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Series A, VOL. 212, pp. 1–32.

BAKERIAN LECTURE.

ON THE VARIATION OF THE SPECIFIC HEAT OF WATER, WITH EXPERIMENTS BY A NEW METHOD.

BY

H. L. CALLENDAR, M.A., LL.D., F.R.S.,
PROFESSOR OF PHYSICS AT THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.

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PHILOSOPHICAL TRANSACTIONS.

I. BAKERIAN LECTURE.—*On the Variation of the Specific Heat of Water, with Experiments by a New Method.*

By H. L. CALLENDAR, *M.A., LL.D., F.R.S., Professor of Physics at the Imperial College of Science and Technology, London, S.W.*

Received December 5, 1911,—Received in extended form as Bakerian Lecture, February 6, 1912,—
Lecture delivered February 22, 1912.

THE question of the mode of variation of the specific heat of water is so fundamental in calorimetry, there are so few experiments between 50° C. and 100° C., and the results in this region obtained by different observers are so discordant, that no apology is needed for the publication of new experimental work tending to throw light on the subject. But in order to elucidate the points at issue, it will first be necessary to review briefly the experimental evidence already in existence, and to exhibit the results graphically as an indication of the order of accuracy of the various methods.

A minor difficulty in comparing the results of different observers arises from the fact that they are expressed in terms of different thermometric scales and units, and that the reduction to a uniform standard of comparison cannot always be effected with certainty. Throughout the present paper, for reasons which have been fully explained elsewhere, all heat quantities are expressed in terms of the specific heat of water at 20° C. taken as unity. The scale of temperature, t, adopted is that deduced from the temperature pt by platinum resistance thermometer by means of the difference formula,*

$$t - pt = 1\cdot50\, t\,(t-100) \times 10^{-4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

---

* Many computers have corrected this formula by assuming values from 444°·8 C. to 445°·0 C., or even 445°·5 C., for the sulphur boiling-point on the perfect-gas scale. But the recent experiments of HOLBORN and HENNING ('Ann. Phys.,' 35, pp. 761–794, 1911) with a quartz-glass bulb give the value 444°·51 C. on the perfect-gas scale. They assume the linear expansion coefficient of quartz-glass constant and equal to $0\cdot54 \times 10^{-6}$, which makes the cubical coefficient $1\cdot62 \times 10^{-6}$. But it appears that the linear coefficient vanishes at − 100° C., and is likely to be smaller between 0° C. and 100° C. than at higher temperatures. In any case it is unsatisfactory to deduce the cubical coefficient from the linear, because the latter is difficult to measure accurately, and may well be different in different directions for a drawn bulb, especially as quartz-glass cannot be annealed owing to its rapid devitrification at temperatures in the neighbourhood of 1,000° C. Direct measurements of the cubical coefficient of a quartz-glass bulb, by E. J. HARLOW ('Proc. Phys. Soc.,' Lond., Nov., 1911), employing the method of the mercury weight

which was proposed at the British Association meeting in 1899 as an easily reproducible scale of reference for the experimentalist. The correction of the practical scale, as above defined, to the absolute scale is so small and uncertain, and has so often been applied incorrectly, that its application appears more likely to lead to confusion than to improved agreement in experimental work.

The specific heat of water at 15° C. has often been adopted as the standard. It exceeds that at 20° C. by little more than 1 in 1,000. The reduction from 15° C. to 20° C. can be effected with comparative certainty, but does not materially affect the question of the variation of the specific heat, since all the values are altered nearly in the same proportion, and few results are accurate to 1 in 1,000.

REGNAULT'S *Experiments*, 100° C. to 200° C.

REGNAULT operated by mixing 10 litres of water from a boiler at various temperatures between 107° C. and 187° C. with 100 litres of water in a calorimeter at the atmospheric temperature. His observations gave directly the mean specific heat* of water from the temperature and pressure of the boiler to the final temperature of the calorimeter at atmospheric pressure in terms of the mean specific heat between the initial and final temperatures of the calorimeter. The results did not give any direct evidence with regard to the variation of specific heat between 0° C. and 100° C., but were fairly consistent over the range 100° C. to 200° C. with the assumption of his well-known parabolic formula

$$s_0^t = 1 + 0{\cdot}002\,(t/100) + 0{\cdot}003\,(t/100)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

for the mean specific heat between 0° C. and t° C.

ROWLAND'S discovery, in 1879, that the specific heat of water diminished by about 1 per cent. between 0° C. and 30° C., showed that REGNAULT'S formula could not possibly be correct at low temperatures, and necessitated a recalculation of his

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thermometer, and assuming the absolute expansion of mercury from the observations of CALLENDAR and MOSS ('Phil. Trans. Roy. Soc.,' A, vol. 211, pp. 1-32) give a value $1 \cdot 00 \times 10^{-6}$ between 0° C. and 100° C., increasing to $1 \cdot 50 \times 10^{-6}$ between 0° C. and 184° C. If this should be correct, the result of HOLBORN and HENNING would require to be raised by 0°·10 C., giving 444°·61 C. on the absolute scale. It is hoped that experiments now in progress by N. EUMORFOPOULOS by the constant-pressure method, with a quartz-glass thermometer of the Callendar type, will throw further light on this important point. It would appear in any case that formula (1) gives a better approximation to the absolute scale of temperature than has previously been supposed. It has been possible for the last twenty years to obtain platinum for thermometric purposes of the same unvarying degree of purity, giving a temperature coefficient approximating to 0·00390, and a practically constant difference-coefficient. It seems, therefore, preferable to eliminate errors of observation of the sulphur boiling-point, and differences of opinion as to its absolute value, by assuming a standard value $1 \cdot 50 \times 10^{-4}$ for the difference-coefficient in the definition of the practical scale.

[*] More accurately, the change of total heat $E + pv$.

experimental results. This was undertaken by J. M. GRAY ('Proc. Inst. Mech. Eng.,' 1899) who found that the data given by REGNAULT did not in all cases agree with his calculated results, the discrepancies occasionally reaching 2 or 3 per cent. It appeared, from measurements of the original apparatus, that in all these cases the recorded quantity of water exceeded the total capacity of the calorimeter. GRAY concluded that REGNAULT'S calculations were probably correct, and that the discrepancies arose from deficient information or erroneous entries in the data columns. Adopting this assumption, it is possible to recalculate REGNAULT'S observations, allowing for the known variation of the specific heat from 0° C. to 30° C., and to express his results for the mean specific heat from 0° C. to t° C. in terms of the specific heat at 20° C. The separate observations, reduced in this manner, are represented by the small crosses in fig. 1. The large crosses surrounded by circles indicate the means of each group. The general effect of this reduction is to bring the results on the average about 2 parts in 1,000 below REGNAULT'S original formula. The correction is fairly certain, and is less than the discrepancies between the observations in any one group.

