedron face all belong to the same form, it is easy to calculate the theoretical readings for the true octahedron faces; they would be

$$\begin{aligned} o &= 328^\circ\ \ 2', \\ \omega &= 257^\circ\ 31', \\ o' &= 148^\circ\ \ 3', \\ \omega' &= \ \ 77^\circ\ 31'. \end{aligned} \qquad \text{so that} \begin{cases} o\omega = 70^\circ\ 31', \\ o'\omega' = 70^\circ\ 32', \end{cases}$$

The angle ($\alpha\beta = \beta\gamma = \gamma\alpha$) of the triakis-octahedron replacing each octahedron face is also easily calculated, and is for the form replacing o $0^\circ\ 5'$,

,, ,, ,, ω $0^\circ\ 9\frac{1}{4}'$,

,, ,, ,, o' $0^\circ\ 6\frac{1}{4}'$,

,, ,, ,, ω' $0^\circ\ 8\frac{3}{4}'$.

This example indicates that—

(1) The octahedron angle of the crystal is really the true octahedron angle (70° 31′–70° 32′);

(2) That there is a different flat triakis-octahedron replacing each face, although they only differ to a slight extent.

In this instance the images, α, β, γ, of each set seem to belong to the same form, for the α and β images are in the same vertical plane; but this is not always the case; the same crystal, measured on November 28, gave the following readings from o and ω (*cf.* figs. 11A, 11B):—

$$\begin{aligned} o_\beta &= 290^\circ\ 58\tfrac{1}{2}', \\ o_\alpha &= 290^\circ\ 55', \\ o_\gamma &= 290^\circ\ 52\tfrac{3}{4}', \\ \omega_\gamma &= 220^\circ\ 29\tfrac{1}{2}', \\ \omega_\beta &= 220^\circ\ 22', \\ \omega_\alpha &= 220^\circ\ 20\tfrac{1}{2}'. \end{aligned}$$

Whereas from ω' $\omega'_\gamma = 40^\circ\ 30'$, $\omega'_\alpha = \omega'_\beta = 40^\circ\ 21'$.

Hence the reading for the true octahedron face ω' is 40° 24′; therefore the reading for ω is 220° 24′, and the three faces replacing ω are unequally inclined to ω, and do not belong to the same form (fig. 11A).

If it be true that the vicinal faces, whether they belong to the same or to different forms, are always triakis-octahedron faces, then of the faces replacing an octahedron plane which should yield an image at o one is always situated on the horizontal wire $o\gamma$, and the other two on the lines $o\alpha$ and $o\beta$, which make an angle of 120° with $o\gamma$ in the field of view (fig. 12). This is a fact which is readily established by means of the micrometer eye-piece; the changes of the images, for example, during the growth of the crystal can be easily followed by the movable cross-wire when it has been adjusted so as to run along the line $o\alpha$. This affords an even safer method of ascertaining the reading corresponding to the true octahedron face o; for after it has been found that the images from the vicinal faces travel along the lines αo, βo, and γo, making angles of 120° with each other, the reading for the true octahedron is known to be that corresponding to their intersection o.

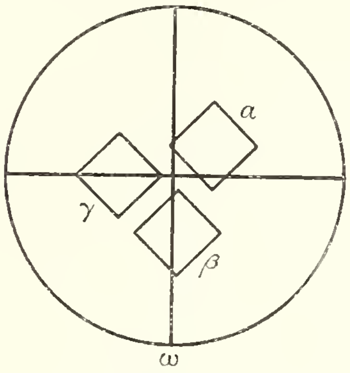

Fig. 11A.

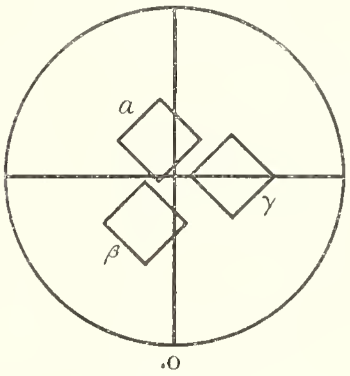

Fig. 11B.

When examined in this way the two adjacent octahedron faces of potash-alum give readings which differ from each other by the true octahedron angle $70^\circ\ 31\frac{3}{4}'$ within errors of observation; it has thus been possible to measure with accuracy the octahedron angle of potash-alum, although the faces of the octahedron are not themselves present. It is not necessary to multiply examples: other crystals led to the same result as that just described: namely, that the octahedron angle of potash-alum is not liable to any variation, but that the octahedron faces themselves are absent and their place is supplied by vicinal planes belonging to triakis-octahedra which are liable to continual variations.

(6.) THE NATURE OF THE VICINAL FACES ON POTASH-ALUM AND AMMONIA-ALUM.

In the course of the present research many attempts were made to discover some regularity in the angles or in the indices of the vicinal faces. That they possess rational indices is rendered possible by the established fact that they lie in certain well-defined zones, but the indices are in that case very complicated. A very well-defined set of faces, for example, on one crystal represented a triakis-octahedron inclined at $6'\ 7''$ to the octahedron; its symbol would, therefore, be (hhl), where $\frac{h}{l} = 1{\cdot}00378$, or something approaching (251.251.250); but it is impossible to say whether these are the indices to be adopted, or some other numbers having nearly the same ratio. Clearly the indices cease to be of much use when they are such high numbers, and the position of the faces can be equally well and conveniently represented by their angles.

In a paper on the vicinal faces of celestite ('Zeits. f. Kryst.,' XI., 1886, p. 220), HINTZE suggested that their relations are better expressed by the angles that they make with each other than by the indices to which they can be referred; and, in fact, that they do not necessarily possess rational indices.

Whether this be so or not, it will be safer for the present purpose to define the vicinal faces of the growing alum crystal by their actual angles than by their possible indices. One reason why I am led to believe that they are really referable to rational, although not to simple, indices is the following:—During the growth of the crystal, one set of vicinal faces is being continually replaced by another along certain zones; each image of the collimator signal fades away like a dissolving view and another makes its appearance; but the change is not gradual, neither are the surfaces curved; one plane reflecting-surface is replaced by another plane; and although the images may for a time be multiple and confused, sharply defined images emerge successively by the substitution of one image for another *per saltum*. This extremely important fact is illustrated by some of the examples quoted above, and instances might be multiplied to any extent.

It is sufficient here to record the well-defined faces which have been observed during the experiments upon potash-alum and ammonia-alum.

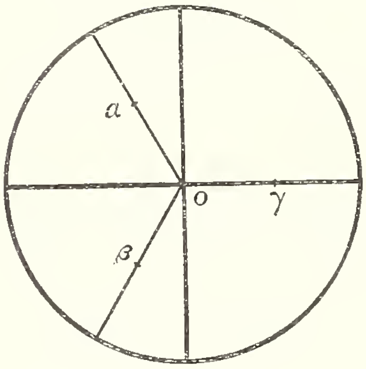

Fig. 12.

If α, β, γ (fig. 12) be the three images obtained from three facets belonging to the same form, then if o be the position of the image which would be yielded by the ideal octahedron face, the readings actually made in the course of the observations are:—

(1) That for which γ coincides with the vertical cross-wire;

(2) That for which α and β simultaneously coincide with the vertical cross-wire.

The difference between these readings is nearly the angle between γ and the face which would truncate the edge $\alpha\beta$; if this face be called μ, the angle between γ and o, *i.e.*, the inclination of the vicinal form to the true octahedron, is given by

$$\tan o\gamma = 2 \tan o\mu.$$

For very small angles $o\gamma$ may be taken as $\frac{2}{3}\gamma\mu$. The best readings obtained on a large number of crystals were the following:—

Potash-alum.		Ammonia-alum.	
$\gamma\mu$.	$o\gamma$.	$\gamma\mu$.	$o\gamma$.
′ ″	′ ″	′ ″	′ ″
2 15	1 30	1 45	1 10
3 15	2 10	3 0	2 0
4 45	3 10	8 30	5 40
6 0	4 0	16 0	10 40
7 30	5 0	17 0	11 20
8 15	5 30	21 0	14 0
9 0	6 0	22 30	15 0
12 0	8 0	24 30	16 20
13 0	8 40	26 30	17 40
15 0	10 0	27 15	18 10
19 30	13 0	28 30	19 0
20 0	13 20	31 0	20 40
21 0	14 0	—	—
22 30	15 0	—	—
24 30	16 20	—	—
25 15	16 50	—	—
28 0	18 40	—	—

and a number of intermediate values were obtained not quite so perfect. The largest values observed for $\gamma\mu$ were 0° 33′ on potash-alum, and 0° 36′ on ammonia-alum, corresponding to inclinations of 0° 22′ and 0° 24′, respectively, to the true octahedron face.

The following examples illustrate the differences in vicinal planes replacing the four octahedron faces of one and the same crystal of potash-alum at the same time :—

	Crystal I.	Crystal II.	Crystal III.	Crystal IV.
$o_\gamma : o_\mu$	7¾′	6¾′	5¼′	28½′
$\omega_\gamma : \omega_\mu$	13¾	8¼	2¼	23½
$o'_\gamma : o'_\mu$	9½	5½	3¼	25¼
$\omega'_\gamma : \omega'_\mu$	12¾	8¼	4¾	28

Similarly on ammonia-alum :—

	Crystal I.	Crystal II.	Crystal III.
$o_\gamma : o$	17′	22′	31¾′
$\omega_\gamma : \omega_\mu$	24½	31	36
$o'_\gamma : o'_\mu$	24½	24	27½
$\omega'_\gamma : \omega'_\mu$	16½	—	—

These examples indicate that the angle of the vicinal faces is generally of the same order of magnitude upon the different faces at any given time, but they do not indicate any cause for the differences, or any special regularity.

In K-alum I., II., opposite faces seem to show nearly the same form, which differs from that on the adjacent faces; but in K-alum IV., and Am.-alum I., the forms which most resemble each other are on adjacent faces.

It is quite clear, at any rate, that there is no constancy of angle in the vicinal faces either of K-alum or of Am.-alum.

Several attempts were made to determine whether, during the growth of a crystal, the changes are progressively in the same direction; whether the flat triakis-octahedron becomes more flat or more acute; also whether the angle varies in any way with the temperature or the barometric pressure.

The following observations on a crystal of ammonia-alum form a continuous and fairly lengthy series:—

o and ω are two adjacent octahedron faces and C is a cube face. o and ω both yielded two images, $\alpha\beta$, in the same vertical plane; C two images, $\alpha\beta$, nearly in a horizontal plane.

February 4, 1894.—The crystal was adjusted for a point halfway between o_α and o_β and a point halfway between ω_α and ω_β.

$$\left[\begin{array}{l} o_{\alpha\beta} = 139^\circ\ 18', \\ C_\beta = \ \ 84^\circ\ 31\tfrac{1}{4}', \\ \omega_{\alpha\beta} = \ \ 29^\circ\ 54', \\ o'_\gamma = 319^\circ\ 25\tfrac{3}{4}', \end{array}\right. \qquad \text{all the images were very good.}$$

At 5 P.M. it was immersed in solution containing loose crystals.

Barometer 769·6 millim.; $t = 12\tfrac{1}{2}^\circ$.

At 7.30 P.M.

$$\left[\begin{array}{ll} o_{\alpha\beta}\ 139^\circ\ 20', & t = 12\tfrac{3}{4}^\circ, \\ \omega_{\alpha\beta}\ \ \ 29^\circ\ 56'. & \end{array}\right.$$

At 10.0 P.M., $t = 12\tfrac{1}{4}^\circ$, o yielded two images.

$$o\left\{\begin{array}{l} 139^\circ\ 20\tfrac{1}{4}', \\ 139^\circ\ 19\tfrac{1}{2}'. \end{array}\right.$$

The crystal having been withdrawn, the solution was then warmed to 35° and the crystal re-immersed at 11.15 when the temperature was 25°.

At 11.45 P.M., $t = 18^\circ$, the crystal was covered with etched triangles.

At 12.0 (midnight), $t = 17^\circ$, the etched figures were disappearing and ω gave a good reading at $29^\circ\ 54'$.

At 12.30 A.M., $t = 15\frac{1}{2}^\circ$, the faces were quite smooth.

THEORETICAL READINGS (from the angles o_γ, $o_{\alpha\beta}$, &c.).

o_γ	$139^\circ\ 34'$,	$o = 139^\circ\ 23\frac{1}{3}'$,	$oo_\gamma = 0^\circ\ 10\frac{2}{3}'$,
$o_{\alpha\beta}$	$139^\circ\ 18'$,		
$\omega_{\alpha\beta}$	$30^\circ\ 0'$,	$\omega = 29^\circ\ 55'$,	$\omega\omega_\gamma = 0^\circ\ 9\frac{1}{2}'$,
ω_γ	$29^\circ\ 45\frac{1}{2}'$,		
o'_γ	$319^\circ\ 36'$,	$o' = 319^\circ\ 24'$,	$o'o'_\gamma = 0^\circ\ 12'$,
$o'_{\alpha\beta}$	$319^\circ\ 18'$.		

At 1.0 A.M. ; $t = 15{\cdot}2^\circ$.

ω_γ	$29^\circ\ 42\frac{1}{4}'$,		
o'_γ	$319^\circ\ 38\frac{1}{2}'$,		
$o'_{\alpha\beta}$	$319^\circ\ 17\frac{1}{2}'$,	$o' = 319^\circ\ 24\frac{1}{2}'$,	$o'o'_\gamma = 0^\circ\ 14'$,

At 1.10 A.M. ; $t = 14{\cdot}9^\circ$.

$\omega_{\alpha\beta}$	$30^\circ\ 3'$,	$\omega = 29^\circ\ 53\frac{1}{2}'$,	$\omega\omega_\gamma = 0^\circ\ 19'$,
ω_γ	$29^\circ\ 34\frac{1}{2}'$,		
o'_γ	$319^\circ\ 40\frac{1}{2}'$,	$o' = 319^\circ\ 24\frac{1}{2}'$,	$o'o'_\gamma = 0^\circ\ 16'$,
$o'_{\alpha\beta}$	$319^\circ\ 16\frac{1}{2}'$.		

At 1.20 A.M. ; $t = 14{\cdot}9^\circ$.

o_γ	$139^\circ\ 35\frac{1}{2}'$,	$o = 139^\circ\ 22\frac{1}{4}'$,	$oo_\gamma = 0^\circ\ 13\frac{1}{4}'$.
$o_{\alpha\beta}$	$139^\circ\ 16\frac{1}{4}'$,		
$\omega_{\alpha\beta}$	$30^\circ\ 9\frac{1}{2}'$,		
$o'_{\alpha\beta}$	$319^\circ\ 15\frac{1}{2}'$,		

The solution was then withdrawn.

February 5.—The solution having been warmed to 35° was allowed to cool to 21°, and the crystal was immersed again at 5.30 P.M., when it at once began to grow.

At 6.30 P.M.; $t = 17°$, barometer 772 millim.

		THEORETICAL	READINGS.
o_{γ}	$139^\circ\ 34'$,		
$o_{\alpha\beta}$	$139^\circ\ 17'$,	$o = 139^\circ\ 22\frac{3}{4}'$,	$oo_{\gamma} = 0^\circ\ 11\frac{1}{3}'$,
$\omega_{\alpha\beta}$	$29^\circ\ 59'$,		
ω_{γ}	$29^\circ\ 39\frac{1}{2}'$,	$\omega = 29^\circ\ 53'$,	$\omega\omega_{\gamma} = 0^\circ\ 13\frac{1}{2}'$,
o'_{γ}	$319^\circ\ 33'$,		
$o'_{\alpha\beta}$	$319^\circ\ 16\frac{1}{2}'$,	$o' = 319^\circ\ 22'$,	$o'o'_{\gamma} = 0^\circ\ 11'$.

At 6.45 P.M.; $t = 15{\cdot}8°$.

$o_{\alpha\beta}$	$139^\circ\ 14'$,		
$\omega_{\alpha\beta}$	$30^\circ\ 0'$,	$\omega = 29^\circ\ 52'$,	$\omega\omega_{\gamma} = 0^\circ\ 15\frac{1}{2}'$,
ω_{γ}	$29^\circ\ 36\frac{1}{2}'$,		
o'_{γ}	$319^\circ\ 41'$,	$o' = 319^\circ\ 22'$,	$o'o'_{\gamma} = 0^\circ\ 19\frac{1}{2}'$,
$o'_{\alpha\beta}$	$319^\circ\ 12\frac{1}{2}'$.		

At 7.10 P.M.; $t = 15°$.

o_{γ}	$139^\circ\ 37'$,		
$o_{\alpha\beta}$	$139^\circ\ 15'$,	$o = 139^\circ\ 22\frac{1}{3}'$,	$oo_{\gamma} = 0^\circ\ 14\frac{2}{3}'$,
$\omega_{\alpha\beta}$	$30^\circ\ 2\frac{1}{2}'$,		
ω_{γ}	$29^\circ\ 31\frac{1}{2}'$,	$\omega = 29^\circ\ 52'$,	$\omega\omega_{\gamma} = 0^\circ\ 20\frac{1}{2}'$,
o'_{γ}	$319^\circ\ 41'$,		
$o'_{\alpha\beta}$	$319^\circ\ 14'$.	$o' = 319^\circ\ 22\frac{2}{3}'$,	$o'o'_{\gamma} = 0^\circ\ 17\frac{1}{3}'$.

At 12.30 A.M.; $t = 14{\cdot}7°$.

o_{γ}	$139^\circ\ 37\frac{1}{2}'$,		
$o_{\alpha\beta}$	$139^\circ\ 15\frac{1}{2}'$,	$o = 139^\circ\ 22'$,	$oo_{\gamma} = 0^\circ\ 13\frac{1}{3}'$,
ω_{β}	$30^\circ\ 0\frac{1}{2}'$,		
ω_{α}	$29^\circ\ 59'$,	$\omega = 29^\circ\ 52\frac{1}{3}'$,	$\omega\omega_{\gamma} = 0^\circ\ 13\frac{1}{3}'$,
ω_{γ}	$29^\circ\ 40'$,		
o'_{γ}	$319^\circ\ 41'$,		
$o'_{\alpha\beta}$	$319^\circ\ 15'$,	$o' = 319^\circ\ 23'$,	$o'o'_{\gamma} = 0^\circ\ 18'$.

The following table sums up the results of these observations, showing the gradual change in the angles made by the vicinal faces with the octahedron face they replace :—

t.	oo_γ.	$\omega\omega_\gamma$.	$o'o'_\gamma$.
$15{\cdot}5^\circ$	$10\frac{2}{3}'$	$9\frac{1}{2}'$	$12'$
$15{\cdot}2$	—	—	14
$14{\cdot}9$	$13\frac{1}{4}$	19	16
17	$11\frac{1}{3}$	$13\frac{1}{2}$	11
$15{\cdot}8$	—	$15\frac{1}{2}$	$19\frac{1}{2}$
15	$14\frac{2}{3}$	$20\frac{1}{2}$	$17\frac{1}{3}$
$14{\cdot}7$	$13\frac{1}{3}$	$13\frac{1}{3}$	18

This indicates that, as the temperature falls, the vicinal forms become in general more acute, their faces make larger angles with each other, but the angle does not depend entirely upon the temperature. At $15\frac{1}{2}^\circ$, for example, $\omega\omega_\gamma$ is at one time $9\frac{1}{2}'$, at another time something between $15'$ and $20'$.

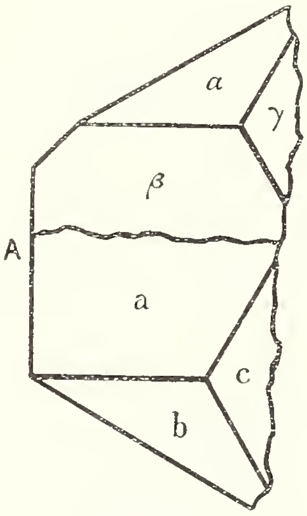

Fig. 13.

The same results were obtained from many other similar series of observations. Variations of barometric pressure also seemed to be without effect upon the angles of the vicinal faces.

One suggestive feature was found to be common to many of the experiments; it sometimes happens that an octahedron face is replaced by two different vicinal forms, one replacing the upper and the other the lower part of the face as it stands vertically in the solution (fig. 13); in such a case it was invariably found that the triakis-octahedron on the lower part of the face is slightly flatter than that of the upper part. For example, a crystal of ammonia-alum, immersed at midnight, $t = 18{\cdot}9^\circ$, barometer 759 millims., gave at 1.30 A.M. the following readings for two apparently perfect octahedron faces o and ω and for the cube face A between them.

$$o_a\ 356^\circ\ 16',$$
$$\mathrm{A}\ 301^\circ\ 42\tfrac{1}{2}',$$
$$\omega_a\ 247^\circ\ 6'.$$

Shortly afterwards ω broke up into three images $\alpha\ \beta\ \gamma$, giving the readings

$$\omega_{\alpha\beta} = 247^\circ\ 2',$$
$$\omega_\gamma = 246^\circ\ 46', \qquad \omega = 246^\circ\ 56\tfrac{2}{3}', \qquad \omega\omega_\gamma = 0^\circ\ 10\tfrac{2}{3}'.$$

At 2.30 A.M., $t = 17^\circ{\cdot}9$, the readings were

$$\left[\begin{array}{lll} o_\gamma \ 356^\circ\ 21', & o = 356^\circ\ 15\tfrac{1}{2}', & oo_\gamma = 0^\circ\ 6', \\ o_{\alpha\beta} \ 356^\circ\ 12\tfrac{1}{2}', & & \\ \mathrm{A} \ 301^\circ\ 36', & & \\ \omega_{\alpha\beta} \ 247^\circ\ 4\tfrac{1}{4}', & \omega = 246^\circ\ 56\tfrac{3}{4}', & \omega\omega_\gamma = 0^\circ\ 15', \\ \omega_\gamma \ 246^\circ\ 41\tfrac{3}{4}', & & \\ \omega'_{\alpha\beta} \ 67^\circ\ 0', & \omega' = 66^\circ\ 54\tfrac{1}{3}', & \omega'\omega'_\gamma = 0^\circ\ 11\tfrac{1}{3}', \\ \omega'_\gamma \ 66^\circ\ 43'. & & \end{array}\right.$$

In addition to these images there were also three close to ω_α ω_β and ω_γ, and proceeding from the lower part of the face (fig. 13); calling these ω_a ω_b and ω_c, the following measurements were obtained :—

At 2.30 A.M.

$$\left[\begin{array}{l} \mathrm{A}\ 301^\circ\ 35\tfrac{3}{4}', \\ \omega_c\ 246^\circ\ 47\tfrac{1}{2}', \\ \omega_\gamma\ 246^\circ\ 41\tfrac{1}{4}'. \end{array}\right.$$

At 2.55 A.M., $t = 17{\cdot}2^\circ$

$$\left[\begin{array}{ll} \mathrm{A}\ 301^\circ\ 36\tfrac{1}{2}', & \\ \omega_\beta\ 247^\circ\ 7\tfrac{1}{4}', & \\ \omega_c\ 246^\circ\ 46\tfrac{3}{4}', & \\ \omega_\gamma\ 246^\circ\ 40\tfrac{3}{4}', & \therefore\ \omega = 246^\circ\ 58\tfrac{1}{4}'. \end{array}\right.$$

So that $\begin{array}{l}\omega\omega_\gamma = 0^\circ\ 17\tfrac{1}{2}' \\ \omega\omega_c = 0^\circ\ 11\tfrac{1}{2}'\end{array}$ and a, b, c is a flatter form than α, β, γ.

Observations of GOUY and CHAPERON and others have shown that solutions are more concentrated in their lower than in their upper layers, and this is of course the case in the present experiments where crystals lie at the bottom of the trough.

The case just quoted, and others like it, suggest that the vicinal form is flatter where the solution is more concentrated. Accordingly many experiments were made in which the trough was successively raised and lowered in order to ascertain the effect of immersing the same crystal to a greater or less depth in the solution.

A crystal of potash-alum gave readings

$$\left[\begin{array}{ll} o_{\alpha\beta}\ 290^\circ\ 58\tfrac{1}{2}', & o_\gamma o_{\alpha\beta} = 0^\circ\ 7', \\ o_\gamma\ 290^\circ\ 51\tfrac{1}{2}'. & \end{array}\right.$$

When immersed deeper they became

$$\left[\begin{array}{ll} o_{\alpha\beta}\ 290^\circ\ 58\tfrac{1}{4}', & o_\gamma o_{\alpha\beta} = 0^\circ\ 6\tfrac{1}{2}', \\ o_\gamma\ 290^\circ\ 51\tfrac{3}{4}'. & \end{array}\right.$$

Another crystal of potash-alum, having been adjusted near the surface of the solution, was immersed to a considerable depth; the image from a brilliant facet was found to move through 0° 22′ (as measured by the micrometer eye-piece) in the direction of a flattening of the form.

A third crystal gave near the surface of the liquid

$$\left[\begin{array}{ll} \omega_{\alpha}\ 208^{\circ}\ 46\tfrac{1}{2}', & \omega_{\alpha}\omega_{\gamma} = 0^{\circ}\ 16\tfrac{1}{2}', \\ \omega_{\beta}\ 208^{\circ}\ 43\tfrac{1}{2}', & \omega_{\beta}\omega_{\gamma} = 0^{\circ}\ 13\tfrac{1}{2}', \\ \omega_{\gamma}\ 208^{\circ}\ 30'. & \end{array}\right.$$

At a greater depth

$$\left[\begin{array}{ll} \omega_{\alpha\beta}\ 208^{\circ}\ 39', & \omega_{\alpha\beta}\omega_{\gamma} = 0^{\circ}\ 7', \\ \omega_{\gamma}\ \ 208^{\circ}\ 32'. & \end{array}\right.$$

Raised to the surface again

$$\left[\begin{array}{ll} o_{\gamma}\ 138^{\circ}\ 11\tfrac{3}{4}', & o_{\gamma}o_{\beta} = 0^{\circ}\ 13\tfrac{1}{4}', \\ o_{\beta}\ 137^{\circ}\ 58\tfrac{1}{2}'. & \end{array}\right.$$

Depressed again

$$\left[\begin{array}{ll} o_{\gamma}\ 138^{\circ}\ 8', & o_{\gamma}o_{\beta} = 0^{\circ}\ 9\tfrac{1}{4}', \\ o_{\beta}\ 137^{\circ}\ 58\tfrac{3}{4}'. & \end{array}\right.$$

The above experiments indicate that in crystals of potassium- or ammonium-alum the vicinal faces, which invariably replace the octahedron planes, belong to different forms $\{hhl\}$ of flat triakis-octahedra, and that, as the crystal grows, these continually change their inclinations; the faces α, β, γ, which replace an octahedron face o, generally belong to the same form, and they make an angle of from 2′ to 30′ with o; when the vicinal facets at the top of the crystal belong to a different form from those at the bottom they generally make a larger angle than the latter with o; similarly as the crystal is immersed deeper in the solution the vicinal form becomes flatter; during the growth of a crystal in a cooling solution the vicinal form usually becomes more acute; but at different times quite different vicinal faces may grow at the same temperature.

(7.) THE VICINAL FACES ON SODIUM CHLORATE, ZINC SULPHATE, AND MAGNESIUM SULPHATE.

(A.) *Sodium Chlorate.*

Cubes of sodium chlorate give multiple images which, in accordance with their symmetry, are usually two images in a horizontal plane yielded by one pair of cube faces, and two images in a vertical plane yielded by the alternate pair, indicating vicinal faces belonging to a form $\{hk0\}$ (fig. 14).

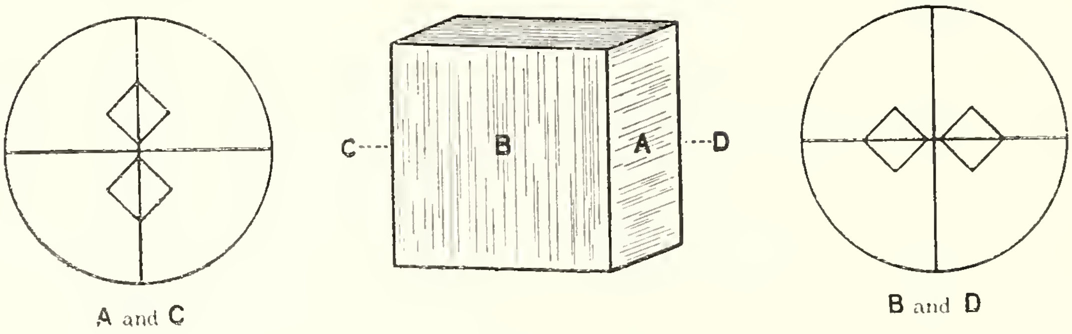

Fig. 14.

Sometimes they are situated obliquely and correspond to two faces of $\{hkl\}$, replacing each cube face.

The following series will serve as an illustration of the results obtained with this substance :—

November 11, 1897.

At 12.45 P.M. ; $t = 17{\cdot}6°$.

A	93° 17′ ;	image	10′ 26″	below	zone.	
B	183° 14′ ;	,,	10′ 26″	,,	,,	
A′	273° 16′ ;	,,	3′ 42″	,,	,,	
B'_α	3° 14′ ;	,,	. . . .	on	,,	∴ B′ = 3° 17½′.
B'_β	3° 21′ ;	,,	. . . .	,,	,,	

After slight re-adjustment :—

At 2.15 P.M., ; $t = 17°$.

B'_α	3° 36′	from the upper part of the face.	All 5′ 40″ below the cross-wire. ∴ B′ = 3° 18½′.
B'_β	2° 59′		
B'_γ	3° 27′	,, ,, lower ,, ,, ,,	
B'_δ	3° 10′		

At 4.15 P.M. ; $t = 17°$.

A_α 93° 25′,
A_β 93° 24′ ; image 20′ 0″ below the cross-wire.

After further readjustment :—

At 4.45 P.M. ; $t = 17°$.

			Approximate readings for true cube faces are therefore
A_α	93° 26′ ;	image 11′ 10″ above cross-wire.	A = 93° 25½′,
A_β	93° 25′ ;	,, 7′ 10″ below ,,	
B'_α	3° 31′ ;	,, . . . on the ,,	B′ = 3° 29½′,
B'_β	3° 28′ ;	,, . . . ,, ,,	
A'_α	273° 26′ ;	,, . . . ,, ,,	
A'_β	273° 19′ ;	,, 3′ 20″ above ,,	A′ = 273° 22½′,
B_α	183° 31′ ;	,, 4′ 10″ below ,,	
B_β	183° 28′ ;	,, 1′ 50″ above ,,	B = 183° 29½.

The crystal was re-immersed at 9.45 P.M. ; $t = 18°$. At 10.15 P.M. ; $t = 18°$; the images from B indicated a re-entrant angle.

B_α 183° 40′.
B_β 182° 58′.
A_α 93° 31′ . . . A_α two images ; one 10′ below, the other 14′ 40″ above
A_β 93° 14′ . . . A_β ,, ,, ,, ,, ,, ,,

∴ B = 183° 19′ ; A = 93° 22½′ ; and AB = 89° 56½′.

This example illustrates the difficulty of adjusting correctly a crystal which is liable to the growth of vicinal faces, and the impossibility of measuring accurately the angles between the faces of the simple forms which are replaced by them, except by tracing these changes. In sodium chlorate the vicinal faces sometimes belong to the form $\{hk0\}$, and they make angles of from 3 to 10 minutes with the ideal cube face ; they sometimes make re-entrant angles with each other, but the difficulties of adjustment and measurement are increased by the fact that the vicinal faces often belong to various forms $\{hkl\}$, and are unequally inclined to the cube faces. The same general features hold as for alum : the vicinal forms usually become more acute as the growth proceeds ; and they are less acute for the parts of the crystal which are most deeply submerged. A cube face of the crystal just described, for example, gave on May 27, 1899, two images separated by 2½ minutes when at a depth of about 1 inch, and two images separated by 12 minutes near the surface of the solution.

Zinc Sulphate and Magnesium Sulphate.

That the same features are also exhibited by crystals belonging to other systems than the cubic, was proved by experiments on these two substances.

The following are examples of measurements upon them :—

ZINC Sulphate ; prism zone ; $m = \mathrm{M} = \{110\}$, $\mathrm{B} = \{010\}$, $\mathrm{A} = \{100\}$.

M 187° 24′,
186° 41′,
m 97° 56′,
97° 53′,
B 52° 19′,
M′ 6° 41′,
6° 36′,
m′ 277° 56′,
B′ 232° 19′,

B*m* = 45° 37′ to 45° 34′,
BM′ = 45° 38′ ,, 45° 33′,
B′*m*′ = 45° 37′.

On the following day :—

M 187° 10′,
186° 42′,
186° 39′,
m 97° 53′,
97° 21′,
B 52° 16′,
52° 8′,
M′ 6° 41′,
6° 39′,
A′ 322° 19′,
322° 17′,
m′ 277° 56′,
277° 52′,
277° 25′,
277° 19′,

B*m* = 45° 41′ to 45° 9′,
B = 52° 12′,
BM′ = 45° 31′ to 45° 33′,
A′ = 322° 18′.

The value generally given for the prism angle of zinc sulphate is 91° 12′ ; in the above crystal various vicinal prism forms are indicated, the angles of which would range from 91° 6′ to 91° 15′ even for the best faces.

MAGNESIUM Sulphate ; prism zone ; $m = \mathrm{M} = \{110\}$.

8.20 P.M. ; $t = 16{\cdot}5°$.

M 12° 30½′,
m′ 282° 59′.

9.30 P.M. ; $t = 16{\cdot}5°$.

m 102° 49′ above zone,
M 12° 32′,
m′ 283° 8½′, three images in vertical plane,
M′ 192° 26½′ below zone.

10.30 P.M. ; $t = 16\cdot5^\circ$.

$$\left[\begin{array}{ll} m & \begin{cases} 103^\circ\ \ 3', \\ 102^\circ\ 50', \end{cases} \\ M & \begin{cases} 12^\circ\ 32\frac{1}{2}', \\ 12^\circ\ 25', \\ 12^\circ\ 17', \end{cases} \\ m' & \begin{cases} 283^\circ\ \ 8', \\ 282^\circ\ 55', \end{cases} \\ M' & 192^\circ\ 17'. \end{array}\right.$$

The value generally given for the prism angle of magnesium sulphate is 90° 35′. The above observations indicate vicinal planes belonging to prisms whose angle would differ from this by more than 20′.

I have given these two examples from the orthorhombic system in order to point out how the mean of a number of measurements may with crystals of comparatively low symmetry give a result very far from the truth. In alum, although the true octahedron angle might never be observed, the mean of a sufficiently large number of measurements would probably give the exact octahedron angle, for the three vicinal planes which replace the octahedron face are, *by the symmetry of the crystal*, inclined to it in three different directions, so that some of the measured angles are too large and some too small. But in the case of a rhombic prism, each face would, in accordance with the symmetry of the crystal, be replaced by only one vicinal plane, and the prism angle, as measured, would be consistently either too large or too small. The true position of the prism face could not be ascertained, as that of the octahedron face was in alum, by the convergence upon it of three zones of vicinal faces, and by the limit to which they tend.

To determine with absolute accuracy the true angles of such crystals it would be necessary to study the variations of their vicinal faces in the manner described above —but by means of a two-circle or three-circle goniometer.

A number of observations were also made upon crystals of sodium arsenate as an example of a substance belonging to the monoclinic system : but since they do not affect the general results they are not described in the present paper.

(8.) The Effect on Alum of Diluting the Solution.

During the experiments described in this paper there were naturally many occasions on which the crystal was not growing in a saturated or supersaturated solution, but was being corroded by a more dilute medium, and in such cases it was sometimes possible to obtain quite good reflections from the prerosion faces ; several experiments were also made in which the solution was purposely diluted or warmed in order to observe the etched faces.

In the case of a bright octahedron of alum, the first effect of slight dilution or warming is to develop small pits having the form of equilateral triangles inscribed in the triangle which bounds the octahedron face; the triangles are small shallow pits and their sides must therefore be vicinal faces, which are still triakis-octahedra, like those of the growing crystal.

Sometimes the growing crystal has its octahedron face covered with flat triangular plates whose outline is parallel to that of the octahedron face; when the solution is diluted, these have their corners rounded and become converted into hexagonal plates, then disappear and become replaced by the inscribed triangular pits.

In one case the prerosion faces (belonging to a triakis octahedron) on one octahedron face made an angle of 0° 57′ with each other; the crystal was then allowed to grow during the night, and in the morning well defined vicinal planes had made their appearance, making an angle of 0° 15′ with each other; as the temperature rose these were replaced by prerosion faces belonging to different forms; that on one edge being inclined at about 0° 5′ to the true octahedron, and that on the adjacent edge at about 0° 18′. This feature was observed in other etching experiments; the prerosion faces replacing an octahedron face generally belong to different forms, whereas the vicinal planes of growth generally belong to the same form.

In one case two well defined prerosion faces belonging to the form {221} made their appearance upon an octahedron edge, inclined at 15° 46′ and 15° 41′ respectively to the adjacent octahedron faces: the theoretical angle for {221} is 15° 47′ 36″.

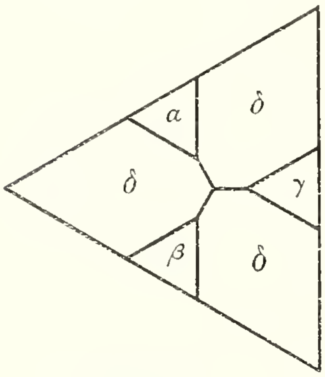

Fig. 15.

The prerosion faces δ which replace the edges of the vicinal triakis octahedron α, β, γ of fig. 15 belong to a different form, the icositetrahedron; and, since the first effect of etching is to round off the edges of the crystal, it generally results in the production of such icositetrahedra; but they do not necessarily truncate the edges α β, &c. Thus the crystal just mentioned yielded the following results three days later, when the corroding action of the solvent happened to be extremely slow.

November 27, 1893.—At 10 A.M., each octahedron face yielded three very perfect images; the actual readings are given on p. 473. A little later, the form replacing o was measured and was found to be a triakis-octahedron inclined at $4\frac{3}{4}'$ to o (previously determined as 5′). At 10.45 the edges of this vicinal form were replaced by facets of an icositetrahedron δ inclined at almost exactly the same angle to o; and the same thing happened on the other faces of the crystal. The angle between δ and the true octahedron face was measured as 0° 2′ on o; 0° 4′ on ω'; 0° $3\frac{1}{2}'$ on o'. The triangular etched pits did not begin to make their appearance until 3.15 P.M.

On the following day the same events recurred: the vicinal faces of growth replacing o belonged to a triakis-octahedron inclined to o at 0° $2\frac{1}{2}'$, and at 11.15 A.M. the edges of this form were replaced by prerosion faces belonging to an icositetrahedron inclined to *o* at 0° 3½′. It is, no doubt, the development of such faces which converts the triangular plates of growth into hexagonal plates, as described above.

These and other instances indicate that the first effect of slow solution is to produce prerosion faces on the edges of the crystal; on the octahedron edge these belong to triakis-octahedra; on the edges of the vicinal faces they belong to icositetrahedra. The latter are inclined to the octahedron at about the same angle as the triakis-octahedron, and they certainly do not truncate its edges. The next effect of the process of solution is to produce etched triangular pits bounded by flat triakis-octahedra.

(9.) Some Possible Causes of the Variations.

With all the substances examined, as with alum, vicinal faces are the rule; they change their position as the crystal grows; they continue to deviate more widely from simple forms, at any rate during the initial growth; the reflections move or oscillate generally in well defined zones, and in accordance with the symmetry of the crystal; their movement is not gradual but *per saltum;* their deviation from the simple forms which they replace generally amounts to from 3 to 20 minutes.

In making the observations great care must be exercised lest deviations due to refraction through layers or currents of more or less concentrated liquid be mistaken for those due to the change of inclinations in the vicinal faces. Such currents are always streaming round a growing crystal, and do produce visible displacements of the images; but these displacements are rather of the nature of irregular oscillations, and may be detected with a little practice.

When beginning the study of alum, I endeavoured to eliminate the action of these currents with the object of ascertaining whether the production of the vicinal faces might not be actually due to them. By means of a suitable clockwork arrangement a wooden vane with four arms was kept revolving in a beaker full of concentrated alum solution during several hours, so as to keep the liquid continually stirred. Small alum crystals were allowed to crystallise on the vane, and were examined at intervals. I came to the conclusion that the crystals were equally perfect, and possessed vicinal faces of the same sort, whether they crystallised in a still solution or in one which was kept continually stirred. In the same way the stirring of the liquid in the goniometer trough seemed to produce no appreciable effect upon the nature of the vicinal faces on a crystal of alum which had been growing in the still solution; the introduction of a stirrer into the trough did not affect the smoothness or the angles of the faces so far as could be observed; the experiments are, however, difficult to carry out, and it is of course impossible to make accurate measurements while the liquid is in violent motion, although the crystal itself is not disturbed.*

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* Other and more precise experiments of this nature are described below on p. 518.

Among other possible causes to which the production of particular vicinal forms might be ascribed are—(1) the temperature at which growth is taking place, (2) the rate at which the temperature is changing. It became important to examine next how far these two factors might contribute to the results observed.

From the example quoted on p. 479 and from other similar examples we may endeavour to trace a connection between the angle of the vicinal form in alum and the rate of fall of temperature. o represents the theoretical octahedron face, γ the vicinal plane.

SERIES I.—Potash-alum.

Time.	Temperature.	$o\gamma$ (mean).	$o\gamma$ (actual values).		
12.30	$15^\circ{\cdot}5$	$0^\circ\ 11'$	$10\frac{2}{3}'$	$9\frac{1}{2}'$	$12'$
1.0	$15{\cdot}2$	14			14
1.10	$14{\cdot}9$	$17\frac{1}{2}$		19	16
1.20	$14{\cdot}9$	$13\frac{1}{4}$			$13\frac{1}{4}$

Hence a fall of about $0{\cdot}6^\circ$ in 50 minutes gives as average $o\gamma = 14'$, ranging from $9\frac{1}{2}$ to 19 minutes.

Temperature nearly stationary at $14{\cdot}9^\circ$ gives $o\gamma = 13\frac{1}{4}'$.

SERIES II.—Potash-alum.

Time.	Temperature.	$o\gamma$ (mean).	$o\gamma$ (actual values).		
6.30	17°	$0^\circ\ 12'$	$11\frac{1}{3}'$	$13'$	$11'$
6.45	$15{\cdot}8$	$17\frac{1}{4}$	$15\frac{2}{3}$	19	
7.10	15	$17\frac{1}{2}$	$14\frac{2}{3}$	$20\frac{2}{3}$	16
12.30	$14{\cdot}7$	15	$13\frac{1}{3}$	$13\frac{1}{3}$	$17\frac{2}{3}$

Hence a fall of 2° in 40 minutes gives as average $o\gamma = 16'$, ranging from 11 to $20\frac{2}{3}$ minutes.

Temperature nearly stationary at $14{\cdot}7^\circ$ gives $o\gamma = 15'$.

SERIES III.—Potash-alum.

Time.	Temperature.	$o\gamma$ (mean).	$o\gamma$ (actual values).		
2.10	$18^\circ{\cdot}3$	$0^\circ\ 10\frac{1}{2}'$	$10\frac{1}{2}'$	$'$	$'$
2.20	$17{\cdot}9$	$9\frac{1}{2}$	15	$2\frac{3}{4}$	$11\frac{1}{2}$

Hence a fall of $0{\cdot}4^\circ$ in 10 minutes gives as average $o\gamma = 10'$, ranging from $2\frac{3}{4}$ to 15 minutes.

Series IV.—Ammonia-alum.

Time.	Temperature.	$o\gamma$ (mean).	$o\gamma$ (actual values).
9.10	15°·1	0° 13′	21½′ 4⅔′
11.25	14·5	18	17⅓ 13 22 19⅓
1.15	14·3	16½	13⅔ 19⅓

Fall of 0·8° in 240 minutes gives as average $o\gamma = 16'$, ranging from 4⅔ to 22 minutes.

Temperature nearly stationary at 14·3° gives $o\gamma = 16\frac{1}{2}'$.

Series V.—Ammonia-alum.

Time.	Temperature.	$o\gamma$ (mean).	$o\gamma$ (actual values).
11.15	12°·2	0° 21′	21′ 24′ 18⅓′
12.45	12·1	16½	18 15⅓

Fall of 0·1° in 90 minutes gives as average $o\gamma = 18\frac{3}{4}'$.
Temperature nearly stationary at 12·1° gives $o\gamma = 16\frac{1}{2}'$.

Series VI.—Ammonia-alum.

Time.	Temperature.	$o\gamma$ (mean).	$o\gamma$ (actual values).
11.30	18°	0° 23⅓′	23⅓′
12.0	16·3	20½	22⅔ 18⅔

Fall of 1·7° in 30 minutes gives an average $o\gamma = 21\frac{3}{4}'$.

Series VII.—Ammonia-alum.

Time.	Temperature.	$o\gamma$ (mean).	$o\gamma$ (actual values).
11.0	12°·8	0° 14½′	16⅓′ 13′
11.30	12·8	13	15 11

Temperature nearly stationary at 12·8° gives $o\gamma = 13\frac{1}{2}'$.

From the above observations it is very difficult to draw any definite general conclusions, since the differences between the various angles in the same crystal are greater than the differences between the mean values in different crystals. This may indicate that the variations are mainly due to local causes.

On the whole, the angle made by the vicinal forms with the octahedron is perhaps slightly greater when the temperature is falling rapidly; and for stationary temperatures it is perhaps slightly greater for low than for high temperatures; but the differences are very small, if, indeed, they really exist, and in many cases quite different vicinal faces are developed at the same temperature, so that in any case the angle of the vicinal form can hardly be a direct result of the particular temperature at which it was produced.

Having found, however, that there seemed to be a general relationship between the acuteness of the vicinal faces and the depth at which the crystal was growing in the solution, I was naturally led next to enquire whether one determining factor is not the concentration of the solution; it is certain that the concentration varies slightly with the depth, especially in solutions which contain loose crystals at the bottom of the trough, and the concentration seemed to be one of the variable factors capable of accounting for the changes of angle.

PART II.

The Concentration of the Solution in Contact with a Growing Crystal.

(A.) *Preliminary Experiments.*

It was pointed out above that in studying the growth of a crystal we are dealing with the conditions of equilibrium between the growing crystal and the liquid in contact with it, and it is therefore a matter of primary importance to know all that can be ascertained about the latter.

Very little seems to be known at present about the nature of this liquid; that it is supersaturated is a reasonable supposition, but to what extent is not certain. The solution is being constantly impoverished by the growth of the crystal, although it is being constantly enriched by the influx of more saturated liquid.

Among the possible factors which determine the different vicinal faces succeeding each other during the growth of the crystal, it appeared from the experiments described above that differences in the degree of concentration of the liquid may conceivably play an important part; but in order to test this possibility it would be necessary to ascertain the composition of the liquid, not merely in the neighbourhood of the crystal, but actually in contact with it. Two methods of attacking the problem suggest themselves; although one cannot hope to analyse the layer of liquid in contact with the crystal, it may be possible to measure either its specific gravity or its refractive index, and from these to determine the degree of concentration.

Now the goniometer used in the earlier part of this research lends itself admirably to the measurement of the refractive indices of solutions by the method of total reflection. If a glass prism be adjusted on the crystal holder, its angles and refractive index can be measured; it may then be immersed in the solution, and if we substitute for the square trough previously used a cylindrical trough (fig. 16, Plate 13)* with a plane glass front set perpendicular to the telescope, it will not be difficult to measure the angle of total internal reflection in the prism, and so the index of refraction of the liquid.

Further, by using a sufficiently small prism, the index of the liquid may be ascertained at any desired point, and by suspending a crystal in the solution and moving it gradually towards the surface of the prism, it may be possible to explore the liquid and to trace the change in refractive index as we approach the growing crystal.

A few observations were made in this way with a small glass prism of about 45°, and a crystal of alum immersed in concentrated solution in the square trough of fig. 1. A face of the crystal and the reflecting surface of the prism were accurately adjusted parallel to each other in the following way. The crystal was fixed for the purpose on a wire rod curved over the edge of the trough and mounted in a crystal holder provided with the ordinary tangent and traversing screws for centring and adjusting; the holder was clamped to a heavy stand placed beside the goniometer. The crystal was first adjusted until it reflected the image of the collimator slit upon the cross-wires of the telescope; it was then parallel to the axis of the goniometer. The crystal having been withdrawn to a short distance by the traversing screw, the prism was next adjusted so that its hypothenuse or totally reflecting surface also reflected the collimator signal on to the cross-wires. The prism being then turned through 180° had its reflecting surface parallel to and facing the crystal plane, and the crystal could be brought as close to it as is desired by means of the traversing screw. The telescope was next set at right angles to the second prism face, and then moved from this position through an angle equal to the angle of emergence for the saturated solution; the front of the trough being also moved so as to remain perpendicular to the telescope. Finally, therefore, the prism and telescope are in the approximate position for measuring the index of the liquid, and the crystal, having a face parallel to the reflecting surface of the prism, can be brought into absolute plane contact with it.

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* The trough is a cylindrical vessel with truncated front; it is held in position by three spring clips, two of which press the plate of glass which constitutes the front against the ground edges of the vessel, and prevent leakage. The trough is adjusted upon its table by three levelling screws, and this table is fixed in any desired position upon the circular table of fig. 1 by means of two catches at the back and a clamping screw in front.

It was found that a perfectly definite reading being obtained with sodium light for total reflection—corresponding to the index of the saturated or slightly supersaturated solution—this reading was only slightly affected when the crystal was moved up and even brought into actual contact with the prism face. The index does actually increase to a certain small extent as the crystal is brought nearer to the prism, and this is shown by Nos. 1–4 in Table II., p. 500.