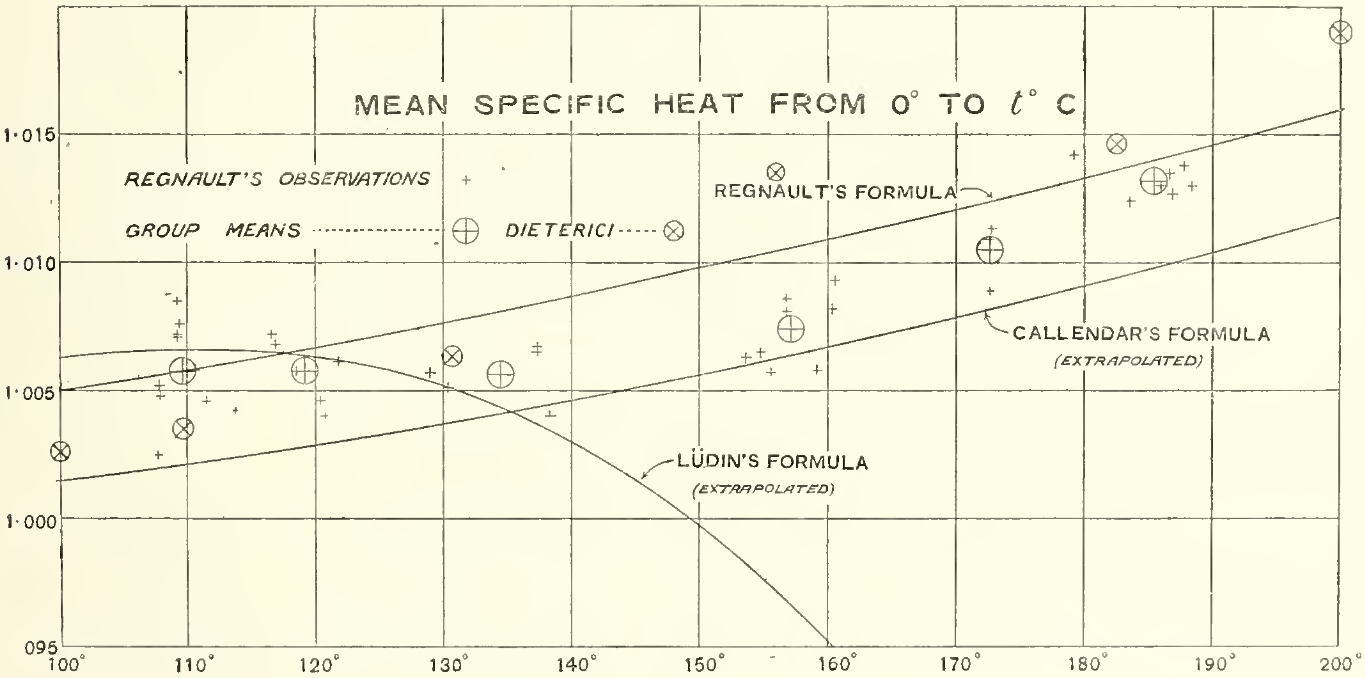

Fig. 1.

The probable errors of REGNAULT'S thermometers remain to be considered. These have not been included in the reduction, as being much less certain, because the original thermometers cannot now be recovered and tested. It appears from recent observations on the absolute expansion of mercury, and on the pressures of steam between 100° C. and 200° C. that REGNAULT'S temperature scale over this range did not differ materially from that given by formula (1). It is certain, however, that REGNAULT was ignorant of the phenomenon of the temporary depression of zero of a mercury thermometer when heated, and that he was unable to detect any systematic difference between the mercury and gas scales of temperature over the range 0° C. to 100° C., both of which facts would appreciably affect the reduction of the readings of the thermometers employed for observing the rise of temperature in the calorimeter. The correction for these two sources of error combined might *reduce* REGNAULT'S values by 5 or 6 parts in 1,000 if the thermometers he employed were of French "*cristal*" glass. In any case the reduction could hardly be less than 2 or 3 parts in 1,000. This would bring the observations into fairly good agreement with my extrapolated formula, indicated by the lower curve in fig. 1, but the corrections involved are so hypothetical that no great stress can be laid on them. The only satisfactory solution is to repeat the observations, for which I have already made such preparations as my scant intervals of leisure will permit. In the meantime we may regard REGNAULT'S observations as giving, with some degree of probability, *the rate of increase* of the mean specific heat between 100° C. and 200° C., although the absolute values given by his formula probably require reduction by about 0·4 per cent. It should be observed that, even if all the corrections could be applied with certainty, the order of accuracy of his final results could not be expected to exceed 1 or 2 parts in 1,000, because the calorimetric thermometers were read to 0°·01 C. only on a rise of temperature of 8° C. to 15° C., and the individual observations in each group show corresponding discrepancies from the means. REGNAULT himself did not claim any higher order of accuracy, and endeavoured to indicate this by the values of the coefficients given in his formula.

Range 0° C. *to* 100° C. (LÜDIN).