This indicates that the index of refraction only varies to a very slight extent, and therefore that the solution is only slightly supersaturated almost up to contact with the growing crystal.

It is clear, however, that this experiment does not really determine the index of the liquid in absolute contact with the crystal, whereas the ultimate layer is precisely that of which we require to know the composition, even if it be only a layer of inappreciable thickness. Is it not possible, however, to make use of the natural faces of the growing crystal as our totally reflecting prism? This, if feasible, appears to be in fact the only method of determining the refractive index of this ultimate layer of the liquid.

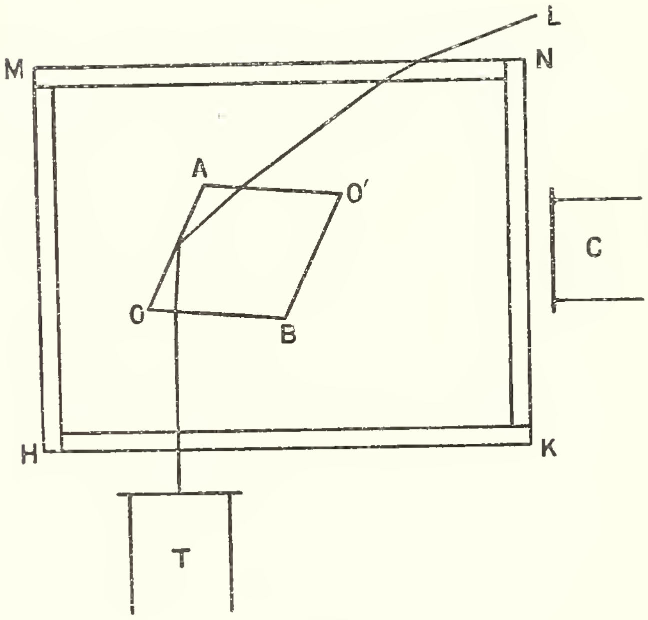

Fig. 17.

Preliminary experiments, in which the square glass trough and an octahedron of potash-alum were employed, presented considerable difficulties, but ultimately yielded a definite and clearly visible line of demarcation in the field of view, and showed that the method is a possible one.

Let OAO′B (fig. 17) be the outline of four faces of an octahedron of alum adjusted upon the goniometer, and growing in the solution; T being the telescope and C the collimator. The angle between the telescope and the collimator is first accurately measured by means of a glass plate mounted on the crystal holder, being twice the angle θ between the position in which the glass plate reflects the collimator signal on to the cross-wires, and that in which the plate is perpendicular to the telescope as determined by the Gauss method. The front HK of the glass trough, HKNM, is then adjusted perpendicular to the telescope by the Gauss method, and the angle AOB is measured. A movable sodium flame at L is next adjusted by trial, and the crystal rotated, until the edge of the dark band indicating total internal reflection at OA is visible in the field of view and can be adjusted upon the vertical cross-wire.

Let the reading for this purpose be ϕ; then, if β be the reading for which the image of the collimator signal is reflected upon the vertical wire from OB, and $\beta + \gamma$ the reading for which OB is perpendicular to T, then $\beta + \gamma - \phi = \theta$ is the angle of emergence of the reflected light; *i.e.*, the angle between the rays entering the telescope from the crystal and the normal to the face OB.

If, then, A be the angle AOB, and n be the refractive index of the crystal, the refractive index, μ, of the liquid is given by the formula

$$\frac{\mu}{n} = \cos p; \quad \text{where} \quad \tan p = 2\,\frac{\sin\left(45^\circ + \frac{\mathrm{A} - \theta}{2}\right)\sin\left(45^\circ - \frac{\mathrm{A} + \theta}{2}\right)}{\sin \mathrm{A}}.$$

A preliminary experiment was made on November 14, 1900, with a good crystal of potash-alum growing at a temperature of 18·6°. The refractive index of the alum crystal for sodium light was measured in two ways: (1) by minimum deviation, using the octahedron as refracting prism; (2) by total internal reflection, making use of the natural faces of the crystal, and was found to be

1·4598 by minimum deviation, 1·4605 by total reflection.

The values previously found by STEFAN, GRAILICH, MULHEIMS, SORET, FOCK, and F. KOHLRAUSCH vary between 1·4549 and 1·4565.

The refractive index of a solution saturated at 18·6° was also determined in two ways: (1) by minimum deviation, using a hollow glass prism filled with the solution; (2) by total reflection, using a glass prism of refractive index 1·51704 immersed in the solution contained in the square trough, and pursuing the process described above.

It was found to be

1·34251 at 18° by total reflection, 1·34280 at 15° by minimum deviation

(the latter corresponding to 1·34250 at 18°).

With a prism of 70° 31′ formed by two octahedron faces, and with 1·4598 for the index of the crystal, and 1·3425 for the index of the liquid, the angle of emergence should be $\theta = 3^\circ\ 57'\ 36''$.

Of course one difficulty introduced by the use of the alum crystal itself is that the angle is not exactly that of the regular octahedron, and is liable to small variations. The faces, A, B, of the crystal used in this experiment did not give multiple images, and were inclined to one another at the angle 70° 24′. For this prism the angle of emergence should be $\theta = 3^\circ\ 50'\ 0''$.

The preliminary experiment gave a smaller angle of emergence, indicating a higher refractive index for the liquid, and showing that the solution in contact with the growing crystal is, in fact, supersaturated.

Before proceeding to determine the exact refractive index of the liquid, it was now necessary to ascertain (1) how the refractive index of strong solutions varies with their concentration; (2) whether there is any sudden change in the index in passing from the saturated to a supersaturated solution; and (3) how the refractive index of supersaturated solutions varies with their strength. So far as I am aware, no previous observations have been made upon the refractive indices of supersaturated, or even of saturated, solutions of the substances investigated in this paper.

(B.) *The Refractive Indices of Supersaturated Solutions.*

The observations were made in two ways:—

(1) By direct measurement of the minimum deviation in a hollow prism containing the solution;

(2) By total reflection, by means of a glass prism of a known index immersed in the solution, using the new goniometer as described on p. 493.

With the minimum deviation method a supersaturated solution containing a known weight of salt to a known weight of water was taken, and a sample of about 6 cub. centims. introduced into the prism; the solution was then diluted with a measured volume of water and another sample examined, and so on. The temperature was measured by a thermometer inserted in the prism.

With the total reflection method it is easier than with the minimum deviation method to carry out a long series of observations upon solutions of slightly varying strength; for it is only necessary to add known volumes of water successively to a known solution. For example, 50 cub. centims. of a supersaturated solution of known strength having been placed in the glass trough, its refractive index was determined by the totally reflecting prism; 1 cub. centim. of water was then added and the index re-determined; this process was repeated until the trough was nearly full; a measured volume of the liquid was then removed from the trough, and the process was repeated and carried on until the solution was quite dilute. The liquid was, of course, kept constantly stirred during these experiments.

As regards the accuracy of the two methods, several examples will be found below of determinations of the same liquid by both; these always agree in the third place of decimals, and sometimes in the fourth.

As regards sensibility, an error of 1 minute in the reading for total reflection corresponds to about 2 in the fourth place of decimals, or to an error of about 2 minutes in the reading for minimum deviation.

Although the readings for total reflection cannot be made so accurately as those for minimum deviation, they could generally be relied upon to within 2 minutes, and sometimes to 1 minute.

Preliminary observations were first made upon solutions of alum and of tartaric acid, chiefly with the object of plotting the results upon a curve in order to ascertain whether there is any sudden change in the curvature, especially on passing from a supersaturated to a saturated solution. In these experiments the constitution of the original saturated solution was not known, but that of the diluted solution at the close of the series was ascertained, and the former was approximately calculated from it.

(1.) *Refractive Indices of Solutions of Potash-alum.*

The refractive index of a saturated solution of potash-alum was approximately determined to be

1·34263 at 14° by total reflection, 1·34220 at 16°·2 by minimum deviation.

The following numbers represent the observations made by the total reflection method, with a prism of angle 44° 58′ and index 1·51704, upon 50 cub. centims. of a saturated solution of alum diluted down by successive additions of 1 cub. centim. of water (up to $\theta = 19° 18'$), and then of 5 cub. centims. (up to $\theta = 19° 8'$), and finally of 25 cub. centims.

Table I.—Series of Consecutive Determinations made by Method of Total Reflection.

m = grammes of salt in 100 grammes of solution.
μ = refractive index of solution.
θ = angle of emergence.

No.	m.	θ.	μ.	t.	μ at 19°.
1	9·023	19° 37½′	1·34274	15°·1	1·3423
2	8·8509	19 35	1·34218	15·3	1·3418
3	8·6852	19 34½	1·34210	15·5	1·3417
4	8·5256	19 33¾	1·34199	15·6	1·3416
5	8·3718	19 32¼	1·34163	15·7	1·3413
6	8·2234	19 32	1·34156	15·9	1·3412
7	8·0802	19 31¼	1·34140	15·9	1·3411
8	7·9419	19 31¼	1·34140	16	1·3411
9	7·8082	19 30	1·34113	16·2	1·3408
10	7·6792	19 29½	1·34103	16·2	1·3407
11	7·5542	19 33½	1·34189	16·6	1·3416
12	7·4332	19 32	1·34156	17	1·3413
13	6·9854	19 30½	1·34124	17·1	1·3410
14	6·4964	19 27½	1·34060	17	1·3404
15	6·0714	19 24½	1·33995	17	1·3397
16	5·6986	19 23½	1·33973	17	1·3395
17	5·3689	19 22½	1·33952	17	1·3393
18	5·0753	19 20½	1·33909	17	1·3389
19	4·8121	19 19½	1·33887	17	1·3387
20	4·5748	19 18	1·33855	17	1·3383
21	4·1643	19 16	1·33812	17·2	1·3379
22	3·8213	19 14½	1·33779	17·3	1·3376
23	3·5306	19 12½	1·33736	17·2	1·3372
24	3·2809	19 12	1·33725	17·2	1·3370
25	3·0642	19 11½	1·33714	17·3	1·3369
26	2·8744	19 10½	1·33693	17·2	1·3367
27	2·7067	19 9½	1·33671	17·2	1·3365
28	2·5575	19 9½	1·33671	17·2	1·3365
29	2·4239	19 9	1·33660	17·2	1·3364
30	2·3036	19 8	1·33638	17	1·3362
31	1·5394	19 3½	1·33541	17	1·3352
32	1·1559	19 1½	1·33497	17	1·3348

The above observations are not represented on Diagram I.

Several determinations were made of the same solution at different temperatures, and indicated that the index is diminished by about ·0001 for each degree of rise in temperature between the above temperatures. The fifth column gives the indices reduced to 19°.

The whole series can only be regarded as a somewhat crude first attempt to trace the changes of refractive index with the composition in strong solutions, and only with a view to the subsequent measurements made with a growing crystal. Samples of several of the liquids were measured at the same time by the hollow prism method in order to check the results.

No. 20 gave, at 17°, the values

1·33855 by total reflection,	1·33825 by minimum deviation.

No. 30 gave, at 17°,

1·33638 by total reflection,	1·33623 by minimum deviation.

No. 32 gave, at 17°,

1·33497 by total reflection,	1·33424 by minimum deviation.

The above results, plotted on a curve with m for abscissa and μ for ordinate (as in Diagram I.), give points which lie nearly upon a straight line, and indicate both that

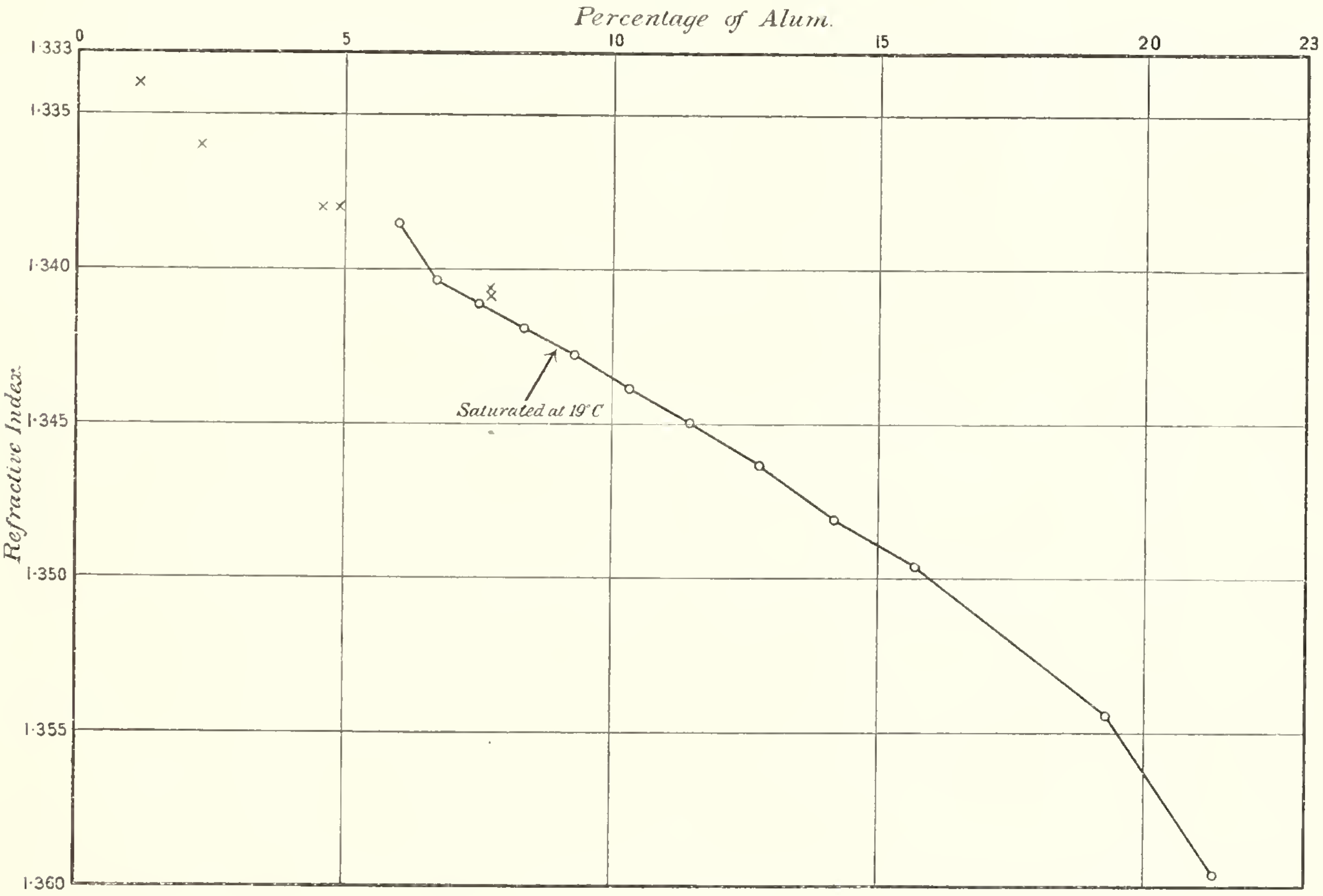

Diagram I.—Alum.

the total reflection method can be relied upon, and that there is no sudden break in the curve.

In this particular series there is a considerable dislocation of the curve between Nos. 10 and 11, due partly to the fact that the corner of the rectangular trough used in this experiment interfered with the illumination, and partly that, for fear of causing the liquid to crystallise, it was not efficiently stirred until this point was reached. For this reason the series is not plotted on Diagram I.

Table II. represents a series of isolated observations made by the method of total reflection upon saturated solutions at the ordinary temperature. In Nos. 1 to 4, which relate to the same solution, the temperature was not recorded; but the effect of approximation to crystals in the solution is here traced; No. 1 is a saturated solution; in No. 2 a few small crystals have been placed in the trough; in No. 3 a mounted crystal is brought near to the prism; in No. 4 it is brought almost into contact with the prism.

TABLE II.—Series of Isolated Determinations made by Method of Total Reflection.

No.	μ.	t.	μ at 19°.	Remarks.
1	1·34232	° —	—	—
2	1·34240	—	—	Some alum crystals placed in the trough.
3	1·34306	—	—	A crystal face adjusted near prism.
4	1·34350	—	—	The crystal nearer to the prism.
5	1·34273	16·6	1·34250	16·6° is the air temperature.
6	1·34251	—	—	—
7	1·34326	15	1·34286	—
8	1·34433	15	1·34396	Prism immersed deep in trough.
9	1·34274	15	1·34234	—
10	1·34210	—	—	Same solution (two determinations).
11	1·34199	—	—	
12	1·34263	14½	1·34210	Some crystals in trough.

All these are solutions saturated, or very slightly supersaturated, at the ordinary temperature; but the observations are not represented on Diagram I. because the exact composition of the several solutions is not certain.

Table III. represents a series of observations made upon a supersaturated solution of known strength gradually diluted down by addition of water, and determined by means of a hollow prism holding about 6 cub. centims. of liquid.

These are denoted by small circles on Diagram I., and serve to establish approximately a curve which shows the relation between composition and refractive index in supersaturated and strong solutions of potash alum.

Table IV. represents a few isolated observations made by the hollow prism upon solutions of known strength; they are denoted by small crosses on Diagram I., and serve to check the curve represented in Table III.

Table III.

No.	m.	μ.	t.
1	21·253	1·35961	19°
2	19·226	1·35439	19
3	15·667	1·34957	19
4	14·134	1·34806	19
5	12·729	1·34627	19
6	11·455	1·34497	19
7	10·298	1·34388	19
8	9·268	1·34274	19
9	8·321	1·34192	19
10	7·466	1·34111	19
11	6·696	1·34035	19
12	6·003	1·33850	19

The above observations are represented by circles on Diagram I.

Table IV.—Isolated Determinations made by Method of Minimum Deviation.

No.	m.	μ.	t.	μ at 19°.
1	7·7198	1·34083	19°	1·34083
2	7·7339	1·34088	16½	1·3406
3	4·897	1·33817	18	1·3381
4	4·575	1·33825	17	1·3380
5	2·304	1·33622	17	1·3360
6	1·156	1·33424	15½	1·3340

The above observations are represented by crosses on Diagram I.

(2.) *Refractive Indices of Solutions of Tartaric Acid.*

The refractive index and composition of a saturated solution of tartaric acid were determined as follows :—

m = grammes of substance in 100 grammes of solution.
μ = refractive index.

m.	μ.	t.	
58·489	1·41672	19°	By minimum deviation.
58·489	1·41667	20	,, ,, ,,
?	1·41649	19	,, ,, ,,

Strongly supersaturated solutions of unknown constitution were next examined by the total reflection method with the prism of angle 44° 58′ and index 1·51704.

In Series I., 50 cub. centims. of a supersaturated solution S_1 were placed in the trough and diluted by successive additions of 2 cub. centims. of water. The results are given in Table V., and are represented by dots in Diagram II.

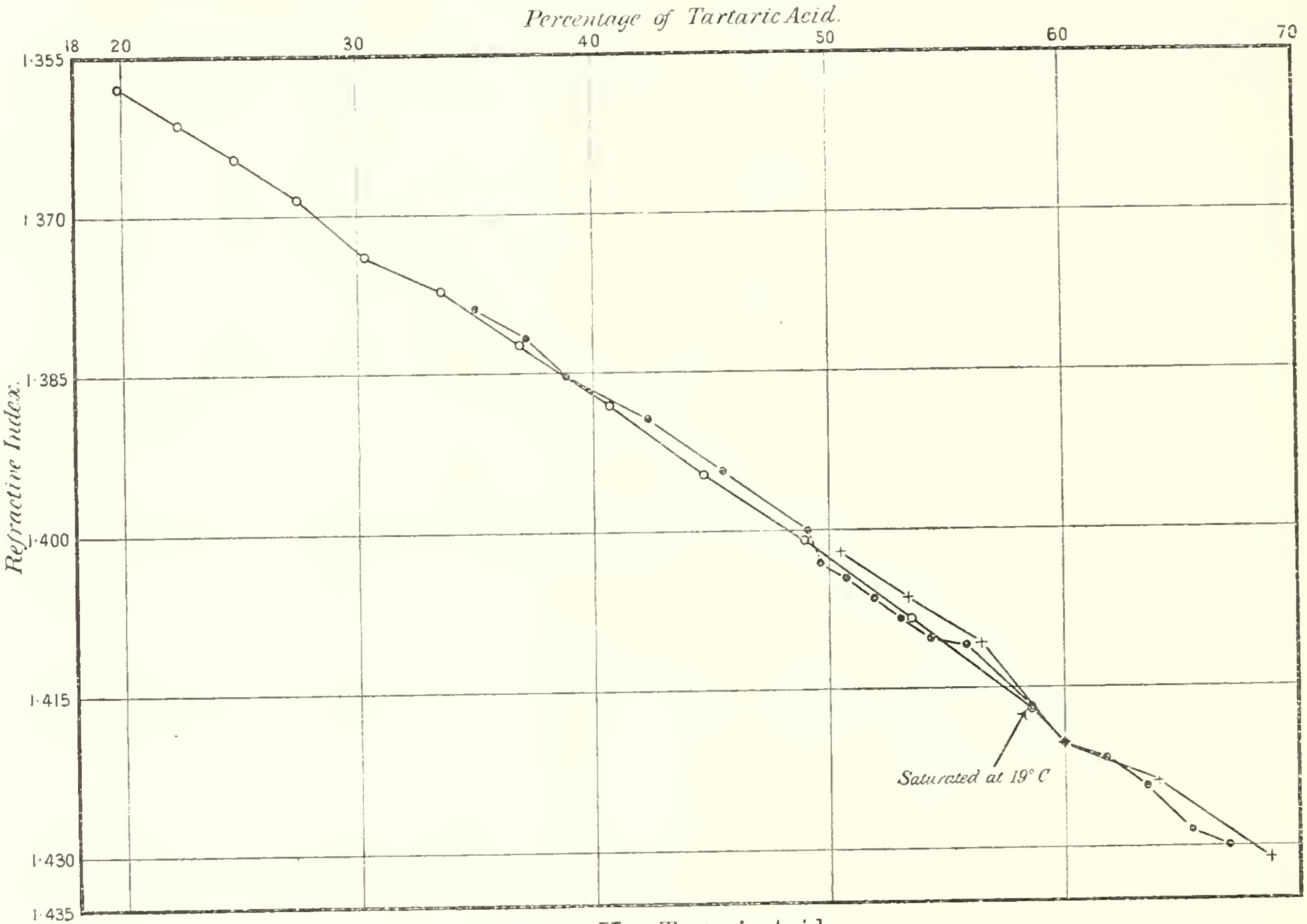

Diagram II.—Tartaric Acid.

The strength of these solutions is obtained by assuming that No. 6 has the same constitution as No. 1 in Table VIII., which possesses practically the same refractive index, *i.e.*, that 50 cub. centims. weigh 64·94 grammes and contain 37·983 grammes of the substance.

50 cub. centims. of the solution S_1 were diluted with 25 cub. centims. of water; and 50 cub. centims. of this new solution (Σ) were then examined in the trough and diluted by successive additions of 5 cub. centims. of water. The results are given in Table VI., and are represented by dots in Diagram II.: this set should, of course, be continuous with the preceding; they are connected by a dotted line on the diagram.

In Series II., 50 cub. centims. of a supersaturated solution S_2 were diluted by successive additions of 5 cub. centims. of water. The results are given in Table VII., and are represented by crosses in Diagram II.

The strength of these solutions is obtained by assuming that No. 3 has the same constitution as No. 5 in Table V., the two having nearly the same refractive index.

Table V.—Series of Consecutive Determinations made by Method of Total Reflection.

Tartaric Acid, Solution S_1.

No.	*m.*	*θ.*	*μ.*	*t.*	*μ* at 19°.
1	67·10	27° 16′	1·43065	16°·8	1·4302
2	65·18	27 5	1·42883	17·8	1·4286
3	63·37	26 40	1·42464	18·5	1·4245
4	61·65	26 23	1·42174	19	1·4217
5	60·03	26 13	1·42002	19·3	1·4200
6	58·489	25 55	1·41690	19·5	1·4169
7	55·63	25 20	1·41069	19·6	1·4108
8	54·31	25 16	1·40997	19·6	1·4101
9	53·04	25 6	1·40816	19·6	1·4083
		25 3	1·40762	19·2	1·4077
10	51·84	24 56	1·40634	19·2	1·4064
11	50·68	24 46	1·40451	19	1·4045
12	49·58	24 38	1·40304	19	1·4030

Table VI.—Series of Consecutive Determinations made by Method of Total Reflection.

Tartaric Acid, Solution Σ.

50 cub. centims. of the solution (50 cub. centims. S_1 + 25 cub. centims. water).

No.	*m.*	*θ.*	*μ.*	*t.*	*μ* at 19°.
13	49·05	24° 22′	1·40007	17°·2	1·4000
14	45·39	23 55	1·39498	16	1·3944
15	42·23	23 29	1·39002	16·4	1·3895
16	38·71	23 8	1·38595	16·6	1·3854
17	37·08	22 49	1·38222	16·8	1·3818
18	34·94	22 35	1·37945	17	1·3790

Table VII.—Series of Consecutive Determinations made by Method of Total Reflection.

Tartaric Acid, Solution S_2.

No.	*m.*	*θ.*	*μ.*	*t.*	*μ* at 19°.
1	68·78	27° 23′	1·43176	16°·6	1·4312
2	64·11	26 37	1·42413	18	1·4239
3	60·03	25 57	1·41724	18·3	1·4171
4	56·43	25 22	1·41105	18·5	1·4110
5	53·25	24 57	1·40653	18·7	1·4065
6	50·40	24 33	1·40211	18·7	1·4021

Table VIII. represents a series of observations made upon a solution of known strength gradually diluted down by addition of water and determined by means of the hollow prism, as in the case of alum. These are represented by small circles on Diagram II. and serve, as before, to establish approximately a curve showing the relation between composition and refractive index in supersaturated and strong solutions of tartaric acid.

TABLE VIII.—Series of Consecutive Determinations made by Method of Minimum Deviation.

No.	m.	μ.	t.
1	58·489	1·41672	19°
2	53·542	1·40843	19
3	48·908	1·40092	19
4	44·588	1·39459	19
5	40·573	1·38817	19
6	36·856	1·38247	19
7	33·427	1·37728	19
8	30·272	1·37292	19
9	27·377	1·36860	19
10	24·729	1·36470	19
11	22·312	1·36149	19
12	19·842	1·35789	19

(3.) *Refractive Indices of Solutions of Sodium Chlorate.*

The refractive index of a saturated solution of sodium chlorate was found as follows :—

μ.	t.	
1·38754	16°·2	By total reflection.
1·38634	19	By minimum deviation.

Supersaturated and strong solutions were next examined by the total reflection method, as in the preceding examples.

In Series I., 20 cub. centims. of a solution containing 13·141 grammes of sodium chlorate were placed in the trough and examined with a totally reflecting prism of angle 44° 51′, and index 1·51704, and diluted down by successive additions of 2 cub. centims. of water. The results are given in Table IX., and are represented by dots in Diagram III.

In Series II., 10 cub. centims. of a supersaturated solution containing 8·026 grammes of sodium chlorate were diluted with successive additions of 4 or 2 cub. centims. of water (warm water being used at first). The results are given in Table X., and are represented by crosses in Diagram II.

TABLE IX.—Series of Consecutive Determinations made by Method of Total Reflection.

No.	m.	θ.	μ.	t.	μ at 19°.
1	46·902	23° 16′	1·38599	20°	1·3862
2	43·780	22 51½	1·38117	20	1·3814
3	41·045	22 38	1·37850	20	1·3787
4	38·632	22 22	1·37530	20	1·3755
5	36·486	22 11	1·37309	20	1·3733
6	34·567	21 59	1·37065	20	1·3708
7	32·839	21 48	1·36841	20½	1·3687
8	31·276	21 39½	1·36668	20¾	1·3670
9	29·855	21 31½	1·36503	20¾	1·3653
10	28·558	21 24	1·36349	21	1·3639
11	27·368	21 17½	1·36215	21	1·3625
12	26·273	21 11	1·36080	21	1·3612
13	25·263	21 6	1·35976	21	1·3602
14	24·328	21 0	1·35851	21	1·3589
15	23·459	20 56	1·35768	21	1·3581
16	21·896	20 47½	1·35590	21	1·3563
17	19·906	20 38	1·35390	21	1·3543

TABLE X.—Series of Consecutive Determinations made by Method of Total Reflection.

No.	m.	θ.	μ.	t.	μ at 19°.
1	55·432	24° 5′	1·39542	29°	1·3974
2	43·432	22 47	1·38029	26	1·3817
3	39·191	22 23	1·37550	25½	1·3768
4	35·704	22 8	1·37247	21½	1·3730
5	32·787	21 52	1·36923	20½	1·3693
6	30·310	21 37½	1·36626	20	1·3665
7	28·182	21 25½	1·36380	19½	1·3639
8	26·333	21 16	1·36184	19½	1·3619
9	24·711	21 5½	1·35966	19¼	1·3597
10	22·002	20 52½	1·35695	19	1·3569
11	19·828	20 40	1·35432	19	1·3543
12	18·044	20 30	1·35222	19	1·3522

Table XI. represents a series of observations made by means of the hollow prism upon 25 cub. centims. of a solution of sodium chlorate concentrated at 19° and diluted by successive additions of 6 cub. centims. of water; the results are represented by small circles upon Diagram III.

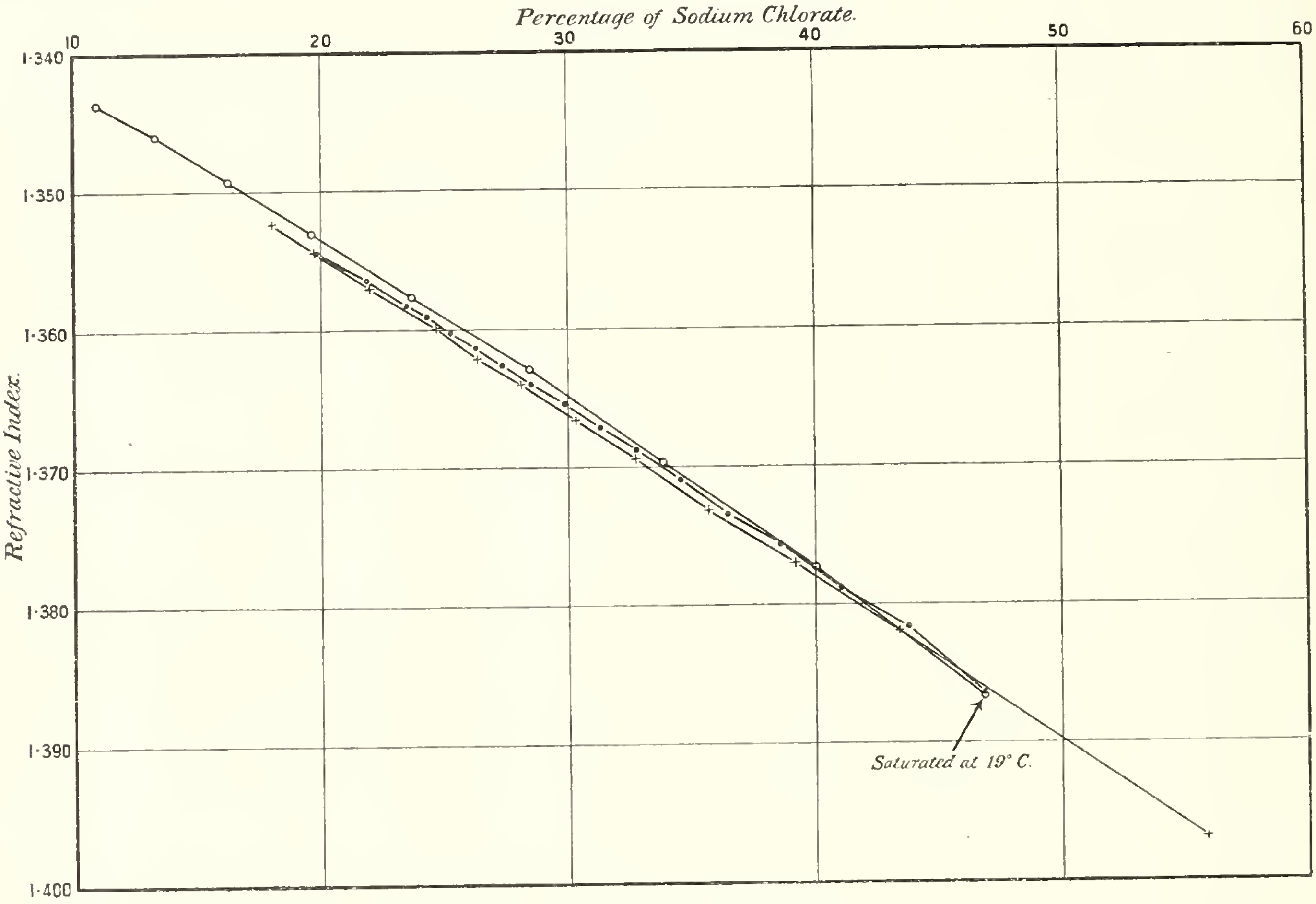

Diagram III.—Sodium Chlorate.

The constitution of the solutions of Table XI. is fixed by assuming that No. 1 has the same constitution as No. 1 of Table IX., which was also a saturated solution, and has nearly the same refractive index.

Table XI.—Series of Consecutive Determinations made by Method of Minimum Deviation.

No.	m.	μ.	t.
1	46·902	1·38634	19°
2	40·044	1·37711	19
3	33·90	1·36953	19
4	28·47	1·36283	19
5	23·75	1·35756	19
6	19·70	1·35287	19
7	16·27	1·34909	19
8	13·33	1·34594	19
9	10·96	1·34361	19

(4.) *Refractive Indices of Solutions of Sodium Nitrate.*

The refractive index of a saturated solution of sodium nitrate was found as follows :—

μ.	t.	
1·38880	19¾°	By minimum deviation.
1·38837	22	,, ,, ,,
1·38770	24·5	,, ,, ,,
1·38873	17·5	,, total reflection.

Supersaturated and strong solutions were next examined by the total reflection method (prism of 44° 52′, index 1·51704). In Series I., 20 cub. centims. of a saturated solution were placed in the trough and examined with the same totally reflecting prism as before, and were diluted by successive additions of 2 cub. centims. of water up to No. 15. Nos. 16 and 17 were taken after addition of 6 cub. centims. and 4 cub. centims. of water respectively. In this series Nos. 1 and 2 were taken on one day and the remainder on the following day. The results are given in Table XII. and are represented by crosses in Diagram IV.

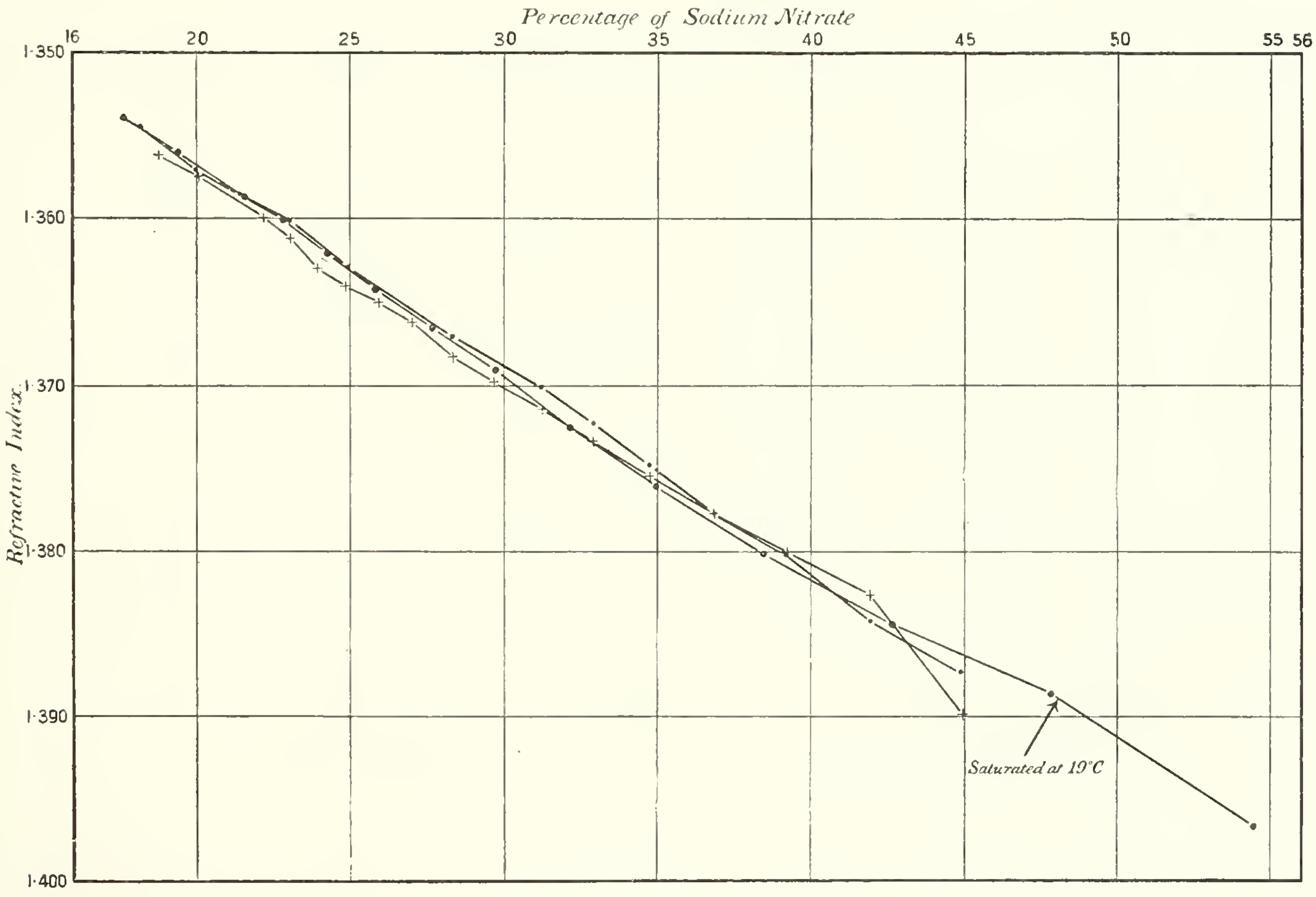

Diagram IV.—Sodium Nitrate.

In Series II., 20 cub. centims. of a saturated solution were examined and diluted down by successive additions of 2, 4, 6, or 8 cub. centims. of water. This series of observations was made in a single day. The results are given in Table XIII. and are represented by dots in Diagram IV.

In Series III., 10 cub. centims. of a supersaturated solution, weighing 14·39 grammes and containing 7·843 grammes of substance, were placed in the trough and diluted by successive additions of 2 cub. centims. of water up to No. 12; warm water being used up to No. 5; water at the ordinary temperature from No. 6 onwards; Nos. 13 and 14 were made after the addition of 4 cub. centims. each.

The results are given in Table XIV. and are represented by dots in Diagram IV.

The irregularity in the series of crosses is fully accounted for by the break in the continuity of the observations.

TABLE XII.—Series of Consecutive Determinations made by the Method of Total Reflection.

No.	m.	θ.	μ.	t.	μ at 19°.
		° ′		°	
1	45·001	23 33	1·38950	20½	1·3899
2	41·920	22 52	1·38150	20½	1·3826
3	39·235	22 48	1·38070	18½	1·3806
4	36·873	22 33	1·37772	18½	1·3776
5	34·779	22 20½	1·37522	19½	1·3754
6	32·910	22 10	1·37311	20	1·3733
7	31·232	21 59	1·37093	20½	1·3714
8	29·717	21 51	1·36926	20½	1·3697
9	28·342	21 43½	1·36773	20¾	1·3683
10	27·088	21 33½	1·36568	21	1·3662
11	25·941	21 27½	1·36445	21	1·3650
12	24·887	21 22	1·36331	21¼	1·3640
13	23·915	21 16½	1·36217	21¼	1·3629
14	23·016	21 8	1·36041	21¼	1·3611
15	22·182	21 2½	1·35927	21¼	1·3599
16	20·008	20 50½	1·35676	21¼	1·3574
17	18·781	20 44	1·35540	21¼	1·3561

The above observations are represented by crosses in Diagram IV.

Table XIII.—Series of Consecutive Determinations made by the Method of Total Reflection.

No.	*m*.	*θ*.	*μ*.	*t*.	*μ* at 19°.
1	45·037	23° 22′	1·38716	18°·2	1·38706
2	41·949	23 7½	1·38433	18	1·3840
3	39·258	22 51	1·38108	18	1·3808
4	36·891	22 34½	1·37780	18	1·3775
5	34·793	22 20½	1·37500	18	1·3747
6	32·922	22 9	1·37268	18	1·3724
7	31·242	22 0	1·37086	18	1·3706
8	28·347	21 42	1·36719	18	1·3669
9	24·888	21 22½	1·36317	18	1·3629
10	23·016	21 11	1·36080	18¼	1·3606
11	21·406	21 1	1·35872	18¼	1·3585
12	20·006	20 54	1·35726	18¼	1·3570
13	18·219	20 45	1·35538	18½	1·3544

The above observations are represented by dots in Diagram IV.

Table XIV.—Series of Consecutive Determinations made by the Method of Total Reflection.

No.	*m*.	*θ*.	*μ*.	*t*.	*μ* at 19°.
1	54·506	23° 54′	1·39332	30°	1·3966
2	47·855	23 10	1·38482	31½	1·3885
3	42·650	22 47	1·38029	32½	1·3843
4	38·467	22 27	1·37630	32½	1·3803
5	35·031	22 15	1·37389	26	1·3760
6	32·158	22 1½	1·37116	23¼	1·3724
7	29·721	21 45	1·36780	23	1·3690
8	27·627	21 34½	1·36565	22	1·3665
9	25·809	21 23	1·36328	22	1·3642
10	24·212	21 13	1·36121	21¾	1·3620
11	22·807	21 7	1·35997	19	1·3600
12	21·554	21 1	1·35872	19	1·3587
13	19·419	20 48	1·35600	19	1·3560
14	17·669	20 38	1·35391	19	1·3539

The above observations are represented by dots in Diagram IV.

All the above experiments indicate that the composition of a supersaturated, a saturated, or a strong solution may be ascertained with a certain degree of accuracy by determining the refractive index by means of a totally reflecting prism; there appears to be no sudden break in the curvature of the curve which expresses the relation between refractive index and constitution.

They must not be regarded as more than a first attempt to establish this fact and to determine the curve for four substances : in the case of the supersaturated solutions, the stirring was not always satisfactory, on account of the danger of making the solution crystallise ; and in the same series of observations the constitution was only deduced by comparison with another series. However, the very fair coincidence between the determinations made quite independently by the two methods gives some confidence in the experiments next to be described, in which a growing crystal itself is employed as the totally reflecting prism.

(C.) *The Refractive Index and Concentration of the Solution in Contact with Growing Crystals of Alum, Sodium Chlorate, and Sodium Nitrate.*

As explained above, the growing crystal itself may in some instances be used as the totally reflecting prism, and it will then give the refractive index of the solution in contact with the crystal by the formula on p. 495. Some difficulty will, of course, be experienced by reason of the vicinal faces ; in the first place, the angle of the prism will have to be measured during, or immediately after, each observation ; this can be done without withdrawing the crystal from the solution if the square trough be employed ; in the second place, and this is a more serious difficulty, the prism faces are no longer single plane surfaces, but sets of vicinal faces, and it will be necessary to select such as are very flat, or to make use of the growing crystal at the precise moment when two large vicinal faces can be employed as a prism and the rest are sufficiently small to be ignored. In spite of these difficulties, observations have been made upon the two cubic substances, alum and sodium chlorate, and upon sodium nitrate, which serve to determine approximately the refractive index of the liquid, and therefore, by the help of the preceding diagrams, its constitution.

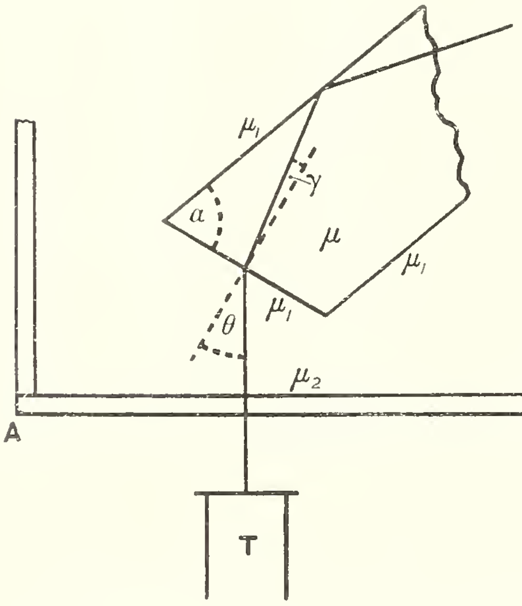

Fig. 18.

Since the light, on emerging from the crystal, traverses a liquid of varying density, and since the crystal face through which it emerges is not parallel to the side AB of the trough nearest to the telescope T, the formula on p. 495 is not rigidly applicable (see fig. 18).

If μ be the index of the crystal, μ_1 the unknown index of the solution in contact with it, and μ_2 the index of a saturated solution, which is known from the preceding experiments, then the light after emergence traverses a liquid whose index changes from μ_1 to μ_2; and, if it be assumed that it changes uniformly, then the index μ_1 can be deduced from the angle of emergence θ and the angle of the crystal α by the formula

$$\mu_1 = \mu \cos \left[\cos^{-1} \frac{\mu_2 \sin \theta}{\mu} - \alpha \right].$$

Under the conditions described below, this formula is practically identical with that given on p. 495.

(1.) *Potash-alum.*

With alum either the acute or the obtuse angle of the octahedron may be employed, and, therefore, a theoretically perfect crystal would admit of four determinations without readjustment, using in turn the four octahedron faces as the totally reflecting surface. In general it was not possible to carry out more than one determination on each crystal in consequence either of vicinal faces, or the difficulty of illumination owing to the shape of the crystal, or the imperfections of the faces. A very perfect crystal giving single reflections from two faces B and C was adjusted, and immersed in concentrated solution one evening and allowed to grow during the night; on the following day no reading could be obtained, but on the second day a reading was obtained for total reflection at C, the light emerging through D (fig. 19).

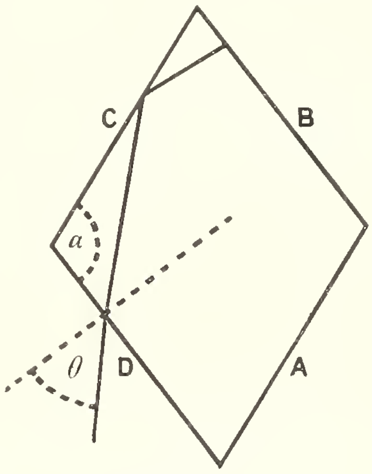

Fig. 19.

Assuming that the angle α is 109° 29′, and calculating from the reading for which C was perpendicular to the telescope (D itself being a somewhat unsatisfactory face), the angle of emergence, θ, was found to be − 46° 54½′. Taking the value 1·4598 for the index of the alum, this leads to the value 1·3455 for the index of the liquid in contact with C, and, therefore, indicates that the liquid is only slightly supersaturated.

If the index of the liquid had been 1·34232, the value found for the saturated solution, the angle of emergence would be − 47° 26′, a difference lying far beyond the errors of observation.

If the angle of the prism was 109° 23½′, as deduced from the measured angle BC, instead of the theoretical angle 109° 29′, the angle of emergence would have been − 46° 49′, indicating that the difference observed cannot be attributed to a small error in the angle of the crystal.

The crystal was re-examined in the evening, and, immediately after the reading for total reflection had been taken, the crystal was dried with a soft tongue of blotting paper and re-measured. The faces CD yielded (in addition to other images) two bright images corresponding to faces inclined to each other at 109° 6′: and the angle of emergence through D was − 46° 51′. This gives the index as 1·34312.

A third determination was made with the same crystal on the following day, using the acute angle of the octahedron as prism, *i.e.*, total reflection taking place at B and emergence through C.

This gave BC = 70° 43′ and the angle of emergence $\theta = -4° 16'$, leading to the value 1·34171 for the index of the liquid; in this case, however, the crystal was probably not growing, but was in contact with a diluted liquid, for the line of total reflection was not well defined, the addition of a little water did not affect the reading, and etched triangles made their appearance on the faces. The value 1·34171 is simply the index of an almost saturated solution. Another crystal was mounted and examined in the same way with the obtuse angle for prism; this gave

$$\alpha = 109° 39\tfrac{1}{2}', \quad \theta = -47° 19\tfrac{1}{2}', \quad \mu = 1{\cdot}34422.$$

The same crystal, examined on the following day at $14\frac{1}{2}°$, gave

$$\alpha = 109° 30\tfrac{1}{2}', \quad \theta = -47° 19\tfrac{1}{2}', \quad \mu = 1{\cdot}34313.$$

But the faces now yielded triple images, so that this determination is possibly not so reliable as the preceding one.

The crystal was then withdrawn and the glass prism inserted in place of it; this gave

$$\alpha = 44° 58', \quad \theta = 19° 37', \quad \mu = 1{\cdot}34263.$$

The above observations are sufficient, I think, to establish conclusively that the liquid in contact with a growing crystal of alum is slightly supersaturated, and that its index differs by about ·0007 from that of a saturated solution at the same temperature. Other observations led to the same result.