Many of the investigations by able experimentalists extending over the range 0° C. to 100° C. have given rates of variation exceeding 10 per cent. per 100° C., which were doubtless due to defective experimental methods and insufficient appreciation of the real difficulties of the problem. Such results are of no value except as an indication that the problem is not quite so simple as it appears at first sight. The first investigation in which sufficient attention was given to the well-known difficulties of mercurial thermometry, was that of E. LÜDIN ('Die Abhängigkeit der specifischen Wärme des Wassers von der Temperatur,' Inaug. Diss. Zurich, 1895), carried out by the method of mixtures under the direction of Prof. PERNET. His observations gave directly the mean specific heat over eight different ranges of temperature above 18° C., and two different ranges below 11° C., in terms of the mean specific heat over the range 11° C. to 18° C. The variation of the actual specific heat was deduced by assuming a formula of the type

$$s = 1 + at + bt^2 + ct^3, \qquad (3)$$

and calculating the values of the coefficients by the method of least squares to agree with the observed ratios of the mean specific heats over the various ranges. This method is somewhat indirect, and makes the result depend to some extent on the particular type of empirical formula chosen. The formula given by LÜDIN for the actual specific heat s was as follows[*] :—

$$\begin{array}{l} s = 1 - 0{\cdot}00076668t + 0{\cdot}000019598t^2 - 0{\cdot}0000001162t^3 \quad . \ . \ . \ . \ . \quad (4) \\ \qquad \pm 0{\cdot}0000025 \quad \pm 0{\cdot}0000040 \quad \pm 0{\cdot}000000030. \end{array}$$

The probable errors of the several coefficients, as calculated by LÜDIN, are given in the second line below the coefficients to which they apply. It would appear that this type of formula is unsuitable for representing the variation of specific heat of water from 0° C. to 100° C., because the coefficients come out relatively large and of opposite signs. For instance, the value of the specific heat at 100° C. is made up as follows, according to LÜDIN's formula :—

$$\begin{array}{rll} s = & 1 - 0{\cdot}076668 & \pm 0{\cdot}00025 \\ & \quad + 0{\cdot}19598 & \pm 0{\cdot}040 \\ & \quad - 0{\cdot}1162 & \pm 0{\cdot}030 \\ \hline \text{Sum} = & 1 + 0{\cdot}0031 & \pm\ ? \\ \hline\hline \end{array}$$

The small difference 0·0031, representing the required variation of the specific heat, is less than 1 per cent. of the sum 0·388848 (taken without regard to sign) of the terms by which it is represented, and is only a tenth of the probable error of either of the last two terms. It is obvious *à priori* that a measurement of the mean specific heat between 18° C. and 89° C., combined with a measurement between 18° C. and

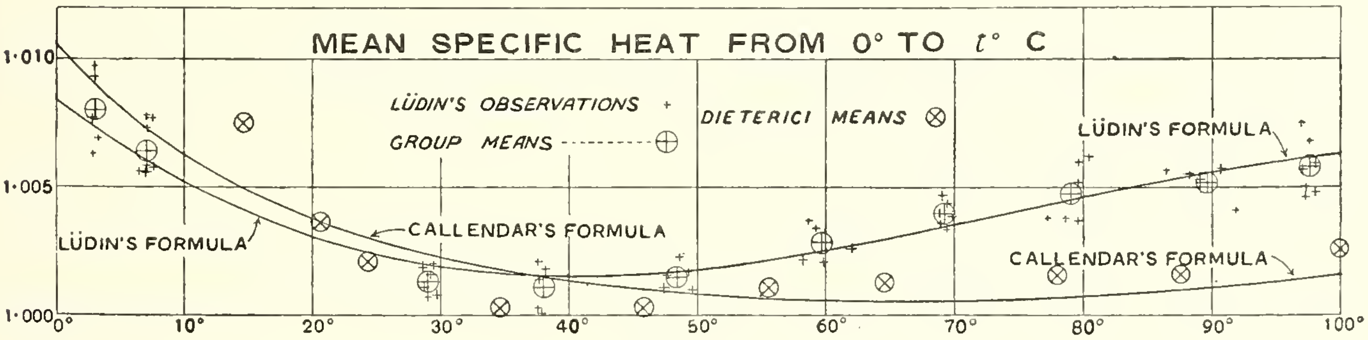

Fig. 2.

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[*] LÜDIN's results have since been corrected by reference to a comparison made by THIESEN, SCHEEL, and SELL between the French "*Verre Dur*" and the Jena 16^{III} glass thermometers. This reduction is somewhat uncertain, and does not affect his values materially except in the neighbourhood of 0° C. His original formula has been retained for purposes of discussion, because it is more nearly correct between 0° C. and 20° C., and because it was employed by Messrs. BOUSFIELD in their comparisons. There is an obvious misprint in LÜDIN's corrected formula as quoted in the 'Fortschritte der Physik,' 1900, II., p. 304, but the tables appear to be correct. LÜDIN's ratio of the mean specific heat from 0° C. to 100° C. to the specific heat at 20° C. is reduced from 1·0063 to 1·0058. His value for the specific heat at 90° C. is reduced from 1·0136 to 1·0127 in terms of the specific heat at 20° C.

97° C., could not give very certain information with regard to the actual specific heat between 89° C. and 97° C. The observations themselves, giving the ratios of the mean specific heats over different ranges, cannot be represented graphically in relation to the curve of actual specific heat represented by formula (4), which is shown by the dotted line in fig. 3. It is easy, however, to deduce the corresponding formula for the mean specific heat from 0° C. to t° C., shown in fig. 2, in relation to which the observations may be represented by a slight reduction (as in the case of REGNAULT's observations) which does not materially affect their relative errors. The individual observations at each point are shown by the small crosses. The large crosses surrounded by circles represent the means of each group. The full curve, marked LÜDIN's formula, represents the equation