The mean of the best determinations for the solution in contact with a growing crystal at 14°,

1·34375, 1·34331, 1·34343, 1·34308, 1·34330, 1·34332, 1·34313 is $\mu = 1{\cdot}34336$.

The best determination for the saturated solution at 14° gave

$$\mu = 1{\cdot}34263.$$

Interpreting these results by the curve of Diagram I, we arrive at the conclusion that at 14° C.:—

(1) A saturated solution of potash-alum contains about 8·5 grammes of the substance in 100 grammes of solution;

(2) The liquid in contact with a growing crystal contains about 9·3 grammes of the substance in 100 grammes of the solution.

Specific Gravity of Solution in Contact with a Growing Crystal of Potash-alum.

The refractive index of the liquid in contact with a growing crystal having been determined, it seemed desirable to determine also its specific gravity.

A solution was therefore made containing 9·3 grammes of K-alum per 100 grammes of solution, and the following observations were made:—

Temperature.	Specific gravity.
14°	1·0458 referred to water at 14° C.

This agrees very closely with the value obtained by constructing a curve from the values found by GERLACH and quoted by LANDOLT and BÖRNSTEIN, 'Physikalisch-Chemische Tabellen,' 1894, p. 203.

The refractive index of this solution was determined by the method of total reflection with a glass prism of 60° 10½′, and refractive index 1·62151, immersed in the liquid. The value obtained was:—

At 14° . . . . . . 1·34310.

The index, as determined from the curve of Diagram I., would be 1·34336 at 14° C.

(2.) *Sodium Chlorate.*

Sodium chlorate has a refractive index of 1·5151 for sodium light, according to KOHLRAUSCH, and we have already found that the index of a saturated solution of the substance at 16° is about 1·38754; with these values, and using cube faces for the surfaces of the reflection and emergence, *i.e.*, using a prism of angle 90°, the angle of total reflection should be 23° 40¾′, and the angle of emergence 26° 0½′.

A fairly good cube of sodium chlorate growing in its solution yielded readings for total reflection from each of the four cube faces in one zone; the best of these corresponded to the angle of emergence $\theta = -26° 5'$.

Assuming the angle α to be 90°, and taking the value 1·5151 for the index of the crystal, we get $\mu = 1·3870$ for the index of the liquid in contact with the crystal.

A second crystal gave $\theta = -25° 56'$, $\alpha = 89° 59'$, and, therefore, $\mu = 1·38801$.

A third crystal gave the following very good readings at 15°, the observations being made late at night when the crystal was growing steadily and uniformly.

Readings for the images of the collimator signal reflected from the four cube faces A, B, C, D :—

$$\left[\begin{array}{ll} A_\alpha & 163^\circ\ 39\tfrac{1}{2}', \\ A_\beta & 163^\circ\ 28', \\ B & 73^\circ\ 33', \\ C_\alpha & 343^\circ\ 38', \\ C_\beta & 343^\circ\ 28', \\ D & 253^\circ\ 33'. \end{array}\right.$$

As explained on p. 484, the faces A, C yield each two images lying in a horizontal plane, and the faces B, D two images lying in a vertical plane.

The readings for total reflection were :—

233° 54′	light reflected at	B	emerging through		A.
143° 48½′	,, ,,	C	,,	,,	B,
53° 56½′	,, ,,	D	,,	,,	C.

The angle between telescope and collimator was 88° 42′.

On the following morning almost precisely the same readings were obtained. There is clearly here a difficulty in deciding what to take as the value of the angle α.

Confining our attention to the case in which total reflection takes place at the face B, and taking in succession the maximum value $A_\alpha B = 90^\circ\ 6\frac{1}{2}'$, the minimum value $A_\beta B = 89^\circ\ 55'$, and the mean value $AB = 90^\circ\ 0'$, the three results are :—

$$\alpha = 90^\circ\ 6\tfrac{1}{2}', \qquad \theta = -25^\circ\ 53', \qquad \mu = 1{\cdot}38951 \text{ at } 16^\circ.$$

$$\alpha = 89^\circ\ 55', \qquad \theta = -26^\circ\ 4\tfrac{1}{2}', \qquad \mu = 1{\cdot}38630 \text{ ,, } 16^\circ.$$

$$\alpha = 90^\circ\ 0', \qquad \theta = -26^\circ\ 0', \qquad \mu = 1{\cdot}38767 \text{ ,, } 16^\circ.$$

Finally, then, we have for the refractive index of the liquid in contact with a growing crystal of sodium chlorate at 16°, $\mu = 1{\cdot}38794$ about.

Interpreting these results by the curve of Diagram III. we arrive at the conclusion that at 16° C :—

(1) A saturated solution of sodium chlorate contains about 47·36 grammes of the substance in 100 grammes of solution ;

(2) The liquid in contact with a growing crystal contains about 47·73 grammes of the substance in 100 grammes of solution.

(3.) *Sodium Nitrate.*

The preceding observations relate to isotropic substances; it appeared advisable to apply the same method to some substance not belonging to the cubic system and possessing strong double refraction. Sodium nitrate lends itself admirably to this purpose and both cleaves and crystallises readily in the form of rhombohedra of 73° 30′. The refractive index of a saturated solution of sodium nitrate was determined above to be about 1·38905 at 19° (mean of 1·38850, 1·38913, 1·38927, 1·38930). With a prism of 73° 30′ this would give for a cleavage rhomb of sodium nitrate in contact with a saturated solution an angle of total reflection of 28° 57′ and an angle of emergence of $-14^\circ\ 15\frac{3}{4}'$, taking $\omega = 1{\cdot}58739$, and using only the ordinary index (see fig. 20).

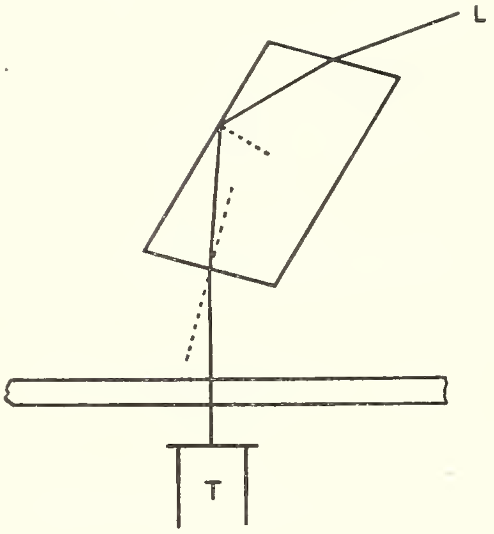

Fig. 20.

A cleavage crystal having an angle of 73° 35′ between two very good faces was immersed in saturated solution and gave an angle of emergence of $\theta = -14^\circ\ 11'$. This leads to the value 1·39085 for the refractive index of the liquid.

Another cleavage fragment gave

$$\alpha = 73^\circ\ 34', \qquad \theta = -14^\circ\ 17\tfrac{1}{2}', \qquad \mu = 1{\cdot}38954 \text{ at } 17\tfrac{1}{2}^\circ.$$

A third cleavage fragment immersed in a saturated solution kept at about the same temperature by surrounding the trough with beakers of ice gave

$$\alpha = 73^\circ\ 33', \qquad \theta = -14^\circ\ 15\tfrac{1}{2}', \qquad \mu = 1{\cdot}38968.$$

A fourth, for which the solution was cooled down to 16° by the same method, gave

$$\alpha = 73^\circ\ 35', \qquad \theta = -14^\circ\ 12', \qquad \mu = 1{\cdot}39067, \qquad t = 16^\circ.$$

A fifth gave

$$\alpha = 73^\circ\ 35', \qquad \theta = -14^\circ\ 13\tfrac{1}{2}', \qquad \mu = 1{\cdot}39042, \qquad t = 17\tfrac{1}{2}^\circ.$$

Finally, then, we have for the refractive index of the liquid in contact with a growing crystal of sodium nitrate (mean of 1·38954 and 1·39042), $\mu = 1{\cdot}38998$ at $17\frac{1}{2}^\circ$.

Interpreting these results by the curve of Diagram IV. we arrive at the conclusion that at $17\frac{1}{2}^\circ$ C:—

(1) A saturated solution of sodium nitrate contains about 47·65 grammes of the substance in 100 grammes of the solution;

(2) The liquid in contact with a growing crystal contains about 48·8 grammes of the substance in 100 grammes of the solution.

It must be remarked that owing to the use of cleavage fragments in these experiments it is not absolutely certain in every case that the crystal was actually growing, and it is possible that the higher values are the most correct.

It will be noticed that the refractive index of a saturated solution of sodium nitrate is greater than the extraordinary index, 1·33608, of the crystallised substance, and less than the ordinary index, 1·58739, so that only the ordinary index comes into operation in these experiments, and with regard to the index of the crystal no account need be taken of the direction in which the light is travelling in the crystal.

With all the three substances examined the result is the same: the liquid in contact with a growing crystal is slightly, and only slightly, supersaturated.

PART III.

THE ACTION OF THE CONCENTRATION STREAMS (CRYSTALLISATION IN MOTION).

Interpretation of the Foregoing Results. A Possible Cause for the Variation of Angle in Alum and other Crystals.

In the preceding pages we have seen that, in the case of alum, the apparent variation of the octahedron angle is certainly due to the production of vicinal faces, and that the same cause is probably sufficient to account for the variations of angles in the forms of other substances. The variations are small, but they lead to the following important results:—

The faces which actually occur upon a crystal are, in general, not those with simple rational indices, but are vicinal faces.

It is true that these probably possess rational indices, but such as can only be expressed by high numbers.

To what are these faces to be attributed?

There is little in crystallographic literature which throws light upon the subject, and, so far as I am aware, absolutely no experimental work.

Only in the recent remarkable and original investigations of G. WULFF, upon the velocity of crystal growth, is a definite explanation of the vicinal faces proposed.*

WULFF finds that the velocity of outward growth of a crystal is different for different faces, and he supposes that it is probably inversely proportional to their reticular density; the actual velocity of growth is, however, largely influenced by the intensity and direction of the concentration streams which flow upwards round the crystal. Experiments upon these led him to the conclusion that the crystals grow

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* "Zur Frage der Geschwindigkeit des Wachsthums und der Auflösung der Krystallflächen," 'Zeitsch. f. Kryst.,' 1901, vol. 34, p. 449.

most regularly when the concentration streams are weakest. In order to eliminate the effect of the concentration streams, his crystals were made to grow in rotating vessels, and very uniform results were obtained. WULFF points out that those faces which grow outwards most slowly increase in area at the expense of those which grow most rapidly, so that the latter are soon eliminated; the actual forms occurring on a crystal are, therefore, those whose rate of growth is least, and these are the faces of greatest reticular density.

The substance used by WULFF in his experiments was ferrous-ammonium sulphate. In an investigation by Z. WEYBERG* the experiments were extended to iron-ammonium-alum, and led to the result that crystals of this substance grow in an aqueous solution, with a supersaturation of about 2 per cent., and at a temperature of 8° C., twice as fast in a direction perpendicular to the dodecahedron faces as perpendicular to the cube faces, and from three to four times more rapidly perpendicular to the cube than to the octahedron.

According to WULFF, therefore, the usual planes on a crystal must be those of high reticular density, and the vicinal planes must be exceptional and due to some disturbing cause, which he describes as follows:—

"Die Concentrationsströmungen verursachen das Erscheinen der Vicinalflächen. Bei der Krystallisation orientiren sich die Molekeln auf den Flächen des Krystalles ganz gleichförmig durch den Einfluss der Richtkraft der Krystallisation.

"Jedoch müssen sich diese Kräfte unbedingt mit den Kräften, durch welche die Molekeln von den Concentrationsströmungen fortgezogen werden, zu einer Kraft zusammensetzen. Die sich ablagernden Molekeln orientiren sich nach den Richtungen, die den resultirenden Kräften entsprechen, und am Ende erhält man Flächentheile, welche um einen mehr oder weniger kleinen Winkel aus ihrer normalen Lage gebracht worden sind. Dieses sind die Vicinalflächen. Es ist klar, dass die Lage solcher Vicinalflächen von folgenden Factoren abhängt: (1) Von der Intensität der Strömungen; (2) von der Richtung der Strömung in Bezug auf die normale Lage der Fläche, und (3) von der Form der Fläche, welche selbstverständlich in einem mehr oder weniger directen Zusammenhange mit der Symmetrie des Krystalles steht. Späterhin werden wir sehen, dass die Energie des Wachsthums der Fläche, bis auf einen gewissen Factor genau, der sich in nicht weiten Grenzen ändert, umgekehrt proportional zur reticulären Dichte der Fläche des Krystalles steht. Bei sehr geringer reticulärer Dichte, wie sie sich für die Vicinalflächen ergiebt, wenn man ihre Symbole nach den beobachteten Winkeln berechnet, wird diese Energie so gross, dass eine solche Fläche verwächst und verschwindet. Deswegen darf man die Vicinalflächen nicht als Flächen mit complicirten Symbolen betrachten, wie es sehr viele Krystallographen zu thun pflegen.

"Ebenso wenig darf man die Vicinalflächen als Flächen mit einfachen Symbolen

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* "Studien über relative Wachsthumsgeschwindigkeit der Krystallflächen," *ibidem*, p. 531.

auffassen, welche aber, nach der Terminologie **Jerofejew's**, zu verschiedenen 'zusammengehäuften' Individuen gehören, und zwar deswegen, weil die Winkel dieser Flächen nicht genau den idealen Grössen, welche die Symmetrie erfordert, entsprechen. Diese Ansicht ist das Resultat eines falschen Begriffes vom Krystalle als von einem Individuum, das sich unbedingt durch einen bestimmten Anfangspunkt des Wachsthums auszeichnet. Wir können den Krystall nur dann als aus mehreren Individuen bestehend betrachten, wenn man in ihm mehrere solche Punkte nachweisen kann. Andererseits erhält man den Begriff 'Zusammenhäufungen der Individuen' in Folge einer einseitigen Vorstellung vom Krystalle, wenn man ihn nur als geometrischen Körper betrachtet. Beide Ansichten über die Vicinalflächen haben nur dadurch entstehen können, dass man den Krystall an und für sich, unabhängig von dem Medium, in welchem er sich bildet, betrachtete."

Now the question whether the vicinal faces are due to the concentration streams is one in which direct appeal can be made to experiment. I have mentioned above the experiments which I made in 1894 with the object of eliminating possible differences of concentration in the mother-liquor. Small crystals of potassium-alum were suspended from the arms of a wooden vane, which was kept rotating in a concentrated solution of the salt for several hours by means of clockwork. No effect whatever seemed to be produced upon the crystals either as regards the presence or absence of vicinal faces or the brilliancy and smoothness of the crystals.

Recently I have made similar, but more precise, experiments in order to ascertain whether the stillness or violent motion of the liquid have any effect in altering the angles of the vicinal forms.

The experiments were made in two ways: a crystal, having been mounted in the platinum clip, was allowed to grow until well developed, and was measured in the solution; without being withdrawn from the solution, it was then attached to a vertical spindle and kept rotating for several hours by means of a small water-motor, and was then measured again. In other experiments the trough of liquid was placed upon a turn-table and set rotating, the crystal remaining fixed within it.

Experiments upon Potassium-alum Crystallising in an Agitated Solution.

An octahedron yielded three well defined vicinal planes upon each of two octahedron faces A and B: the angle between one facet α and the edge of the other facets, β, γ, was measured as in fig. 10.

$$A_{\alpha} : A_{\beta\gamma} = 0^{\circ}\ 30' ; \quad B_{\alpha} : B_{\beta\gamma} = 0^{\circ}\ 31'.$$

At 4 P.M. the crystal was set rotating, the temperature being 19° C.

At 7.30 P.M., $t = 11^{\circ}$, the crystal was stopped and measured, and gave

$$A_{\alpha} : A_{\beta\gamma} = 0^{\circ}\ 48' ; \quad B_{\alpha} : B_{\beta\gamma} = 0^{\circ}\ 31' ;$$

but these were now accompanied by other and less distinct images.

The crystal was re-immersed at 7.45 P.M., and allowed to rotate during the whole night.

Next morning at 9.30 A.M., $t = 11°$, it was measured again and gave upon another octahedron face

$$C_\alpha : C_{\beta\gamma} = 0° \; 37\tfrac{1}{2}',$$

these readings being again very good.

The same crystal was re-immersed at 3.30 P.M., $t = 17°$, and the trough was set rotating.

At 9.0 P.M., $t = 10\frac{1}{2}°$, it gave

$$C_\alpha : C_{\beta\gamma} = 0° \; 39\tfrac{1}{2}',$$

the readings being very good.

The corresponding readings for the other vicinal forms were :—

	Before rotation.	After rotation.
On A	0° 32′	0° 33½′
,, B	0° 31½′	0° 31′
,, D	0° 33′	0° 29′

As a result of these experiments it may be asserted that, in alum at any rate, the vicinal faces are neither produced nor appreciably affected by the concentration streams in the solution.

The vicinal faces may, however, vary with the average concentration of the solution in their neighbourhood, or—what may amount to the same thing—with their rate of growth. In fact, it is difficult to think of any other nearly constant, but slightly variable, condition to which they may reasonably be attributed. In any case, the fact to which I wish to draw attention is that the faces which actually occur upon a crystal are not those with simple indices and great reticular density, but those with complex indices and low reticular density.

The faces of alum whose angles were measured by BRAUNS, and whose rate of growth was measured by WEYBERG, were, therefore, not octahedron faces at all, but vicinal faces, and in the arguments relating to them we are not at liberty to assume that they are faces of high reticular density.

Whatever structures may be necessary to account for other features of crystals, there is little doubt that we are justified in regarding their faces as the planes of a space-lattice. Now there is one remarkable property of the space-lattice which bears closely upon the present problem. In general, two planes of the lattice which are nearly coincident in direction are by no means alike in other respects. In the cubic lattice, for example, the cube face is the most dense, and the faces which approximate most closely to it in density are not the planes which most nearly coincide with it but the dodecahedron and octahedron. To replace the cube or the octahedron by vicinal planes nearly coincident with them is to replace planes of the greatest possible reticular density by planes of the least possible reticular density. And yet the crystal is bounded by the latter rather than by the former. Is it not possible that the supersaturated liquid in immediate contact with the growing alum crystal consists of particles of alum uniformly mingled with particles of water, and that the act of crystallisation consists in the escape of the water, and consequent solidification of the alum? Immediately before the act of crystallisation the alum particles in the solution cannot be so closely packed as those in the crystal, since they are separated by particles of water; if, then, they are to be laid down in plane layers, and are yet to find their places at once as constituent parts of the crystal structure, they will be laid down not along planes of great reticular density but along vicinal planes.

Fig. 21 gives a crude representation* of a cubic structure in which the particles are so widely spaced immediately before the act of crystallisation that they solidify along the plane (025). The density in the cube face is 5·385 times as great as the density in this plane; for in the cube plane the mesh is a square (side = a), and in the plane (025) the mesh is a rectangle whose sides are a and $5{\cdot}385a$ respectively.

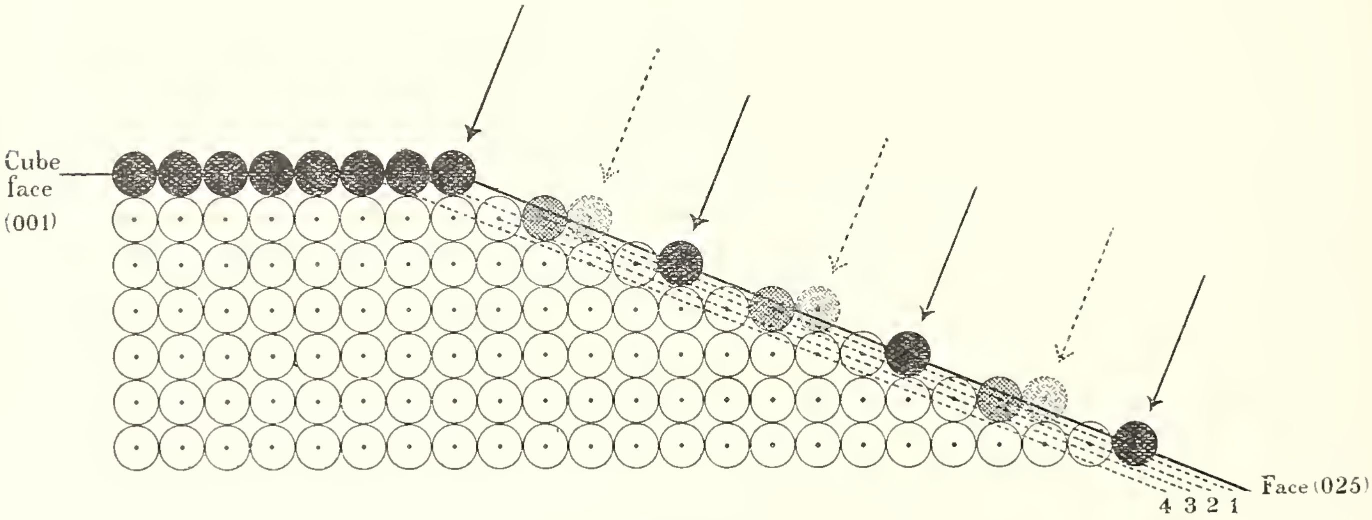

Fig. 21.

It is, of course, impossible from the constitution of a single layer of particles to deduce that of the solution in the neighbourhood of the crystal as a whole; and the refractive index presumably only gives the average constitution of a certain layer of the solution, thin though that layer may be. Nevertheless, the figure indicates that, if the crystallising particles be regarded as a shower falling normally upon the surface, the shower is so dense upon a growing cube face that it would leave little space for the escape of the solvent, whereas upon the face (025), although equally dense as measured along lines perpendicular to the plane of the diagram, it is more than five

---

[*] The particles are only represented as circles in contact with each other, in order to make the structure more clear.

times more open as measured in the plane of the diagram. [With vicinal faces of the sort actually observed, the difference is, of course, very much greater; for example, a vicinal plane ($0kl$) in the cubic lattice inclined at 0° 30′ to the cube face has a rectangular mesh whose sides are a and $114a$ (about), and the density in the cube face is therefore about 114 times that in the vicinal plane.] Although the plane (025) has a comparatively open structure, the successive layers of particles parallel to this plane are far more closely packed than successive cube layers, as is clear from the figure (lines 1, 2, 3, 4). The black circles represent the particles which, at a given moment, bound the crystal; the plane which preceded it is represented by shaded circles whose centres lie on the line 1, and the set of particles in the act of crystallising is represented by dotted circles.

If we are to speculate concerning the arrangement of the material in layers further removed from the surface of the crystal, we may perhaps suppose that along lines normal to the surface (the arrows of fig. 21) the particles are even as closely packed as along an edge of the cube. Each successive layer is then formed as the crystal solidifies by the particles immediately behind those of the newly solidified layer slipping sideways into their places.

Further, in the case contemplated, each dotted circle in the figure may be taken to represent a line of particles perpendicular to the plane of the drawing, which are packed as closely as the particles along a cube edge in the crystal, *i.e.*, as closely as the horizontal lines of particles. The act of crystallisation will then consist in the deposition of such lines all parallel to the cube edge, but so widely spaced as to lie in a vicinal plane ($0kl$). This corresponds with the fact that the vicinal planes, though they vary in inclination, always belong to well defined zones; in this instance they will lie in the cube zone, and sodium chlorate possibly affords an example of vicinal planes of the sort depicted in fig. 21.

The determinations made above enable us to compare the weight of material contained in a given volume of the crystal with the weight of the same material in the same volume of the solution; that is to say, the density of the substance in the crystal with its density in the immediate neighbourhood of the crystal, ignoring the solvent. Thus for *alum*:—Taking the specific gravity of the crystallised salt to be 1·72, then 100 cub. centims. of the solid will contain 172 grammes of alum; and 100 cub. centims. of a solution containing 9·3 per cent. alum, and of specific gravity 1·048, will contain 9·74 grammes of alum. The density of alum in the crystal is, therefore, about 17⅔ times that in the adjacent solution.

For *sodium chlorate*:—Specific gravity of the crystallised salt = 2·289; 100 cub. centims. of the solid will contain 228·9 grammes of sodium chlorate; and 100 cub. centims. of a solution containing 47·73 per cent. of the salt will contain 65·27 grammes of sodium chlorate. The density of sodium chlorate in the crystal is, therefore, about 3½ times that in the adjacent solution.

For *sodium nitrate*:—Specific gravity of the crystallised salt = 2·244; 100 cub.

centims. of the solid contain 224·4 grammes of $NaNO_3$; 100 cub. centims. of a 48·8 per cent. solution contain 66·88 grammes $NaNO_3$. The density of sodium nitrate in the crystal is, therefore, about $3\frac{1}{3}$ times that in the adjacent solution.

Without knowing something more concerning the nature of the liquid, it is difficult to establish any relation between these numbers and the particular vicinal face produced.