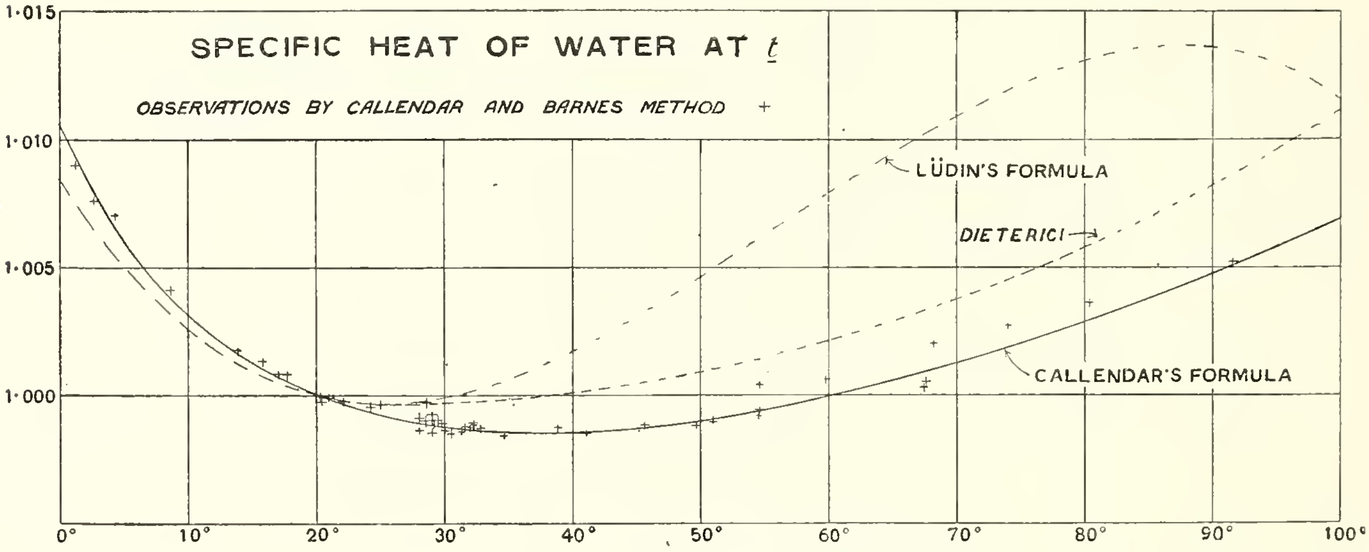

Fig. 3.

$$s_0^t = 1{\cdot}0084 - 0{\cdot}00038656t + 0{\cdot}000006588t^2 - 0{\cdot}00000002929t^3 \quad . \quad . \quad . \quad (5)$$

which gives the mean specific heat from 0° C. to t° C. by LÜDIN's formula in terms of the specific heat at 20° C. taken as unity. The group means are seen to differ by less than 1 in 1,000 from LÜDIN's curve. It must be remembered, however, that the observations in each group were all taken consecutively under the same conditions with the same calorimeter and thermometers, and would give no indication of possible constant errors. Thus in LÜDIN's method of operation it was necessary to vary the quantity of hot water introduced into the calorimeter from 460 gr. at 30° C. to 102 gr. at 90° C., with a corresponding variation in the initial water content of the calorimeter, and in the temperature of the walls above the water level. In spite of the great care taken in reading the thermometers and applying all corrections to 0°·001 C., the results of consecutive observations under the same conditions often differ by 2 or 3 parts in 1,000, especially near the ends of the range. This is probably due to the uncertainty of heat loss or gain during the transference of the hot water to the calorimeter, of which no account could be taken. Such gain or loss would vary, on the whole, systematically with the temperature of the hot water, and would inevitably lead to constant errors.

It will be observed, on reference to fig. 1, that LÜDIN'S formula for the mean specific heat, when extrapolated, gives results agreeing closely with REGNAULT'S observations up to 130° C. But this is really without significance, because REGNAULT'S results, as plotted, are not corrected for the probable errors of his calorimetric thermometers, and would certainly require to be further reduced. LÜDIN'S curve, if extrapolated to 200° C., would give results about 10 per cent. too low, and is obviously of a type which cannot be trusted for extrapolation. It is almost inconceivable on any theoretical grounds that the specific heat of water, after reaching a maximum at 87° C., should then diminish and increase again. LÜDIN'S method, as already explained, could not be trusted to give certain results with regard to the variation of the specific heat near the ends of his range. The experimental evidence for the drop in the curve near 100° C. is very weak, and, such as it is, may be most readily explained by a slight loss of heat due to evaporation of the nearly boiling water on its way to the calorimeter. It would appear almost hopeless to obtain reliable results by the method of mixtures with an *open* calorimeter. REGNAULT'S method, employing a nearly closed calorimeter of large volume, permanently connected to the heater by a tube for introducing the water, appears to be the only satisfactory means of avoiding the uncertainty of heat loss in transference if the ordinary method of mixtures is employed.

Continuous-Electric Method (CALLENDAR *and* BARNES).

The continuous-electric method, in which a steady current of water at any desired temperature is heated through a small range of temperature by a steady electric current, has the great advantage that it gives directly the actual specific heat over a small range at the desired point in place of the mean specific heat over a large range, and appears for this reason peculiarly suited for determining the *variation* of the specific heat. The method has been very fully described and discussed in previous papers (CALLENDAR, 'Phil. Trans.,' A, 1902, vol. 199, pp. 55–148; BARNES, *loc. cit.*, pp. 149–263), but it appears desirable to enumerate briefly its principal features. The form of the calorimeter, being merely a fine-bore tube about half a metre long with enlargements at either end for the thermometers, gives a very small water equivalent and radiating surface, and permits complete enclosure in a hermetically sealed vacuum-jacket, which reduces the external heat-loss to a minimum. The vacuum-jacket is surrounded by a water-jacket maintained at a steady temperature. The water current is brought to the same temperature as the jacket before passing the inflow thermometer. The rise of temperature of the water passing through the tube is obtained by a single reading on a pair of differential platinum thermometers, sensitive to 0°·0001 C., and probably in all cases accurate to 0°·001 C., thus avoiding nearly all the difficulties of mercurial thermometry. The electric heating current passes through a conductor of bare platinum wire, extending throughout the length of the fine-flow tube, and connected at either end to massive terminals of negligible resistance in the form of thick copper tubes enclosing the thermometers. These terminals serve to define accurately the resistance of the heater, and also to equalise the temperature along the length of the bulbs of the thermometers. The fineness of the flow tube renders any insulation of the conductor unnecessary. Sufficient stirring is obtained by causing the water to flow spirally round the thermometer bulbs and along the fine tube, or by subdividing the heating conductor. The heat generated by the friction of the water current in passing through the tube could be accurately measured by observing the difference of pressure between the ends of the tube, but its effect on the results was in all cases less than 1 part in 40,000. The electric current of 4 to 6 amperes was maintained steady by a battery of very large cells (300 ampere rate of discharge) because this permitted an order of accuracy of 1 or 2 parts in 100,000 in the electrical readings and appeared preferable to discontinuous hand regulation. For this and other reasons the potential difference on the heating conductor was not directly balanced against an integral number of Clark cells, but was measured on a carefully calibrated potentiometer, together with the potential difference due to the same current passing through a specially designed standard resistance of platinum-silver maintained at a constant temperature in an oil-bath.

As is usual in calorimetric experiments, the accuracy obtainable was limited chiefly by the determination of the heat-loss, which was deduced from experiments in which the electric and water currents were varied in such a way as to maintain the same rise of temperature. The heat-loss for the same rise of temperature was found to be not quite independent of the flow. It was also found to vary slightly owing to slight changes in the vacuum, when the apparatus was maintained for some time at a high temperature. It was inferred, however, that the uncertainty from all causes combined could not have exceeded 1 in 1,000 even at the limit of the range, and was probably much less at lower temperatures.

The experiments have been criticised chiefly on the ground of the uncertainty of the absolute values of the electrical units ten years ago, but this would not affect the question of the *variation* of the specific heat with temperature, as there was no question of the *constancy* of the standards employed. It is true that it was not at that time possible to secure a direct comparison of the Clark cells with the international standards which have since been established. In default of this I made, with the assistance of Mr. King, an absolute determination of the E.M.F. of the cells at that time in use in the laboratory, by means of an electro-dynamometer specially designed to read to 1 or 2 parts in 100,000. I was confident that the result of this determination, namely, 1·4334 volts for this type of cell at 15° C., would prove accurate to at least 1 in 10,000. This has since been verified independently by Wolff and Waters ('Bull. American Bureau of Standards,' vol. 4, p. 64, 1907), who give the value 1·43330 volts at 15° C., in terms of modern standards, for Clark cells constructed with washed mercurous sulphate according to the specification then adopted.

The idea that the absolute values of the mechanical equivalent deduced from the continuous-electric method were uncertain to the extent of more than 1 in 1,000, and had recently required correction, appears to have arisen from the fact that some of the results were originally expressed in terms of the conventional, or legal, value, 1·4342 volts at 15° C., of the Clark cell, adopted twenty years ago. This value was known at the time to be inaccurate, and was employed merely for the purpose of comparing results with those of other observers who had also assumed the conventional value.

The resistance of the standard platinum-silver coil employed in the current measurements was probably known to 1 in 10,000 in terms of then existing standards, but it has been suggested that some uncertainty existed with regard to the heating effect of the current. The coil was designed with eight wires in parallel, so that its rise of temperature in a well-stirred oil-bath when carrying 8 amperes (4 watts in each wire), should not exceed 1° C., or 1 in 4,000 increase of resistance. The currents actually employed in the specific-heat determinations gave about 2·5 watts in each wire. It is, therefore, unlikely that the increase of resistance could have been greater than 1 in 5,000, even if allowance is made for slight differences between the experimental coil on which the design was based and the actual standard.

The experiments, made by Profs. VIRIAMU JONES and W. E. AYRTON, with the Lorenz apparatus, which I ordered for McGill College in 1895, had shown (CALLENDAR, *loc. cit.*, p. 71) that the Board of Trade Standard Ohm was probably 2 or 3 parts in 10,000 larger than 10^9 C.G.S. Since the absolute values of the Clark cells as well as the platinum-silver resistance were determined with reference to this standard, the absolute values of the mechanical equivalent would require to be raised on this account by 2 or 3 parts in 10,000. Correction for the heating effect of the current would require the results to be lowered to nearly the same extent. Since these corrections were nearly equal and of opposite sign, and since both were so small and uncertain, it did not appear desirable at the time to correct for either.

Formula for the Variation from 0° C. *to* 200° C.

When the preliminary results of the continuous-electric method were first announced at the meeting of the British Association at Dover in 1899, I suggested two simple formulæ to represent the variation empirically, one covering the range of minimum specific heat from 20° C. to 60° C., and the other, a simple modification of REGNAULT'S, fitting the first at 60° C. and representing REGNAULT'S corrected and reduced results up to 200° C. The first formula was subsequently modified by the addition of a small term below 20° C. to represent more accurately the rapid increase of specific heat as the freezing-point was approached. It is for many purposes inconvenient to have to deal with different formula covering limited ranges, however carefully they may have been fitted together. I have, therefore, devoted some attention to devising a single formula of a suitable type to cover the whole range. Of the many possible types of formula which might be devised for the purpose, the following has appeared to me, after exhaustive trials of many types from different points of view, to be the simplest and the most generally convenient :—

$$s = 0{\cdot}98536 + 0{\cdot}504/(t+20) + 0{\cdot}0084\,(t/100) + 0{\cdot}009\,(t/100)^2. \quad . \quad . \quad . \quad (6)$$

This formula was obtained by combining a formula with REGNAULT'S coefficients to represent the variation from 100° C. to 200° C., with a formula containing a reciprocal term to represent the rapid fall in the neighbourhood of 0° C. The value of the constant term 0·98536 is adjusted to make $s = 1$ when $t = 20°$ C., which is the most convenient temperature in practice to use as a standard of reference. The other terms are all small and positive, and can be calculated with sufficient accuracy for all possible purposes by means of a 10-inch slide-rule, which is far from being the case if a formula of the LÜDIN type is employed.

This formula is represented by the full line in fig. 3. The observations of BARNES, represented by the crosses, have been reduced to a unit at 20° C., and corrected for the variation of the temperature-gradient in the flow-tube, as explained in my paper (*loc. cit.*, p. 129). The results are plotted in terms of the temperature scale defined by formula (1), and are not reduced to the hydrogen scale on account of the smallness and uncertainty of this correction, as previously stated. It may be observed that the agreement of the observations with the curve would be slightly improved if the mean of the large group of observations near 30° C. had been taken as the basis of reduction in place of the few observations near 20° C. This would have the effect of depressing all the points by 0·00014, but would not alter the form of the curve. It happens that the absolute value of the specific heat can be most easily determined by the continuous-electric method in the neighbourhood of 30° C., which would naturally be selected as the standard temperature if this method were the only one to be considered. None of the observations deviate from the curve by more than 1 in 1,000, and only seven by more than 1 in 2,000. The agreement is very good considering that the observations were taken with several different calorimeters and thermometers at dates extending over more than a year. Taking account of all the changes of condition which were made in testing the method, it seems hardly likely that the variation of the specific heat given by the formula (6) can be in error by so much as 1 in 1,000 even at 80° C.

0° C. *to* 300° C. (DIETERICI).

The earlier experiments of DIETERICI ('WIED. Ann.,' 33, p. 417, 1888), in which he determined the absolute value of the mean calorie (0° C. to 100° C.) by passing a current of 0·5 ampere to 0·7 ampere, measured with a silver voltameter, through a resistance of 1·71 ohms in a Bunsen ice-calorimeter, gave a result 4·2436 ± 0·0017 joules per gr. ° C., assuming the constant of the calorimeter as 15·44 mgr. of mercury per mean calorie from the mean of the values given by BUNSEN 15·41, SCHULLER and WARTHA 15·44, and VELTEN 15·47. Taking ROWLAND'S values for the mechanical equivalent from 0° C. to 30° C., and assuming a linear increase from 30° C. to 100° C. to fit with his own value for the mean calorie, DIETERICI deduced a table (*loc. cit.*, p. 441) for the variation of the specific heat from 0° C. to 100° C., which has been frequently quoted and employed for reducing observations. According to this table, the mean calorie exceeded that at 20° C. by 1·5 per cent. The specific heat at 90° C. was 3 per cent. greater than the value subsequently found by the continuous-electric method, but appeared to be in fair agreement with older observations.