If we assume that not only the particles in the layer of liquid in immediate contact with the face, but also those in consecutive layers for an appreciable distance, have the same arrangement as in the face itself; then, if the consecutive layers in the crystal are separated by a distance D, and if A be the area of the elementary parallelogram in the growing face,

$$AD = \text{constant} = \text{volume of the elementary parallelepiped in the lattice.}$$

And if consecutive layers in the liquid be separated by an interval X, then the volume of the elementary parallelepiped in the liquid is AX.

The ratio of the density of the material in the crystal to that in the liquid is therefore X/D, and in the substances considered above this quantity would be from $17\frac{2}{3}$ to $3\frac{1}{3}$.

If the relative distances be calculated on the assumption that X be, as suggested above, not less than the least distance which separates adjacent particles in the crystal, the numbers obtained for vicinal faces inclined at 30′ to the octahedron are not identical with these, but are more than five times as great, whether the structure be the cube, the centred cube, or the cube with centred faces; and for vicinal faces inclined at only about 10′ to the octahedron the disproportion is far greater.

It will be noticed, however, that to assume any uniform distribution of the crystallisable material in the liquid is to endow it with a crystalline structure before it solidifies. There is, perhaps, nothing impossible in the idea that the material may be already arranging itself immediately before the act of crystallisation. (There is, however, no evidence that this is the case.) Under these conditions, the solution could not possess the ordinary properties of a liquid, and, *inter alia*, might be expected to exhibit double refraction; it was with this possibility in view that the strongly birefringent sodium nitrate was chosen above as a substance to be experimented upon, in the hope that evidence of birefringence might be detected in the solution in contact with the growing face; but no such evidence could be found by the method of total reflection within the crystal.

To obtain anything like a correct estimate of the relative sizes of the meshes in the vicinal faces, and therefore of the distance which separates consecutive layers parallel to them, it would be necessary to measure their angles accurately not to minutes, but to seconds. To determine from the constitution or specific gravity of the liquid any relation between the arrangement of the particles in the vicinal face and in the solution, some assumption must be made concerning the successive layers in the latter.

Such speculations are, however, at present beyond the test of experiment, neither is it possible to say what particular vicinal faces correspond to a certain concentration of the solution until more is known concerning the nature of these layers of solution immediately adjacent to the crystal. In particular, it will be necessary to make accurate determinations of the change of volume produced by dissolving the crystals.

It is sufficient to point out that the wider spacing of the material before it solidifies is a reason why the crystallising substance should descend upon the growing crystal in a shower which is not very dense; and this again is a reason why the growth should take place along vicinal planes, and not along planes with simple indices. That the growth does take place along vicinal planes has been abundantly proved, at any rate for alum, in the preceding pages; that the spacing is very much wider in the liquid than in the crystal has been proved by showing that the liquid about to crystallise is scarcely more than saturated.

Very slight variations in the concentration of the solution would probably correspond to considerable differences in the vicinal planes produced.

The observations recorded above raise many interesting questions; but I have thought it better to confine myself in this paper mainly to observed facts, and to reserve further speculation for another occasion, hoping in the meantime that the enquiry into the nature of the liquid in contact with a growing crystal, which is here opened, will be pursued by others in a more systematic and exhaustive manner.

Note.—A brief statement of some of the results recorded in Part I. (pp. 459–492) was published in the Report of the British Association for 1894, p. 654.

In the latter part of the research I have received useful help from my assistant, Mr. RICHARD GRAHAM, by whom many of the observations in Part II. were made.

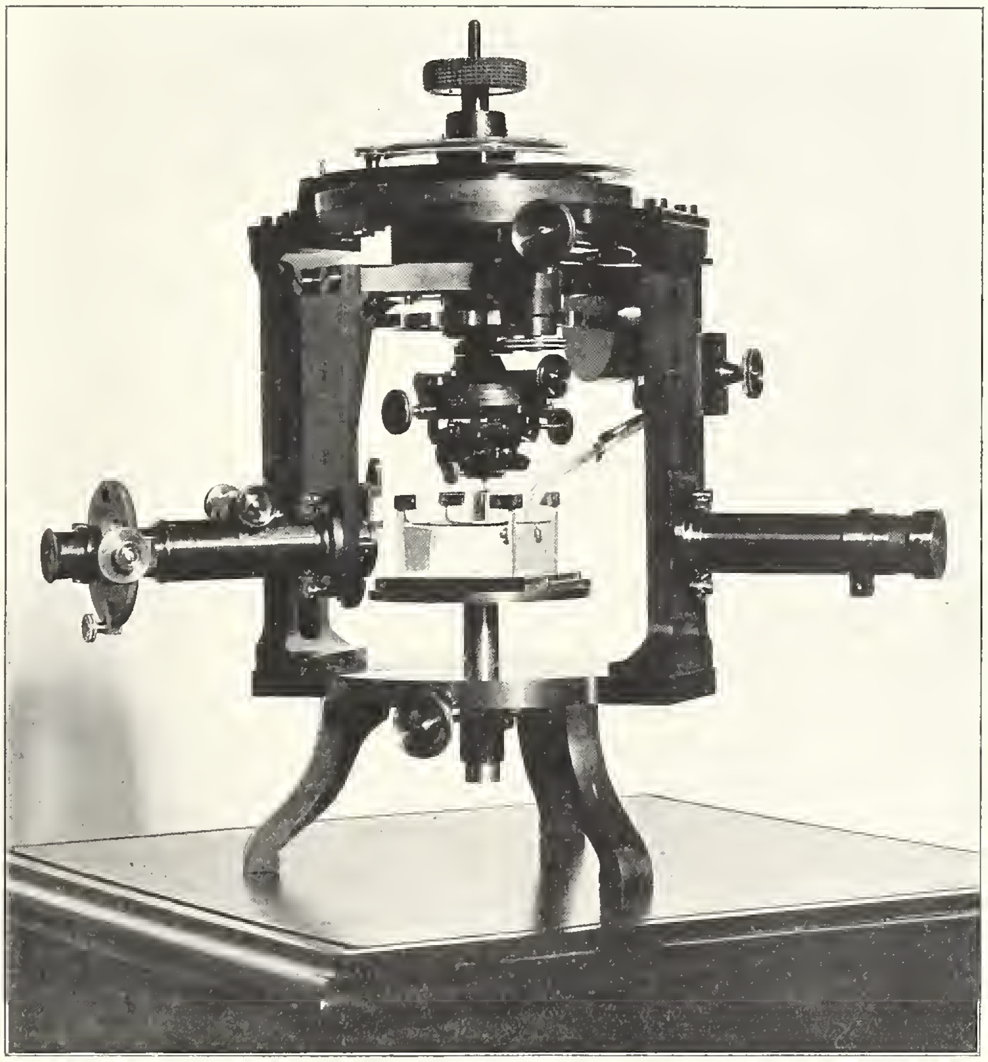

Fig. 1.

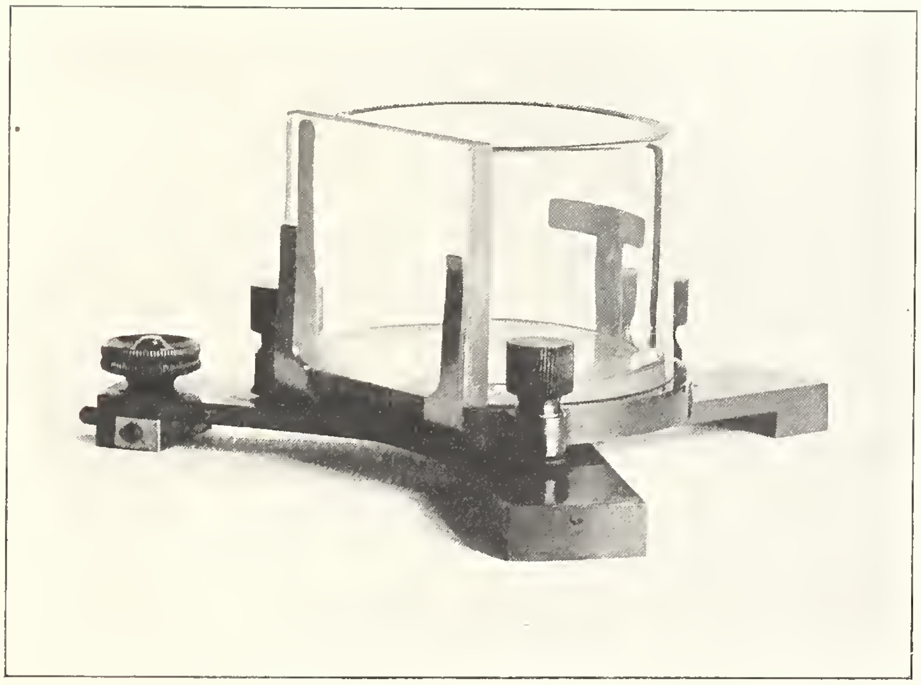

Fig. 16.

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RADIATION IN THE SOLAR SYSTEM: ITS EFFECT ON TEMPERATURE AND ITS PRESSURE ON SMALL BODIES

BY

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XII. *Radiation in the Solar System: its Effect on Temperature and its Pressure on Small Bodies.*

By J. H. Poynting, *Sc.D., F.R.S., Professor of Physics in the University of Birmingham.*

Received June 16,—Read June 18, 1903.

PART I.

Temperature.

When a surface is a full radiator and absorber* its temperature can be determined at once by the fourth-power law if we know the rate at which it is radiating energy. If it is radiating what it receives from the sun, then a knowledge of the solar constant enables us to find the temperature. We can thus make estimates of the highest temperature which a surface can reach when it is only receiving heat from the sun. We can also make more or less approximate estimates of the temperatures of the planetary surfaces by assuming conditions under which the radiation takes place,† and we can determine, fairly exactly, the temperatures of very small bodies in interplanetary space.

These determinations require a knowledge of the constant of radiation and of either the solar constant or the effective temperature of the sun, either of which, as is well known, can be found from the other by means of the radiation constant. It will be convenient to give here the values of these quantities before proceeding to apply them to our special problems.

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* A surface which absorbs, and therefore emits, every kind of radiation, is usually described as "black," a description which is obviously bad when the surface is luminous. It is much better described as "a full absorber" or "a full radiator."

† This was pointed out by W. Wien in his report on "Les Lois Théoriques du Rayonnement" ('Congrès International de Physique,' vol. ii., p. 30). He remarks that Stefan's law enables us to calculate the temperatures of celestial bodies which receive their light from the sun, by equating the energy which they radiate to the energy which they receive from the sun, and states that for the earth we obtain nearly the mean temperature, using the reflecting power of Mars, while the temperature of Neptune should be below $-200°$ C.

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The Constant of Radiation.

If R is the energy radiated per second per square centimetre by a full radiator at temperature θ° A (where A stands for the absolute scale), the fourth-power law states that

$$R = \sigma\theta^4,$$

where σ is the constant of radiation.

According to KURLBAUM* the constant is

$$\sigma = 5{\cdot}32 \times 10^{-5} \text{ erg}.$$

The Solar Constant.

The solar constant is usually expressed as a number of calories received per minute by a square centimetre held normal to the sun's rays at the distance of the earth. The determinations by different observers differ so widely that it is not necessary for our present purpose to consider whether the constant really exists or whether there are small periodic variations from constancy.

ÅNGSTRÖM estimated the value as 4 calories per square centimetre per minute, and this value is adopted by CROVA as very probable.† When converted to ergs per second this gives

$$S_a = 0{\cdot}28 \times 10^7 \text{ ergs/cm.}^2 \text{ sec.},$$

where the suffix denotes that it is ÅNGSTRÖM's value.

LANGLEY‡ assumed that the atmosphere transmits about 59 per cent. of the energy from a zenith sun and from his measurement of the heat reaching the earth's surface he estimated the value of the constant at 3 calories. This gives

$$S_l = 0{\cdot}21 \times 10^7 \text{ ergs/cm.}^2 \text{ sec.},$$

ROSETTI§ assumed a transmission of 78 per cent. from the zenith sun, but WILSON and GRAY|| consider that 71 per cent. represents ROSETTI's numbers better than 78 per cent. If in LANGLEY's value we replace 59 per cent. by 71 per cent. we get 2·5 calories. This gives

$$S_r = 0{\cdot}175 \times 10^7 \text{ ergs/cm.}^2 \text{ sec.}$$

---

* 'Wied. Ann.,' vol. 65, 1898, p. 748.

† 'Congrès International de Physique,' vol. 3, p. 453.

‡ 'Phil. Mag.,' vol. 15, 1883, p. 153, and 'Researches on Solar Heat.'

§ 'Phil. Mag.,' vol. 8, 1879, p. 547.

|| 'Phil. Trans.,' A, 1894, p. 383.

The Radiation from the Sun's Surface.

If s is the radius of the sun's surface, R the radiation per square centimetre, then the total rate of emission is $4\pi s^2\mathrm{R}$. This passing through the sphere of radius r, at the distance of the earth and with surface $4\pi r^2$, gives

$$4\pi s^2\mathrm{R} = 4\pi r^2\mathrm{S},$$

where S is the solar constant.

Hence

$$\mathrm{R} = \frac{r^2}{s^2}\mathrm{S} = \left(\frac{9{\cdot}23 \times 10^7}{4{\cdot}3 \times 10^5}\right)^2 \mathrm{S} = 46{,}000\mathrm{S}.$$

Corresponding to the three values of S just given we have three values of R, viz.,

$$\mathrm{R}_a = 1{\cdot}29 \times 10^{11}\,; \qquad \mathrm{R}_l = 0{\cdot}945 \times 10^{11}\,; \qquad \mathrm{R}_r = 0{\cdot}805 \times 10^{11}.$$

The Effective Temperature of the Sun.

If we equate the sun's radiation to $\sigma\theta^4$, where σ is the radiation constant, we get θ, the "effective temperature" of the sun, that is the temperature of a full radiator which is emitting energy at the same rate.

Thus

$$5{\cdot}32 \times 10^{-5}\,\theta_a{}^4 = 1{\cdot}29 \times 10^{11},$$

whence

$$\theta_a = 7000^\circ\,\mathrm{A}\ \text{approximately.}$$

Similarly

$$\theta_l = 6500^\circ\,\mathrm{A}\,; \qquad \theta_r = 6200^\circ\,\mathrm{A}.$$

Wilson[*] made a direct comparison of the radiation from the sun with that from a full radiator at known temperature. Assuming a zenith transmission of 71 per cent., he obtained 5773° A as the effective solar temperature. If we put

$$46{,}000\mathrm{S} = 5{\cdot}32 \times 10^{-5} \times 5773^4,$$

we get

$$\mathrm{S} = 0{\cdot}128 \times 10^7.$$

This is no doubt too low a value. Either then Wilson's zenith transmission was less than 71 per cent. or Kurlbaum's constant is too small.

The low value is probably to be accounted for chiefly by the first supposition. Wilson points out that if x is the true value of the transmission, his value of the temperature is to be multiplied by $(71/x)^{\frac{1}{4}}$. If we take $\theta_r = 6200^\circ$ as the true value then x will be given by

$$x = \left(\tfrac{5773}{6200}\right)^4 \times 71 = 53.$$

This low value is not necessarily inconsistent with the much higher value 71 per cent.

---

[*] 'Roy. Soc. Proc.,' vol. 69, 1901–2, p. 312.

used above in finding ROSETTI's solar constant, for no doubt the transmission varies widely with time and place, and we have no reason to assume that 1·77 calories per minute, obtained by LANGLEY, would have been received from the zenith at the time and in the place where WILSON was making his determination.

The Effective Temperature of Space.

In determining the steady temperature of any body as conditioned by the radiation received from the sun, we have to consider whether it is necessary to take into account the radiation from the rest of the sky. If it receives S from the sun, ρ from the rest of the sky, and if its own radiation is R, then in the steady state

$$R = S + \rho \quad \text{or} \quad R - \rho = S.$$

It behaves therefore as if it were receiving S from the sun, but as if it were placed in a fully radiating enclosure of such temperature that the radiation is ρ. This temperature is the "effective temperature of space."

The temperature may perhaps be more definitely described as that of a small full absorber placed at a distance from any planet and screened from the sun. Various well-known attempts have been made to estimate this temperature, but the data are very uncertain. The fourth-power law however shows that it is not very much above the absolute zero, if we can assume that the quality of starlight is not very different from that of sunlight.

According to L'HERMITE[*] starlight is one-tenth full moonlight. Full moonlight is variously estimated in terms of full sunlight. LANGLEY[†] takes it as $\frac{1}{400,000}$. These two values combined give sunlight as 4×10^6 starlight. But starlight comes from the whole hemisphere, while the sun only occupies a small part of it. In comparing temperatures we have to use the brightness of sunlight as if the whole hemisphere were paved with suns.

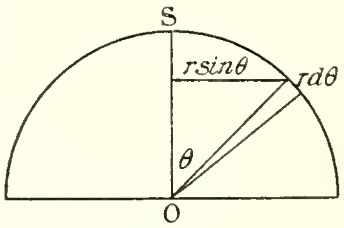

Fig. 1.

If B is the illumination of a surface at O, fig. 1, lighted by the sun in the zenith at S, and if πs^2 is the area of the sun's diametral plane, then $B/\pi s^2$ is the illumination at O due to each square centimetre. If the hemisphere were all of the same brightness as the sun, the illumination at O due to the ring of sky between θ and $\theta + d\theta$ would be

$$\frac{B}{\pi s^2} 2\pi r^2 \sin\theta \cos\theta \, d\theta,$$

where r is the distance of the sun.

---

[*] 'L'Astronomie,' vol. 5, p. 406.

[†] "First Memoir on the Temperature of the Surface of the Moon." 'National Academy of Sciences vol. 3.

Integrating from $\theta = 0$ to $\theta = \pi/2$, we have

$$\text{Total illumination} = \mathrm{B}r^2/s^2 = 46{,}000 \text{ B}.$$

The illumination from a hemisphere paved with suns is therefore $46{,}000 \times 4 \times 10^6 = 1{\cdot}84 \times 10^{11}$ times that from the stellar sky.

If we assume that the quality of the radiation is the same in both cases, that is, if we assume that the energy is proportional to the light part of the spectrum, we have by the fourth-power law

$$\text{Effective temperature of space} = \frac{\text{effective temperature of sun}}{({\cdot}184 \times 10^{12})^{\frac{1}{4}}}$$

$$= \frac{\text{effective temperature of sun}}{655}.$$

As the temperature of the sun probably lies between 6000° A and 7000° A, this gives

$$\text{Effective temperature of space} = 10^\circ \text{ A}.$$

If, then, a body is raised by the sun to even such a small multiple of 10° as, say, 60°, the fourth-power law of radiation implies that it is giving out and therefore receiving from the sun more than a thousand times as much energy as it is receiving from the sky.

The sky radiation may therefore be left out of the account when we are dealing with approximate estimates and not with exact results, and bodies in the solar system may be regarded as being situated in a zero enclosure except in so far as they receive radiation from the sun.

Temperature of a Planet under Certain Assumed Conditions when placed at a distance from the Sun equal to that of the Earth.

The real earth presents a problem of complexity far too great to deal with. I shall therefore consider an ideal earth for which certain conditions hold, more or less approximating to reality, and determine the temperature of its surface on the assumption that it receives heat from the sun only.

Let us suppose :—

1. That the planet is rotating about an axis perpendicular to the plane of its orbit, which is circular.

This will give us too high a temperature at the equator, and the absolute zero, which is too low, at the poles. The mean, however, over the planet, will probably be not much affected by the supposition.

2. That the effect of the atmosphere is to keep the temperature in any given latitude the same, day and night.

This is not a great departure from reality. On the sea, which is more than two-thirds of the earth's surface, the daily range is very small, of the order of 1° or 2° C., while even on the land it is, in extreme cases, not more than 15° C., which is not a large fraction of the absolute temperature.

3. That the surface and the atmosphere over it at any one point have one effective temperature as a full radiator. This is no doubt a departure from reality. How wide a departure we have no present means of estimating.

4. That there is no convection of heat from one latitude to another.

This is a very wide departure from reality. But, as we shall see below, the mean temperature of the planet is very little affected by convection, even if we assume that it is so extensive as to make the surface of uniform temperature.

5. That the reflexion at each point is $\frac{1}{10}$th of the radiation received.

This is probably of the order of the actual reflexion from the earth. According to LANGLEY* the moon reflects about $\frac{1}{8}$th of the radiation received. The earth certainly reflects less. The temperatures determined hereafter are proportional to the 4th root of the coefficient of absorption. Even if this coefficient is as low as 0·9 its 4th root is 0·974. Hence if the actual value is anywhere between 0·9 and 1, the assumed value of 0·9 will not make an error of more than $2\frac{1}{2}$ per cent. in the value of the temperature.

6. That the planet ultimately radiates out all the heat received from the sun, no more and no less.

This again is very near the condition of the real earth, which, on the whole, radiates out rather more than it receives—perhaps on the average a calorie per square centimetre in three days.

Making these six suppositions, let us calculate the temperature of various parts of this ideal planet.

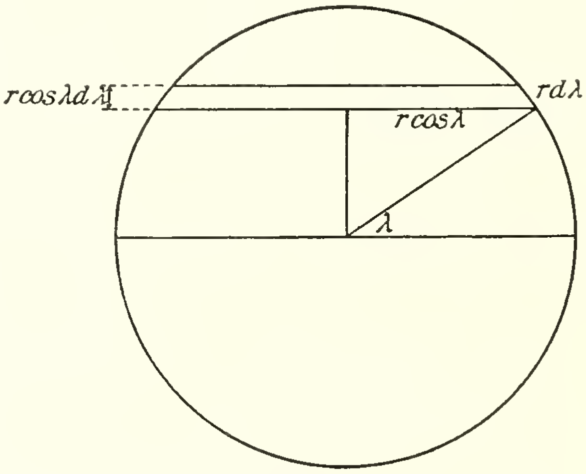

Fig. 2.

Consider a band between latitudes λ and $\lambda + d\lambda$. The area receiving heat from the sun at any instant, if projected normally to the stream of solar radiation, is (fig. 2)

$$2r\cos\lambda \, r d\lambda \cos\lambda = 2r^2\cos^2\lambda d\lambda,$$

where r is the radius of the planet.

If S is the solar constant, this band is absorbing, with coefficient 0·9,

$$0{\cdot}9\mathrm{S} \times 2r^2\cos^2\lambda d\lambda.$$

But the band all round the globe is radiating equally, according to the second supposition, and the radiating area is

$$2\pi r\cos\lambda \, . \, r d\lambda = 2\pi r^2\cos\lambda d\lambda.$$

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* "Third Memoir on the Temperature of the Moon." 'National Academy of Sciences,' vol. 4, Part 2, p. 197.

Hence the radiation emitted per square centimetre is

$$\frac{0{\cdot}9\ \mathrm{S}\ 2r^2 \cos^2\lambda\, d\lambda}{2\pi r^2 \cos\lambda\, d\lambda} = \frac{0{\cdot}9\ \mathrm{S} \cos\lambda}{\pi}.$$

If the effective temperature in this latitude is θ_λ, we have

$$\frac{0{\cdot}9\ \mathrm{S}\cos\lambda}{\pi} = 5{\cdot}32 \times 10^{-5}\theta_\lambda{}^4,$$

or

$$\theta_\lambda = \left(\frac{0{\cdot}9 \times 10^5\mathrm{S}}{5{\cdot}32\pi}\right)^{\frac{1}{4}} \cos^{\frac{1}{4}}\lambda.$$

If we put $\lambda = 0$, we get the equatorial temperature corresponding to each of the different values of S given above, viz. :

Equatorial $\theta_a = 350°$ A approximately.
,, $\theta_l = 325°$ A ,,
,, $\theta_r = 312°$ A ,,

The temperature in latitude λ is

$$\theta_\lambda = \text{equatorial temperature} \times \cos^{\frac{1}{4}}\lambda.$$

Thus, in latitude 45°, it is 0·917 equatorial temperature.

The average temperature over the globe is

$$\frac{2}{4\pi r^2}\int_0^{\frac{\pi}{2}} 2\pi r^2 \cos\lambda\theta_{\mathrm{E}} \cos^{\frac{1}{4}}\lambda\, d\lambda,$$

where θ_{E} is the equatorial temperature

$$= \theta_{\mathrm{E}}\int_0^{\frac{\pi}{2}} \cos^{\frac{5}{4}}\lambda\, d\lambda = \theta_{\mathrm{E}}\frac{\sqrt{\pi}}{2}\frac{\Gamma\left(\frac{9}{8}\right)}{\Gamma\left(\frac{5}{8}\right)} = 0{\cdot}93\theta_{\mathrm{E}}.$$

The average temperature, then, is little more than 1 per cent. above the temperature in latitude 45°.

If we use the three values of θ_{E} just given, we have

Average $\theta_a = 325°$ A approximately.
,, $\theta_l = 302°$ A ,,
,, $\theta_r = 290°$ A ,,

Our fourth supposition was that there is no convection by wind or water from one latitude to another. Let us now go to the other extreme and suppose that the convection is so great that the temperature is practically uniform all over the globe.