DIETERICI'S later determinations of the mean calorie ('Ann. Phys.,' 16, p. 593, 1905) by a similar method, in which the current was reduced to 0·05 ampere and the resistance increased to 40 ohms in order to diminish errors due to conduction and generation of heat in the leading wires, gave a result 4·1925 joules per gr. ° C., exceeding the value 4·187 given by the continuous-electric method by only 1·4 in 1,000, which is almost, if not quite, within the possible limits of error of the ice-calorimeter. Accepting DIETERICI'S value of the specific heat at 20° C., namely, 0·9974 in terms of the mean calorie, his value for the mechanical equivalent at 20° C. would be 4·1815, which agrees to 1 in 3,000 with the continuous-electric method. DIETERICI'S value of the calorie at 20° C. has accordingly been taken in place of the mean calorie in reducing his results for comparison with those of other observers. It should be remarked, however, that the rate of heat supply in his experiments with the ice-calorimeter was 300 times smaller than in the continuous-electric method, and that, in order to obtain equally good results with the ice-calorimeter, it would be necessary that the uncertainty of the heat-loss should also be 300 times smaller, the probability of which is open to doubt.

DIETERICI also redetermined the constant of the ice-calorimeter by an improved method, employing sealed tubes of quartz-glass to contain the water at 100° C. The value thus found was 15·491 mgr. per mean calorie, exceeding the value previously employed by 1 in 300. His results by the same method for the mean specific heat from 0° C. to t° C., reduced to his calorie at 20° C. as unit, are indicated by the diagonal crosses in figs. 1 and 2. Between 0° C. and 100° C., his results, as shown in fig. 2, agree to 1 in 1,000 with my formula, except for one observation at 14°·6 C., where, as he admits, an inferior degree of accuracy was to be expected. For temperatures above 35° C. he represents his results for the mean specific heat from 0° C. to t° C. in terms of the mean calorie by the formula

$$s_{0,t} = 0{\cdot}99827 - 0{\cdot}005184\,(t/100) + 0{\cdot}006912\,(t/100)^2$$

which gives a minimum at 35° C., agreeing with his observations. He points out that the corresponding formula for the specific heat at t,

$$s_t = 0{\cdot}99827 - 0{\cdot}010368\,(t/100) + 0{\cdot}020736\,(t/100)^2,$$

being obtained by differentiation, has an inferior degree of accuracy, which he sets at 0·3 per cent. in the neighbourhood of 100° C. The curve marked DIETERICI, in fig. 3, represents this formula reduced to a unit at 20° C. by dividing by the factor 0·9974, representing his value at 20° C. DIETERICI employs this formula for the actual specific heat, s_t, in calculating the values given in his table down to a temperature of 25° C., although it does not strictly apply below 35° C. Below 25° C. his values for the specific heat are calculated in a different way, but agree so closely with my formula that his curve could not be shown separately. This agreement is very satisfactory, but gives rise to a somewhat sharp change of curvature at 25° C., which is repeated at 35° C. in his formula for the mean specific heat, and introduces some uncertainty in the interpretation or application of the tabulated results. Below 35° C. his table of mean specific heat appears to represent his experimental results between 35° C. and 20° C. (neglecting the discordant observation at 14°·6 C.) with an almost linear extrapolation which follows my curve very closely from 20° C. down to 0° C. Values of the actual specific heat calculated from this table show a rapid fall from 1·0075 at 0° C. to 0·9912 at 30° C., and a sudden jump from below 0·9900 up to the value 0·9973 at 35° C. If, on the other hand, his table of actual specific heat is taken as the basis of calculation, the value of the mean specific heat from 0° C. to 40° C. comes out 0·9992 in place of 0·9973, given in his other table. The observations themselves do not afford any valid evidence for the existence of these discontinuities, which might prove very troublesome in the practical application of his tables. A single continuous formula, such as (6), presents many advantages in this respect, especially for representing observations on the mean specific heat, which ought not to show sudden changes of curvature. The deduction of the true specific heat at any temperature from the mean specific heat is most uncertain in any case, and the observations cannot be said to support the minimum at 25° C., shown in DIETERICI'S curve for the actual specific heat. The uncertainty in the reduction of the results from 0° C. to 35° C. must affect the whole form of the curve, and even the apparent discrepancy of 0·4 per cent. at 100° C., shown in fig. 3, does not exceed the limits of possible error in the calculation.

Apart from variations in the fundamental constant (depending possibly on the quality of the ice formed), and uncertainty of the correction for creep of zero, which might give rise to accidental errors, the main source of systematic error in DIETERICI'S method would lie in the correction for the water equivalent of the quartz-glass bulbs, and in loss or gain of heat during transference from the heater to the calorimeter. The water equivalent of each bulb was calculated from its mass by means of a formula for the variation of the specific heat of quartz, which is appropriate if there is no heat-loss in transference. It appears probable, however, that bulbs of different form and thickness would experience different losses in transference. In fact, a small systematic error of this kind is indicated by the observations themselves, and might produce appreciable errors at the higher temperatures.

Below 100° C. the uncertainty would probably not exceed 1 in 1,000, as the thermal capacity of the bulbs employed was only a quarter of that of the contained water. From 130° C. to 220° C. all the observations, except one at 130° C., were made with bulbs having a thermal capacity nearly equal to that of the contained water. In the observations at 100° C., 109° C., and 130° C., where both thick and thin bulbs were employed, the results deduced from the thick bulbs, assuming the same formula for the specific heat of quartz-glass, were systematically higher by 0·12, 0·17, and 0·23 per cent. respectively than those deduced from the thin bulbs. The point shown at 156° C. in fig. 1, which is the lowest depending entirely on observations with the thick bulbs, shows so great an increase, when compared with REGNAULT'S observations, as to suggest a systematic error of this kind. Assuming that the error might amount to 0·1 per cent. in the mean specific heat at 100° C. with the thin bulbs, and that it would probably increase in proportion to the temperature and to the relative thermal capacity of the bulbs, it would amount to 0·8 per cent. at 200° C., which would be more than sufficient to bring the results of DIETERICI into agreement with the most probable reduction of REGNAULT'S observations as indicated by my formula. A similar uncertainty would apply with greater force to the experiments at higher temperatures where the thermal capacity of the quartz-glass bulbs amounted to four times that of the contained water. The heat-loss in transference might have been in part eliminated from the results for water by using *the same bulbs* full and empty at each temperature, but even in this case the accuracy of the results for water would have been reduced to about a fifth with the thickest bulbs.