We then have a receiving surface virtually πr^2, and a radiating surface $4\pi r^2$. Then we get the radiation emitted per square centimetre

$$\frac{0\cdot9\text{S}\pi r^2}{4\pi r^2} = \frac{9\text{S}}{40};$$

and if θ is the temperature required for this,

$$5\cdot32 \times 10^{-5}\theta^4 = \frac{9\text{S}}{40};$$

whence

Uniform $\theta_a = 330°$ A approximately

,, $\theta_l = 307°$ A ,,

,, $\theta_r = 293°$ A ,,

values not more than 5° above those obtained for the average on the supposition of no convection.

Comparing these results with the temperature of the real earth, it is seen at once that they are of the same order.

The average temperature of the earth's surface is usually estimated at about 60° F., say 289° A. The temperature of the atmosphere is on the whole decidedly lower than that of the surface below it. We should therefore conclude that the earth's effective temperature is somewhat below 289° A.

Again, the earth and the atmosphere, taken as one surface, do not constitute a full absorber, but are to some extent selective. Hence we should expect the earth to be, if anything, of a higher temperature than a full absorber and radiator under the same conditions.

For both these reasons, then, the ideal planet might be expected to have a temperature below rather than above 289° A. The lowest estimate obtained above is therefore probably nearest to the truth, and it would appear that even that is somewhat too high. This tends to show that, if we accept KURLBAUM's value of the radiation constant, we cannot put the solar constant so high as 3 or 4, but must accept a value much nearer to that which I have called ROSETTI's value, viz., 2·5.

In what follows I shall therefore take ROSETTI's value and the resulting value of the solar temperature, viz., 6200° A.

The calculation made above may be turned the other way round, and may be used for a

Determination of the Effective Temperature of the Sun from the Average Temperature of the Earth.

Assuming that the real earth may be replaced by the ideal planet already considered, the radiation per square centimetre from the equatorial band is $\frac{0\cdot9\text{S}}{\pi}$. But the radiation per square centimetre from the sun's surface is 46,000S. If then θ_E is the earth's equatorial temperature, and θ_S is the solar temperature,

$$\frac{0{\cdot}9S}{\pi} : 46{,}000S = \theta_E{}^4 : \theta_S{}^4,$$

whence

$$\theta_E = \theta_S/20.$$

The average temperature of the earth is 0·93 of the equatorial temperature. If this average is θ_A, then

$$\theta_A = \theta_S/21{\cdot}5.$$

If we take the temperature of the real earth as 289° A, and as being equal to that of the ideal,

$$\theta_S = 21{\cdot}5 \times 289^\circ = 6200^\circ \text{ A approximately}.$$

Upper Limit to the Temperature of a Fully Radiating Surface exposed normally to Solar Radiation at the Distance of the Earth from the Sun.

The highest temperature which a full radiator can attain is that for which its radiation is equal to the energy received. This will only hold when no appreciable quantity of heat is conducted inwards from the surface.

To obtain the upper limit in the case under consideration, we have to equate the radiation to the solar constant, which we shall now take as $S_r = 0{\cdot}175 \times 10^7$. Then,

$$5{\cdot}32 \times 10^{-5}\theta^4 = 0{\cdot}175 \times 10^7,$$

and

$$\theta = 426^\circ \text{ A}.$$

If the surface reflects some of the radiation and absorbs a fraction x of that falling on it, then the effective temperature is

$$x^{\frac{1}{4}} \times 426^\circ \text{ A}.$$

The Limiting Temperature of the Surface of the Moon.

We may apply this result to find an upper limit to the temperature of the moon's surface. This upper limit can only be attained when it is sending out radiation as rapidly as it receives it, and is therefore conducting no appreciable quantity inwards.

We shall take LANGLEY's estimate (*loc. cit.*) of $\frac{\text{reflected radiation}}{\text{emitted radiation}} = \frac{1}{6{\cdot}7}$. This is represented nearly enough by $x = \frac{7}{8}$.

The upper limit of temperature of the surface exposed to a zenith sun is, therefore,

$$\theta = 426 \times (\tfrac{7}{8})^{\frac{1}{4}} = 426 \times 0{\cdot}967 = 412^\circ \text{ A}.$$

This, then, is the upper limit to the temperature of the hottest part of an airless moon.

For a surface at angle λ with the line to the sun,

$$\theta_\lambda = 412 \cos^{\frac{1}{4}} \lambda.$$

If we take this as the law of temperature of the side of the moon exposed to the sun, we can find the effective temperature of the full moon as seen from the earth, *i.e.*, the uniform temperature of a flat disc of radius equal to that of the moon, sending to us the same total radiation.

If $N d\omega$ is the normal stream of radiation from 1 sq. centim. of surface of the moon immediately under the sun sent out through a cone angle $d\omega$, that sent out in direction λ to the normal is $N \cos \lambda \, d\omega$. But 1 sq. centim. on the moon's surface inclined at λ to the sun's rays only receives $\cos \lambda$ of the radiation received by the surface immediately under the sun. It therefore sends in the direction of the earth, also at λ to the normal, only $N \cos^2 \lambda \, d\omega$. Hence the total radiation to the earth, obtained by putting $d\omega = 2\pi \sin \theta \, d\theta$ and integrating is

$$\int_0^{\frac{\pi}{2}} \frac{N \cos^2 \lambda \; 2\pi m^2 \sin \lambda \, d\lambda}{r^2},$$

where m is the radius of the moon and r is its distance from the earth

$$= \frac{2\pi}{3} \frac{m^2}{r^2} N.$$

Let N_D be the normal stream from the equivalent flat disc, then

$$\frac{\pi m^2 N_D}{r^2} = \tfrac{2}{3}\pi \frac{m^2}{r^2} N$$

and

$$N_D = \tfrac{2}{3} N.$$

The effective temperature of the flat disc is therefore $\sqrt[4]{\frac{2}{3}}$ that of the surface immediately under the sun at the same distance from it.

Then the effective average $= 412 \times \sqrt[4]{\frac{2}{3}} = 412 \times 0{\cdot}9 = 371°$ A. The upper limit, then, to the average effective temperature of the moon's disc is just below that of boiling water.

This is very considerably above LANGLEY's estimate, that the surface of the full moon is a few degrees above the freezing-point. There can be no doubt that a very appreciable amount of heat is conducted inwards. The observations during eclipses by LANGLEY* and by BOEDDICKER show that some heat is still received from the moon's surface when it has entered the full shadow, and that it takes time after the eclipse has passed to establish a steady temperature again. It might be possible to

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* 'Third Memoir,' p. 159.

make some rough estimate of the amount conducted inwards from the Fourier equation, but the problem is not an easy one. Perhaps we get the best estimate by comparing the actual temperature with that above found.

If the actual temperature is taken as about $\frac{4}{5}$ the upper limit, say 297° A, then the radiation outwards is of the order $\sqrt[4]{\frac{4}{5}} = 0{\cdot}41$ of that where no conduction exists. Then nearly $\frac{3}{5}$ of the heat is probably conducted inwards.

If the moon always turned the same face to the sun instead of to the earth, the upper limit would be approached.

Temperature of a Spherical Absorbing Solid Body of the Order 1 *centim. in diameter at the Distance of the Earth from the Sun.*

The calculation of the temperature of such a body is interesting for two reasons. Firstly, the body will be at nearly the same temperature throughout, and secondly, as we shall show in the second part of this paper, the mutual repulsion of two such bodies, due to the pressure of their radiation, is of the same order as their gravitative attraction.

If the radius of the body is a, its effective receiving area is πa^2, and it receives

$$\pi a^2 \mathrm{S} \text{ ergs/sec.}$$

Its radiating surface is $4\pi a^2$, and therefore its average radiation per square centimetre in the steady state is

$$\pi a^2 \mathrm{S}/4\pi a^2 = \tfrac{1}{4}\mathrm{S}.$$

If we take $\mathrm{S} = 2{\cdot}5$ cal./min. or 0·04 cal./sec., and if the conductivity is of the order of that of terrestrial rock lying, say, between 0·01 and 0·001, it is evident that a difference of temperature of only a few degrees between the receiving and the dark surfaces will convey heat sufficient to supply radiation, 0·01 cal./sec., equal to the average. Thus, if the conductivity is 0·001 and the diameter is 1 centim., a difference of temperature of 10° suffices.

We may therefore take the temperature of the surface as approximately uniform when the steady state is reached. Let the temperature be θ, and let the solar temperature be θ_{S}. Then we have

$$\theta^4 : \theta_{\mathrm{S}}^4 = \frac{\mathrm{S}}{4} : 46{,}000\ \mathrm{S}$$

and

$$\theta = \frac{\theta_{\mathrm{S}}}{20{\cdot}7}.$$

If

$$\theta_{\mathrm{S}} = 6200^\circ \text{ A},$$

$$\theta = 300^\circ \text{ A approximately.}$$

This will be the temperature of fully absorbing bodies smaller than 1 centim., so long as they are not too small to absorb the radiation falling on them.

Variation of Temperature with Distance from the Sun.

Since the radiation received varies inversely as the square of the distance from the sun, that given out varies in the same ratio. The temperature of the radiating surface varies therefore as the fourth root of the inverse square, that is inversely as the square root of the distance.

This enables us to deduce at once the temperatures of the various surfaces and bodies which we have considered, if placed at the distances of different planets as well as at the distance of the earth. We have merely to multiply the results hitherto found by $\sqrt{\frac{\text{Earth's distance}}{\text{Planet's distance}}}$.

The following table contains the values of the temperatures at selected distances, all on the absolute scale :—

TABLE of Temperatures of Surfaces at Different Distances from the Sun. All on the Absolute Scale.

At the distance of the planet. I.	Distance. Earth's distance = 1. II.	Square root of (distance)$^{-1}$. III.	Equatorial temperature of ideal planet. IV.	Average temperature of ideal planet. V.	Upper limit of a surface reflecting one-eighth under zenith sun. VI.	Average temperature of equivalent disc. VII.	Temperature four-fifths that of equivalent disc. VIII.	Temperature of small absorbing sphere. IX.
Mercury .	0·3871	1·61	502	467	664	598	478	483
Venus .	0·7233	1·18	368	342	486	438	350	358
Earth . .	1·0000	1·00	312	290	412	371	297	300
Mars . .	1·5237	0·81	253	235	337	300	240	243
Neptune .	30·0544	0·18	56	52	74	67	53	54

We have omitted the larger planets except Neptune, since in all probability they radiate heat of their own in considerable proportion. Neptune is inserted merely to show how low temperatures would be at his distance if there were no supply of internal heat.

The results given in the table may not be exactly applicable to any of the planets, but they at least indicate the order of temperature which probably prevails.

If, for instance, Mars is to be regarded as having an atmosphere with regulating properties like our own, his equatorial temperature, Column IV., is probably far below the temperature of freezing water, and his average temperature, Column V., must be not very different from that of freezing mercury. If, on the other hand, we suppose that his atmosphere has no regulating power, we get the upper limits not very different from those in Columns VI. and VII. These are the limits for the bright side, and they imply nearly absolute zero on the dark side. If we regard Mars as resembling our moon, and take the moon's effective average temperature as 297° A, the corresponding temperature for Mars is 240° A, and the highest temperature is $\frac{4}{5} \times 337 = 270°$. But the surface of Mars has probably a higher coefficient of absorption than the surface of the moon—it certainly has for light—so that we may put his effective average temperature on this supposition some few degrees above 240° A, and his equatorial temperature some degrees higher still.

It appears exceedingly probable, then, that whether we regard Mars as like the earth, or, going to the other extreme, as like the moon, the temperature of his surface is everywhere below the freezing-point of water. The only escape from this conclusion that I can see is by way of a supposition that an appreciable amount of heat is issuing from beneath his surface.

We cannot draw any definite conclusions as to the temperatures of Mercury and Venus till we know whether they have atmospheres and whether they rotate on their own axes. If we make both these suppositions and further suppose that their conditions approximate to those of the ideal planet at their distances given in Columns IV. and V., then they may well be surrounded by hot clouds, as is sometimes supposed, entirely screening their solid bodies from us. If, on the other hand, their atmospheres are ineffective as regulators and if they always present the same face to the sun, the hottest part of Mercury is probably not far from 650° A, and that of Venus not far from 500° A.

If a comet consist of small solid particles of diameter of the order 1 centim. or less, then the temperatures of these particles are given in Column IX. At one-quarter of the earth's distance, say 23 million miles from the sun, the temperature is 600°, about the melting-point of lead. At one-twenty-fifth, say $3\frac{3}{4}$ million miles, it will be about 1500°, say the melting point of cast-iron. Nearer than this the temperature no doubt increases rapidly, but the law of temperature, deduced from the inverse square law for the radiation received, requires amendment, as that law was based on the supposition that a hemisphere only is lighted by the sun, and that the whole of his disc is visible from every part of that hemisphere. Both of these suppositions cease to hold when the distance from the sun is only a small multiple of his radius.

PART II.

RADIATION PRESSURES.

The pressure of radiation against a surface on which it falls, first deduced by MAXWELL from the Electromagnetic Theory of Light, is now established on an experimental basis by the work of LEBEDEW, confirmed by that of NICHOLS and HULL.

Though this pressure was first deduced as a consequence of the Electromagnetic Theory, Bartoli showed, independently, that a pressure must exist without any theory as to the nature of light beyond a supposition which may perhaps be put in the form that a surface can move through the ether, doing work on the radiation alone and not on the ether in which the radiation exists. Professor Larmor[*] has given a proof of this pressure and has shown that it has the value assigned to it by Maxwell, viz., that it is numerically equal to the energy density in the incident wave, whatever may be the nature of the waves, so long as their energy density for given amplitude is inversely as the square of the wave-length. We may, in fact, regard a pencil of radiation as a stream of momentum, the direction of the momentum being the axis of the pencil. If E is the energy density of the pencil, U its velocity, the momentum density may be regarded as E/U.

If the stream of radiation is being emitted by a surface, the surface is losing the momentum carried out with the issuing stream, and is so being pressed backwards. If the stream is being absorbed by the surface, then it is gaining the momentum and is still being pressed backwards, the forces being in the line of propagation.

As the expressions for the radiation pressure in various cases are probably not very well known, it may be convenient to state them here for use in what follows.

Values of Radiation Pressure in Different Cases.

If 1 sq. centim. of a full radiator is emitting energy R per second, and if $\mathrm{N}\,d\omega$ is the energy it is emitting through a cone $d\omega$, with axis along the normal, then in direction θ its projection is $\cos\theta$, and it is emitting $\mathrm{N}\cos\theta\,d\omega$ through a cone $d\omega$. Putting $d\omega = 2\pi\sin\theta\,d\theta$, and integrating over the hemisphere, we have

$$\mathrm{R} = \int_0^{\frac{\pi}{2}} \mathrm{N}\cos\theta \,.\, 2\pi\sin\theta\,d\theta = \pi\mathrm{N}.$$

If we draw a hemisphere, radius r, round the source as centre, the energy falling on area $r^2 d\omega$ is $\mathrm{N}\cos\theta\,d\omega$ per second, and, since the velocity is U per second, the energy density just outside the surface on which it falls is $\mathrm{N}\cos\theta/\mathrm{U}r^2$, and this is the rate at which the momentum is being received, that is, it is the normal pressure. The total force on area $r^2 d\omega$ is $\mathrm{N}\cos\theta\,d\omega/\mathrm{U}$. This is the momentum sent out by the radiating square centimetre per second through the pencil with angle $d\omega$, in the direction θ, and is therefore the force on the square centimetre due to that pencil.

Resolving along the normal and in the surface we have

$$\text{Normal pressure} = \mathrm{N}\cos^2\theta\,d\omega/\mathrm{U}.$$

$$\text{Tangential stress} = \mathrm{N}\cos\theta\sin\theta\,d\omega/\mathrm{U}.$$

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[*] 'Brit. Assoc. Report,' 1900; 'Encyc. Brit.,' vol. 32, Art. "Radiation."

Putting $d\omega = 2\pi \sin\theta\, d\theta$ and integrating over the hemisphere, we get

$$\text{Total normal pressure} = \int_0^{\frac{\pi}{2}} (\text{N} \cos^2\theta \,.\, 2\pi \sin\theta d\theta/\text{U}) = 2\pi\text{N}/3\text{U} = 2\text{R}/3\text{U}.$$

Total tangential stress = 0, since the radiation is symmetrical about the normal.

If the surface is receiving radiation, let us suppose that the stream is a parallel pencil S per second per square centimetre held normal to the stream, and that it is inclined at θ to the normal to the receiving surface. The momentum received per second is S cos θ/U. This produces

$$\text{Normal pressure} = \text{S} \cos^2\theta/\text{U}.$$

$$\text{Tangential stress} = \text{S} \cos\theta \sin\theta/\text{U}.$$

If the stream is entirely absorbed both these forces exist.

If the stream is entirely reflected, the reflected pencil exerts an equal normal force and an equal and opposite tangential force, and we have only normal pressure of amount 2S $\cos^2\theta$/U.

If only a fraction μ is reflected, the incident and reflected streams will give

$$\text{Normal pressure} = (1 + \mu)\, \text{S} \cos^2\theta/\text{U}.$$

$$\text{Tangential stress} = (1 - \mu)\, \text{S} \cos\theta \sin\theta/\text{U}.$$

To the normal pressure must be added the pressure due to the radiation emitted from the surface.

Radiation Pressure in Full Sunlight.

If a full absorber is exposed normally to the solar radiation at the distance of the earth the pressure on it is S/U, or $\dfrac{0{\cdot}175 \times 10^7}{3 \times 10^{10}} = 5{\cdot}8 \times 10^{-5}$ dyne/sq. centim.

The Radiation Pressures Between Small Bodies. Comparison with their mutual Gravitation.

It is well known that the radiation force on a small body, exposed to solar radiation, does not decrease so rapidly as gravitative pull on the body as its size decreases. If the body is a sphere of radius a and density ρ, and with a fully absorbing surface, and if it is so small that it is practically at one temperature all through, it is receiving a stream of momentum

$$\pi a^2\text{S}/\text{U}$$

directed from the sun. Its own radiation outwards being equal in all directions has zero resultant pressure.

The gravitative acceleration towards the sun at the distance of the earth is about 0·59 centim./sec.^{2}. Then we have

$$\frac{\text{Radiation pressure}}{\text{Gravitation pull}} = \frac{\pi a^2 S}{U \times \frac{4}{3}\pi a^3 \rho \times 0{\cdot}59}.$$

The two will be equal when

$$a = \tfrac{3}{4}\frac{S}{U\rho \times 0{\cdot}59}.$$

If we put

$$\rho = 1;\ S = 0{\cdot}175 \times 10^7;\ U = 3 \times 10^{10};$$

we get

$$a = 74 \times 10^{-6}.$$

This is the well-known result that a body of diameter about two wave-lengths of red light would be equally attracted and repelled if we could assume that a surface so small still continued to absorb. But, of course, when we are getting to dimensions comparable with a wave-length that assumption can no longer be made.

It is not, I think, equally well recognised that if the radiating body is diminished in size, the radiation pressure due to it also decreases less rapidly than the gravitative pull which it exerts. For the radiation decreases as the square of the radius of the emitting body and its gravitative pull as the cube.

We can easily compare the radiation and gravitation forces between two bodies, if for simplicity we assume that their distance apart is very great compared with the radius of either.

Let AB, fig. 3, be two spheres with full radiating surfaces. Let their radii be a, b and let their centres oo' be d apart. If this distance is great compared with a and b, each may be regarded as receiving a parallel stream from the other.

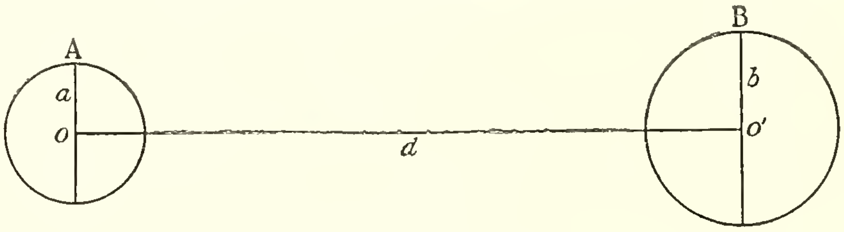

Fig. 3.

Let A send out a normal stream N $d\omega$ per square centimetre through cone $d\omega$, while B sends out N$'$ $d\omega$.

B receives the stream of cross section πb^2 or the angle of the cone is $\pi b^2/d^2$, and it issues virtually from area πa^2, for at B, A will appear as a uniformly bright flat disc.

Then the total force on B is

$$\frac{\pi a^2 N}{U} \times \frac{\pi b^2}{d^2} = \frac{\pi a^2 b^2 R}{U d^2},$$

where

$$R = \pi N.$$

The force on A due to B is $\pi a^2 b^2 R'/Ud^2$, where $R' = \pi N'$.

These are not equal unless $R = R'$, *i.e.*, unless the two bodies have the same temperature, an illustration of the fact that equality of action and reaction does not hold between the radiating and receiving bodies alone. They no longer constitute the whole of the momentum system. The ether, or whatever we term the light-bearing medium, is material, and takes its part in the momentum relations of the system.

If the surfaces are partially or totally reflecting, the forces are easily obtained. Thus if one is totally reflecting, it can be shown that the force is only half as great as when it is fully absorbing. But it will be sufficient to confine ourselves to the case of complete absorption, followed by radiation of the absorbed heat equally in all directions from all parts of the surface. More general assumptions do not alter the order of the forces found.

If G is the constant of gravitation $= 6{\cdot}67 \times 10^{-8}$, and if ρ, ρ' are the densities of A and B, the gravitation pull is $G\,\dfrac{16\pi^2 a^3 b^3 \rho\rho'}{9\,d^2}$.

Then on B

$$\frac{\text{Radiation push F}}{\text{Gravitation pull P}} = \frac{9\pi a^2 b^2 R}{16 G U \pi^2 a^3 b^3 \rho\rho'},$$

or

$$\frac{F}{P} = \frac{9R}{16 G U \pi a b \rho\rho'}.$$

If $a = b$; $\rho = \rho'$; $R = 5{\cdot}32 \times 10^{-5}\theta^4$, we have

$$a = \frac{2{\cdot}18\theta^2 \times 10^{-4}}{\rho} \sqrt{\frac{P}{F}}.$$

If we suppose the two bodies to have the temperature of the sun say, 6200° A, and its density, say 0·25, then $F = P$, when

$$a^2 = \frac{4{\cdot}75 \times 6200^4 \times 10^{-8}}{0{\cdot}25^2},$$

then $a = 33{,}500$ centims. or 335 metres.

Of course two globes of this size would soon cool far below the temperature of the sun, even if for an instant they could be raised up to it.

If we suppose $\theta = 300°$ A—the approximate temperature of small bodies at the distance of the earth from the sun—and if we take $\rho = 1$, then $F = P$, when $a = 19{\cdot}62$ centims.

Thus two globes of water—probably nearly full absorbers at 300° A—will at that temperature neither attract nor repel each other if their radii are about 20 centims.

If the density of the spheres is 11, about that so often used for masses in the Cavendish experiment, $F = P$ when

$$a = 1{\cdot}78 \text{ centims.}$$

This does not throw any doubt on the results of Cavendish experiments, for it only holds when the radiators are in an enclosure of very low absolute temperature. In all Cavendish experiments the greatest care is taken to make the attracted body and its enclosure of one uniform temperature.

The really interesting case is that of two small meteorites, in interplanetary space. To judge from the specimens which succeed in penetrating the earth's atmosphere they are very dense. Let us suppose them to have density 5·5—that of the earth—and temperature 300° A, that which they will have at the earth's distance. Then $F = P$ when

$$a = 3{\cdot}4 \text{ centims.}$$

If the radii of the bodies are less than the values found for equality of F and P in the different cases, the net effect is repulsion.

The ratio of F to P is inversely as the square of the radius, so that, as the radii are decreased from the values giving $F = P$, the radiation repulsion soon becomes enormously greater than the gravitation pull, and the latter may be neglected in comparison. Thus for two drops of water at 300° A in a zero enclosure, with radii 0·001 centim., the pressure is nearly 400,000,000 times the pull.

It is not, however, that the radiation force is great, or even its acceleration. The force becomes exceedingly minute, but the gravitation much more minute.

Thus consider two drops of water at 300° placed in a zero enclosure at a distance $d = 10a$ apart. Our assumption of parallel radiation from one to the other is now only a rough approximation, but the result will be of the right order.

The radiation push is $\pi a^4 R/Ud^2$, and the acceleration is $3aR/4Ud^2 = \frac{1}{10^7} \times \frac{1}{a}$ approximately.

This only becomes considerable when the drops approach molecular dimensions, and long before this they cease to absorb fully the stream of momentum falling on them. Still, even molecules are selective absorbers, and absorb especially each other's radiations. And we may expect that if two gas molecules collide and set each other radiating much more violently than before, they will be practically in an enclosure of much lower temperature than their own, and their mutual radiation may result in very rapid repulsion—repulsion of the order of the fourth power of the temperature reached.