The large correction for the water equivalent of the bulbs, which could not easily be reduced, is a serious objection to DIETERICI'S method as compared with REGNAULT'S at the higher temperatures. Below 100° C. this source of error is unimportant as compared with evaporation losses incurred in transferring hot water when exposed to evaporation, as in LÜDIN'S method. On this account there would probably be little hesitation in preferring DIETERICI'S results to LÜDIN'S between 0° C. and 100° C., if it were not that, within the last year, Messrs. W. R. and W. E. BOUSFIELD ('Phil. Trans. Roy. Soc.,' A, 1911, vol. 211, pp. 199–251) have succeeded in reproducing LÜDIN'S results with remarkable fidelity by a method of electric heating with a vacuum-jacket calorimeter, which presents many ingenious and novel features. Owing to the uncertainty in the reduction of DIETERICI'S results for the specific heat at 20° C., it might naturally be argued that his curve for the mean specific heat should be fitted to LÜDIN'S at a higher temperature, such as 60° C. or 70° C. This could easily be done by raising all the points representing DIETERICI'S observations in fig. 2 by only 0·25 per cent., in which case they would nearly all agree with LÜDIN'S curve to 1 in 1,000 except those below 30° C., where DIETERICI admits a larger possible error. It would then appear that Messrs. BOUSFIELD, LÜDIN, and DIETERICI were in fair agreement in assigning a much higher value to the mean specific heat from 0° C. to 80° C. than that assigned by the continuous-electric method, and that the error probably lay with the latter. It is usual to take the curves for the actual specific heat in making these comparisons, but these do not represent the observations themselves, except in the case of the continuous-electric method, and little can fairly be deduced from such a comparison (though DIETERICI, LÜDIN, BOUSFIELD, and many others have adopted this method), owing to the great uncertainty involved in deducing the actual from the mean specific heat. There is no similar uncertainty in deducing the mean from the actual specific heat, so that the method adopted in fig. 2 is the more appropriate. Since the evidence for the slow rate of increase of the specific heat between 60° C. and 100° C., in the continuous-electric method, rested chiefly on half-a-dozen observations taken under conditions of exceptional difficulty, it appeared desirable to confirm them, if possible, over this range by an entirely different method, at least equal in accuracy.

Continuous-Mixture Method.

If two steady currents of fluid at different temperatures are passed through an arrangement of concentric tubes called a "heat exchanger," it is clear that, neglecting external heat-loss or gain, the loss of total heat by the hot current will be equal to the gain of total heat by the cold current. By measuring the currents and the temperatures of inflow and outflow, we have all the data required for determining the ratio of the mean specific heats over the respective ranges. This method does not appear to have been applied to any extent in accurate calorimetry, on account of the experimental difficulties involved in regulating and measuring the currents and the temperatures simultaneously to a sufficient order of accuracy. As applied to the variation of the specific heat of a single fluid, the method permits of a most important simplification which does not appear to have been hitherto noticed. In place of employing two separate currents, each of which must be measured and regulated to the limit of accuracy, *the same current* is passed twice through the heat exchanger, first as a hot current, and then, after suitable cooling, as a cold current, or *vice versâ*. If there is no leakage the ratio of the currents is always one of equality, and a comparatively rough determination of the absolute value of the current suffices for the application of small corrections. The experimental problem is reduced to the regulation and measurement of the temperatures, which, taken by itself, is comparatively easy. The method possesses the advantage, common to all continuous-flow methods, that a knowledge of the water equivalent of the calorimeter and of its variation with temperature is not required provided that the conditions are fairly steady. There is no uncertainty of heat-loss in transference, or by evaporation, as with an open calorimeter. It is also easy, by a suitable arrangement of the flow-tubes, to reduce the external heat-loss almost to a vanishing quantity without the employment of vacuum-jackets or elaborate precautions in lagging. The method requires considerable variation in detail to suit different ranges of temperature, and is in some ways less direct than the electric method, but it is peculiarly suitable as a means of independent verification.

General Arrangement of the Apparatus.

The continuous-mixture method was primarily designed for determining the variation of the total heat of water at temperatures above 100° C., where the continuous-electric method appeared to present greater difficulties. But, as the arrangements for this were not complete, it was decided to apply the method in the first instance as an independent test of the accuracy of formula (6) over the range 60° C. to 100° C., where it differed most widely from those of Lüdin and Bousfield. The arrangement adopted for this purpose will be readily understood from the diagrammatic scheme in fig. 4.