Radiation Pressure between Small Bodies at Different Distances from the Sun.

We have seen above, that if two small spheres of density 5·5 are at the distance of the earth from the sun, their gravitation will be balanced by their radiation pressure when the radius of each is 3·4 centims. Now the balancing radius is proportional to the square of the temperature, that is, inversely proportional to the distance, since the temperature (Part I.) is inversely as the square root of the distance. Thus, at the distance of Mercury, the radii would be about 9 centims.; a million miles from the sun's surface they would be about 200 centims.; out at Neptune they would be about 1 millim.

We see then that the mutual action between small bodies of density that of the earth, will, at different distances, change sign for different sizes of body, ranging from something of the order of 4 metres diameter near the sun to the order of 2 millims. diameter at the distance of Neptune. A ring of small planets, each of radius 3·4 centims., and density 5·5, would move round the sun at the distance of the earth without net mutual attraction or repulsion, and each might be regarded as moving independently of the rest. It appears possible that if Saturn is hot enough, considerations of this kind may apply to his rings.

The repulsion between small colliding bodies, even if not heated by the sun, must lead to some delay in their final aggregation. This is obvious when there are only two small bodies, and their temperature is very considerably raised by the collision. But there is also delay, if instead of a single pair we suppose two swarms to collide. Near the boundary of the colliding region, a body will experience radiation pressure chiefly on one side, and will tend to be driven out of the system. Of course, if the swarms are so dense that a member near the outside cannot see through the rest, this effect will be less. A body in front of another entirely screens its radiation, but the gravitation is not screened. Hence, a body near the boundary of a densely-packed region of collision may be repelled only by the colliding bodies just round it, while it will be attracted by all; or, to put the same idea in another way, a body in a spherical swarm of uniform temperature will only be pulled equally in all directions at the centre of the swarm, but it will be equally repelled in all directions as soon as it is sufficiently deep to be surrounded by its fellows wherever, so to speak, it looks.

Inequality of Action and Reaction between Two Mutually Radiating Bodies.

We have seen that two distant spheres push each other with forces $\pi a^2 b^2 \mathrm{R}/\mathrm{U}\, d^2$ and $\pi a^2 b^2 \mathrm{R}'/\mathrm{U}\, d^2$, and that these, though opposite, are not equal unless $\mathrm{R} = \mathrm{R}'$.

It would be easy to imagine cases in which the forces were not even opposite or in the same directions. At first sight, then, it would appear that we have two bodies acting upon each other with unequal forces, but of course this statement is inexact. The bodies do not act upon each other at all; each sends out a stream of momentum into the medium surrounding it. Some of this momentum is ultimately intercepted by the other, and in its passage the momentum belongs neither to one body nor to the other. If we assume that the momentum is conserved, and of course everything in the methods of this paper depends on that assumption, the action on one of the bodies is equal and opposite to the reaction on the light-bearing medium contiguous to it. There is no failure of the law of action and reaction, but an extension of our idea of matter to include the medium. There should be no difficulty in this extension; indeed, we have made it long ago in endowing the medium with energy-carrying properties. Whether the momentum in the medium is in the form of mass m moving with velocity v in the direction of propogation is perhaps open to doubt. We may, perhaps, have different forms of momentum just as we may have different forms of energy, and possibly we ought not to separate the momentum in radiation into the factors m and v, but keep it for the present as one quantity M.

An interesting example of inequality of the radiation forces on two mutually radiating bodies is afforded by two equal spheres, for which, at a given temperature, the radiation push F balances the gravitation pull P. Raise one in temperature so that the push on the other becomes F′. Lower the other so that the push on the first becomes F″, but adjust so that

$$F' + F'' = 2F = 2P,$$

then

$$P - F'' = F' - P.$$

There will then be equal accelerations of the two in the same, *not* in opposite directions, and a chase will begin in the line joining the centres, the hotter chasing the colder. If the two temperatures could be maintained, the velocity would go on increasing; but the increase would not be indefinitely great, inasmuch as a Doppler effect would come into play. Each sphere moving forward would crowd up against the radiation it emitted in front, and open out from the radiation it emitted backwards. This would increase the front and decrease the back pressure, and ultimately the excess of front pressure would balance the accelerating force due to mutual radiation.

Let us examine the effect of motion of a radiating surface on the pressure of its radiation against it.

Application of Doppler's *Principle to the Radiation Pressure against a Moving Surface.*

If a unit area A, fig. 4, is moving with velocity u in any direction AB, making angle ψ with its normal AN, the effect on the energy density in the stream of radiation issuing in any direction AP is two-fold. If the motion is such as to shorten AP, the waves and their energy are crowded up into less space, and if such as to lengthen AP, they are opened out. At the same time, in the one case A is doing work against the radiation pressure and in the other is having work done on it. We shall assume, as in the thermodynamic theory of radiation, that this work adds to or subtracts from the energy of radiation. Both effects (1) the crowding, and (2) the work done, or the reverse of each, combine to alter the energy and therefore the radiation pressure. We have no data by which we can determine whether the

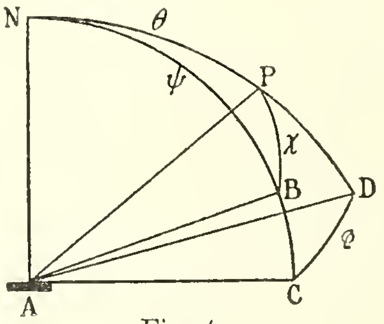

Fig. 4.

motion alters the rate at which the surface is emitting radiation, but it appears worth while to trace consequences on the assumption that the radiation goes on as if the surface were at rest,* but that it is crowded up into less space or spread over more, and that we can superpose on this the energy given out to, or taken from, the stream by the work done by or on the moving surface by the radiation pressure. This work can evidently be calculated to the first order of approximation by supposing the pressure equal to its value when the surface is at rest.

Let us draw from A as centre a sphere of radius U, equal to the velocity of radiation. The energy which, in a system at rest, would be radiated into a cone with A as vertex, length U, and solid angle $d\omega$, in the direction AP making χ with the direction of motion AB, will now be crowded up into a cone of length $\mathrm{U} - u\cos\chi$, since $u\cos\chi$ is the velocity of A in the direction AP. We shall suppose that u/U is very small. Hence the energy density in the cone is increased in the ratio $\mathrm{U} + u\cos\chi : \mathrm{U}$ or by the factor $1 + u\cos\chi/\mathrm{U}$.

Considering now the effect of the work done, the force on A due to the stream in $d\omega$ is $\mathrm{N}\cos\theta\, d\omega/\mathrm{U}$, and the work done in one second is $(\mathrm{N}\cos\theta\, d\omega/\mathrm{U}) \times u\cos\chi$.

When A is at rest the energy in this cone is

$$\mathrm{N}\cos\theta\, d\omega.$$

When A is moving it is increased to

$$\mathrm{N}\cos\theta\, d\omega + \frac{\mathrm{N}\cos\theta\, d\omega}{\mathrm{U}}\, u\cos\chi,$$

that is

$$\mathrm{N}\cos\theta\, d\omega\left(1 + \frac{u\cos\chi}{\mathrm{U}}\right).$$

Thus the effect of the work done is equal to that of the crowding and the energy density on the whole is increased in the ratio

$$1 + \frac{2u\cos\chi}{\mathrm{U}} : 1.$$

The pressure is increased in the ratio of the energy density. Then the force on A due to the radiation through $d\omega$ is increased from

$$\frac{\mathrm{N}\cos\theta\, d\omega}{\mathrm{U}} \quad \text{to} \quad \frac{\mathrm{N}\cos\theta\, d\omega}{\mathrm{U}}\left(1 + \frac{2u\cos\chi}{\mathrm{U}}\right).$$

---

* *Added August* 20, 1903.—Since the above was written Professor LARMOR has pointed out to me that the results obtained in the text from this assumption, along with the hypothesis of crowding of the radiation and its increase by an amount equivalent to the work of the radiation pressure, can be justified by an argument based on the following considerations. A perfect reflector moving with uniform speed in an enclosure, itself also moving at that speed, and so in a steady state, must send back as much radiation of every kind as a full radiator in its place. Now the electrodynamics of perfect reflexion are known; hence the effect of motion of a full radiator on the amount of its radiation can be determined. The result is equivalent to the statement that the amplitudes of the excursions of the optical vibrators are the same at the same temperature whether the source to which they belong is moving or not.

If we resolve this along the normal to the surface A and integrate over the hemisphere we obtain the total normal pressure. As we only want to know the change in pressure P we may neglect the first term which gives the pressure on A at rest, and we have

$$\mathrm{P} = \int \frac{\mathrm{N}\cos^2\theta}{\mathrm{U}} \cdot \frac{2u\cos\chi}{\mathrm{U}}\,d\omega.$$

If ϕ is the angle between the normal planes through B and P we have

$$\cos\chi = \cos\theta\cos\phi + \sin\theta\sin\phi\cos\phi.$$

Putting $d\omega = \sin\theta\,d\theta\,d\phi$,

$$\begin{aligned}\mathrm{P} &= \int_0^{\frac{\pi}{2}}\int_0^{2\pi} \frac{2u\mathrm{N}}{\mathrm{U}^2}\cos^2\theta\sin\theta\,(\cos\theta\cos\psi + 2\theta\sin\psi\cos\phi)\,d\theta\,d\phi \\ &= \frac{\pi\mathrm{N}u\cos\psi}{\mathrm{U}^2} \qquad = \frac{\mathrm{R}u\cos\psi}{\mathrm{U}^2}.\end{aligned}$$

The change in the tangential stress is evidently in the direction AC, that of the component of u in the plane of A.

We may therefore resolve each element of tangential stress in the direction AC. Omitting the first term again, since in this case it disappears on integration, the element due to $d\omega$ in the direction AP will contribute

$$\frac{\mathrm{N}\cos\theta\sin\theta\cos\phi}{\mathrm{U}} \cdot \frac{2u\cos\chi}{\mathrm{U}}\,d\omega,$$

and integrating over the hemisphere we have

$$\begin{aligned}\mathrm{T} &= \int_0^{\frac{\pi}{2}}\int_0^{2\pi} \frac{2u\mathrm{N}}{\mathrm{U}^2}\cos\theta\sin^2\theta\cos\phi\,(\cos\theta\cos\psi + \sin\theta\sin\psi\cos\phi)\,d\theta\,d\phi \\ &= \frac{\pi\mathrm{N}u\sin\psi}{2\mathrm{U}^2} \qquad = \frac{\mathrm{R}u\sin\psi}{2\mathrm{U}^2}.\end{aligned}$$

Force on a Sphere moving with Velocity "u" in a Given Direction.

If a sphere, radius a, is moving with velocity u, we may from symmetry resolve the forces on each element in the direction of motion. The resolutes will be $\mathrm{P}\cos\psi$ and $\mathrm{T}\sin\psi$. Evidently it is sufficient to integrate over the front hemisphere and then double the result. We have the

$$\begin{aligned}\text{Retarding Force} &= 2\int_0^{\frac{\pi}{2}}\left(\frac{\mathrm{R}u\cos^2\psi}{\mathrm{U}^2} + \frac{\mathrm{R}u\sin^2\psi}{2\mathrm{U}^2}\right)2\pi a^2\sin\psi\,d\psi \\ &= \tfrac{8}{3}\,\frac{\mathrm{R}u}{\mathrm{U}^2}\cdot\pi a^2.\end{aligned}$$

It is noteworthy that one half of this is due to the normal, the other half to the tangential stresses.

If the sphere has density ρ the acceleration is obtained by dividing by $\frac{4}{3}\pi a^3\rho$, then

$$du/dt = -2\mathrm{R}u/\mathrm{U}^2\rho a.$$

Effect on Rotation.

If the sphere radius a is rotating with angular velocity ω, then any element of the surface λ from the equator is moving with linear velocity at $\omega \cos \lambda$ in its own plane. This does not affect the normal pressure, but it introduces a tangential stress opposing the motion

$$\mathrm{R}u/2\mathrm{U}^2 = \mathrm{R}a\omega \cos \lambda/2\mathrm{U}^2.$$

Taking moments round the axes and integrating over the sphere, we obtain a couple

$$\tfrac{4}{3}\pi a^3 \,.\, \tfrac{2}{5}\, a^2 \frac{d\omega}{dt} = \frac{\mathrm{R}a\omega}{2\mathrm{U}^2}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} 2\pi a^3 \cos^3 \lambda \, d\lambda,$$

whence

$$d\omega/dt = -\tfrac{5}{2}\,\mathrm{R}\omega/2\mathrm{U}^2\rho a.$$

The rate of diminution of ω is therefore of the same order as that of u.

To obtain an idea of the magnitude of the retardation of a moving sphere, let us suppose that one is moving through a stationary medium. Let its radius be $a = 1$ centim., its density $\rho = 5{\cdot}5$, its temperature 300° A.

Then

$$\frac{1}{u}\frac{du}{dt} = -\frac{2 \times 5{\cdot}32 \times 10^{-5} \times 300^4}{9 \times 10^{20} \times 5{\cdot}5}$$
$$= 1{\cdot}75 \times 10^{-16}.$$

This will begin to affect the velocity by the order of 1 in 10,000 in, say, 10^{12} seconds, or taking the year as $3{\cdot}15 \times 10^7$ seconds, in about 30,000 years.

The effect is inversely as the radius, so that a dust particle 0·001 centim. radius will be equally affected in 30 years.

The effect is as the fourth power of the temperature, so that with rising temperature it becomes rapidly more serious.

Equation to the Orbit of a Small Spherical Absorbing Particle Moving in a Stationary Medium Round the Sun.

It is evident from the above result, that the effect of motion on radiation pressure may be very considerable in the case of a small absorbing particle moving round the sun.

We shall take the particle as spherical, of radius a and distance r from the sun. We shall suppose the radius so small that the particle is of one temperature throughout, the temperature due to the solar radiation which it receives, but that it is still so large as to be attracted much more than it is repelled by the sun. Both attraction and repulsion are inversely as the square of the distance, so that we shall have a central force which we may put as producing acceleration A/r^2, where A is constant.

We know that at the distance of the earth, putting $r = b$, $A/b^2 = 0{\cdot}59$ centim./sec.^{2}, say 0·6 centim./sec.^{2} Then $A = 0{\cdot}6b^2$. The force acting against the motion produces retardation $- 2Ru/U^2\rho a$.

If S is the solar constant at the distance b, its value at distance r is

$$Sb^2/r^2.$$

Putting

$$4\pi a^2 R = \pi a^2\, Sb^2/r^2$$

$$R = (S/4)\,(b^2/r^2),$$

then the acceleration in the line of motion is

$$- \frac{Sb^2}{2U^2\rho a} \cdot \frac{u}{r^2} = - \frac{T\dot{s}}{r^2},$$

where $T = Sb^2/2U^2\rho a$, and $\dot{s}$ is now written for the velocity u.

The accelerations along and perpendicular to the radius vector give the equations

$$\ddot{r} - r\dot{\theta}^2 = - \frac{A}{r^2} - \frac{T\dot{s}}{r^2}\frac{dr}{ds} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta}) = - \frac{T\dot{s}}{r^2}\frac{rd\theta}{ds} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

From (2) we get

$$\frac{d}{dt}(r^2\dot{\theta}) = - \frac{Td\theta}{dt},$$

whence

$$r^2\dot{\theta} = C - T\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

where C is the constant of integration.

If θ is 0 when $t = 0$, then C is the initial value of $r^2\dot{\theta}$. Further, as θ increases $r^2\dot{\theta}$ decreases and is 0 when $\theta = C/T$. This gives a limit to the angle described.

Equation (1) may be written

$$\ddot{r} - r\dot{\theta}^2 = - A/r^2 - T\dot{r}/r^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Putting u for r^{-1}

$$\dot{r} = \frac{dr}{d\theta}\dot{\theta} = - \frac{1}{u^2}\frac{du}{d\theta}\dot{\theta} = - (C - T\theta)\frac{du}{d\theta} \text{ from (3),}$$

$$\ddot{r} = T\dot{\theta}\frac{du}{d\theta} - (C - T\theta)\frac{d^2u}{d\theta^2}\dot{\theta}$$

$$= T(C - T\theta)u^2\frac{du}{d\theta} - (C - T\theta)^2 u^2\frac{d^2u}{d\theta^2} \text{ from (3)}$$

Substituting in (4)

$$\frac{d^2u}{d\theta^2} + u = \frac{A}{(C - T\theta)^2}.$$

This can probably only be integrated by approximation. We can see the effect on the motion at the beginning by putting

$$\frac{d^2u}{d\theta^2} + u = \frac{A}{C^2}\left(1 + \frac{2T}{C}\,\theta\right),$$

since T/C is small if we begin at the distance of the earth and with a particle having the velocity of the earth.

An integral of this is

$$u = \frac{A}{C^2}\left(1 + \frac{2T}{C}\,\theta\right).$$

The complementary function will be periodic and may be omitted. To the order of approximation adopted

$$r = \frac{C^2}{A}\left(1 - \frac{2T}{C}\,\theta\right) \qquad \text{and} \qquad \dot{r} = -\frac{2CT}{A}\,\dot{\theta}.$$

Then initially

$$\dot{r}/r = -(2T/C)\,\dot{\theta}.$$

In applying these results, we may note that $T = Sb^2/2U^2\rho a$ is constant for all distances, and that b, the earth's distance, is 493 U. Inserting the value of the solar constant, $0{\cdot}175 \times 10^7$, and taking $\rho = 5{\cdot}5$, we get

$$T = 3{\cdot}9 \times 10^{10}\,.\,a^{-1}.$$

C will depend on the initial conditions. Assuming that the body considered is initially moving in a circle, then, at the beginning

$$r\dot{\theta}^2 = \frac{A}{r^2} \quad \text{or} \quad \dot{\theta} = \sqrt{\frac{A}{r^3}} = \sqrt{\frac{0{\cdot}6b^2}{r^3}},$$

since at $r = b$ the acceleration to the centre is $0{\cdot}6$.

Then

$$C = r^2\theta = \sqrt{0{\cdot}6b^2r}.$$

Substituting these values in $\dot{r}/r$ we have

$$\frac{\dot{r}}{r} = -\frac{7{\cdot}8 \times 10^{10}}{r^2a}.$$

This gives only the initial value of $\frac{\dot{r}}{r}$ and cannot be taken to hold for a time which will make $T^2\theta^2/C^2$ appreciable. But by (3) we see that $r = 0$ if $\theta = C/T$, so that

$C/2\pi T$ is a superior limit to the number of revolutions, even if we suppose the way clear right up to the centre.

Putting the numerical values we get

$$C/2\pi T = 61 r^{\frac{1}{2}} a.$$

Suppose, for example, that $r = b = 493 \times 3 \times 10^{10}$; $a = 1$, then

$$\dot{r}/r = -\,3{\cdot}5 \times 10^{16}.$$

If we multiply by $3{\cdot}15 \times 10^7$, the seconds in a year, $(\dot{r}/r) \times 3{\cdot}15 \times 10^7 = 1{\cdot}1 \times 10^{-8}$.

This implies that a sphere 1 centim. radius and density 5·5, starting with the velocity of the earth, and at its distance from the sun, will move inwards $\frac{1}{10{,}000}$ of its distance in about 10,000 years. It cannot in all make so many as $61 \times b^{\frac{1}{2}} = 2{\cdot}35 \times 10^8$ revolutions.

If we put $a = 0{\cdot}001$ centim., since the effects are inversely as a, then its distance will decrease by about 1 in 10,000 in 10 years, and it cannot make in all so many as $2{\cdot}35 \times 10^5$ revolutions.

If instead of starting from the distance of the earth, the particle starts from, say, 0·1 the distance, the effect in the radius is 100 times as great and the number of revolutions is $\sqrt{10}$ times less. Then with radius 1 centim. the distance decreases by $\frac{1}{10{,}000}$ in 100 years, and there are not so many as 80,000 revolutions, while with radius 0·001 centim. the distance decreases by $\frac{1}{10{,}000}$ in 0·1 year, and there are not so many as 80 revolutions.

Small particles, therefore, even of the order of 1 centim. radius, would be drawn into the sun, even from the distance of the earth, in times not large compared with geological times, and dust particles if large enough to absorb solar radiation would be swept in in a time almost comparable with historical times. Near the sun the effects are vastly greater. The application to meteoric dust in the system is obvious.

There should be a similar effect with dust and small particles circulating round the earth. If, for example, any of the Krakatoa dust was blown out so far beyond the appreciable atmosphere, and was given such motion that the particles became satellites to the earth, at no long time the dust will return. A ring of dust particles moving round a planet and receiving heat either from the sun or from the planet will tend to draw in to the planet.

[*Note added October* 31.—Since the foregoing paper was printed I have re-examined the theory of the pressure on a fully radiating surface when in motion, and have come to the conclusion that the change in pressure due to the motion is only half as great as that obtained on p. 545. In that investigation the pressure was assumed to be equal to the energy density, whether the surface was at rest or in motion, whereas it appears, if the following mode of treatment is correct, that the pressure on a radiating surface moving forward is only $1 - \frac{u}{U}$ of the energy density of the radiation emitted.

Let us suppose that a surface A, a full radiator, is moving with velocity u towards a full absorber B, which, with the surroundings, we will suppose at 0° A. Consider for simplicity a parallel pencil issuing normal from A with velocity U towards B. Let the energy density in the stream from A be E when A is at rest, and E′ when it is moving. Let the pressure on A be $p = E$ when it is at rest, and p' when it is moving. When moving, A is emitting a stream of momentum p' per second and this momentum ultimately falls on B. Let A start radiating and moving at the same instant; let it move a distance d towards B, and then let it stop radiating and moving. It emits momentum p' per second for a time d/u and therefore emits total momentum $p'd/u$. Since B is at rest, the pressure on it, the momentum which it receives per second, is E′. But since A is following up the stream sent out, B does not receive through a period as long as d/u, but for a time less by d/U. If we assume that the total momentum received by B is equal to the total sent out by A, we have

$$p'd/u = E'(d/u - d/U),$$

or

$$p' = E'(1 - u/U).$$

To find E′ in terms of E we must make some assumption as to the effect of the motion on the radiation emitted. In the paper I have assumed that the emitting surface converts the same amount of its internal energy per second into radiant energy as when it is at rest, but that $p'u$ of the energy of motion of the radiating mass is also converted into radiant energy. Since the radiation emitted in one second is contained in length $U - u$, we have

$$E'(U - u) = EU + p'u = EU + E'\left(\frac{U-u}{U}\right)u,$$

whence

$$E' = E\frac{U^2}{(U-u)^2} = E(1 + 2u/U).$$

The same result is obtained if we assume that the amplitude of the emitted waves is the same whether the surface is moving or not, and that the energy density is inversely as the square of the wave-length for given amplitude.

We have, therefore, if the above application of the equality of action and reaction is justified,

$$p' = E'\left(1 - \frac{u}{U}\right) = E\frac{U}{U-u} = p\left(1 + \frac{u}{U}\right).$$

In a similar way we can find the effect of motion of an absorber on the pressure against it due to the incident radiation.

Let a stream of energy density E be incident on a fully absorbing surface moving towards the source with velocity u. Let the surface be at 0°A, so as to obtain the effect of the incident radiation only. When the surface is at rest, we may regard the stream as bringing up momentum E per second, or as containing momentum ot density E/U brought up with velocity U to it. If the surface is moving towards the source, it takes up in one second the momentum in length $\mathrm{U} + u$, or receives $\frac{\mathrm{E}}{\mathrm{U}}(\mathrm{U} + u)$, and the pressure on it is $p' = \mathrm{E}\left(1 + \frac{u}{\mathrm{U}}\right) = p\left(1 + \frac{u}{\mathrm{U}}\right)$.

It is easy to show that when a perfect reflector is moving, the pressure upon it is altered from p to $p\left(1 + \frac{2u}{\mathrm{U}}\right)$.

In the paper, the case of a full radiator in an enclosure at zero has alone been considered, so that the correcting factor is $1 + \frac{u}{\mathrm{U}}$ or $1 + \frac{u \cos \chi}{\mathrm{U}}$ when the motion is at χ to the line of radiation. Hence the forces obtained in the paper when the factor was $1 + \frac{2u}{\mathrm{U}}$ are all double those obtained with the factor now given. The process of drawing in small particles to the sun is correspondingly lengthened out.

It is, perhaps, worth noting that the motion of a body round the sun produces a small aberration effect. If the body is a sphere, the sunlight does not fall on the hemisphere directly under the sun, but on one turned round through an angle u/U. The pressure of the radiation, though still straight from the sun, does not act through the centre but through a point $\frac{u^2}{2\mathrm{U}^2}$ × radius of sphere in front of the centre. Thus, in the case of the earth, it will tend to stop the rotation. But the effect is so minute that if present conditions as to distance and radiation were maintained, it would take something of the order of 10^{19} years to stop the whole of the rotation.]

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