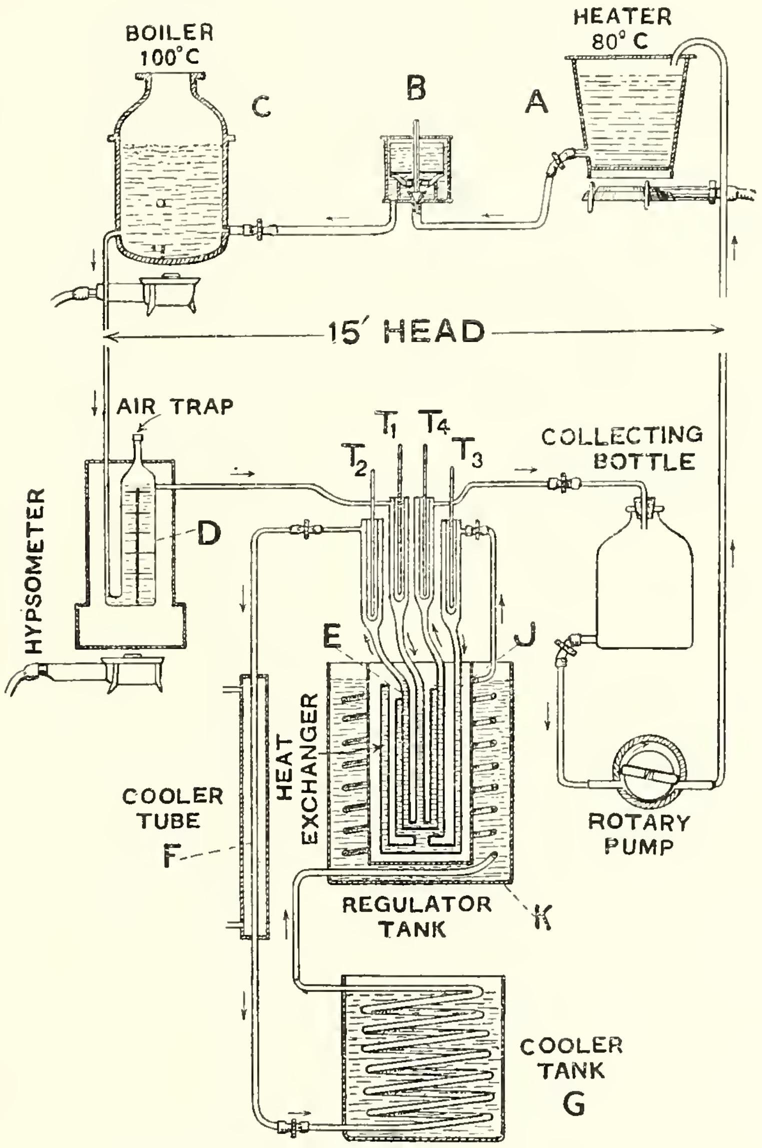

Fig. 4.

The current of air-free distilled water is supplied from a boiler C in which the level is kept constant by means of a float-feed B, from an auxiliary tank A, maintained at a temperature of about 80° C. From the boiler the current passes with a fall of about 15 feet to a reservoir D_1 surrounded by a steam-jacket, in which it is again raised to the boiling-point before entering the exchanger E. There is an air-trap at the top of the reservoir D, and similarly at each of the highest points of the circulating system, to facilitate filling the apparatus completely with water before starting the flow. Just before entering the exchanger E, the current passes through thermometer-pocket T_1, the construction of which is shown on a larger scale in the section of the exchanger, fig. 5. In order to protect the thermometer-pocket itself from loss of heat, the current is made to circulate upwards through a jacket-tube surrounding the thermometer-pocket before circulating downwards past the thermometer. Any small loss of heat which may occur before reaching the thermometer is immaterial. The thermometer-pockets and other tubes throughout the exchanger are made of thick copper, with deep screw-threads carefully fitted to produce a spiral circulation of the current. After passing thermometer T_1 the current flows downwards through the central tube to the bottom of the exchanger and thence upwards through a concentric tube, where it loses heat to the cold current. Its temperature on first leaving the exchanger is taken by a thermometer T_2 in a pocket constructed similarly to T_1, but not shown in fig. 5, in order to avoid confusion. The thermometer-pockets are all connected to the exchanger by thin tubes about 2 cm. to 3 cm. long and 0·5 cm. bore. These connections are exaggerated in the diagram, fig. 4, so as to permit the general course of the circulation to be more easily followed. After leaving T_2 at a temperature between 60° C. and 70° C., the current passes through a cooling-tube F surrounded by an easily regulated jacket of cooling water; thence through a long tin spiral immersed in a large cooling tank G to steady the temperature, before reaching a similar spiral in the regulator tank K, where its temperature is reduced precisely to that required for the cold current. From the regulator tank the current passes directly through the thermometer-pocket T_3 before entering the exchanger again as a cold current. In order to prevent loss of heat from the exchanger to the regulator tank in which it is immersed, the current, at very

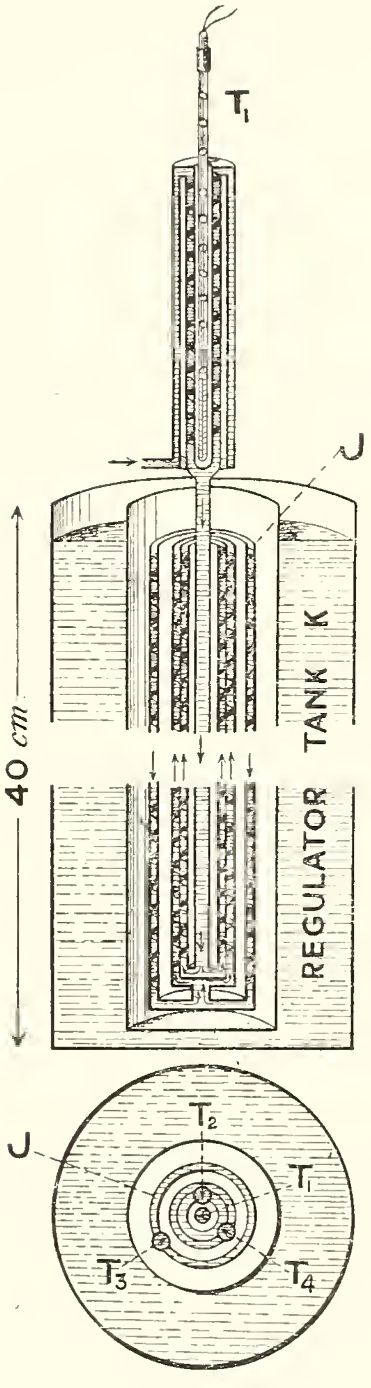

Fig. 5.

nearly the same temperature as the regulator tank, first circulates downwards through the outer jacket J and then upwards through the next inner tube, where it comes in contact with the hot current, emerging finally through the thermometer-pocket T_4, whence it passes to the collecting bottle, where the flow is measured from time to time. The head being maintained constant, steady currents of suitable values are obtained by fitting exit tubes of various bores between T_4 and the collecting bottle. From the collecting bottle the water is continuously returned to the heater on the floor above by means of a small rotary pump. With the exception of the heat exchanger itself, the details require considerable modification for different ranges of temperature. But the arrangement above described has been found to work very well for comparing the mean specific heat from 70° C. to 100° C. with the mean specific heat from 30° C. to 60° C., and will sufficiently illustrate the general nature of the method.

With a flow of 10 c.c. per second the heat-exchange amounts to about 300 calories per second, and the external heat-loss with the arrangement above described can be reduced to less than a tenth of a calorie per second, or about 1 in 3,000 of the total quantity measured. Owing to the relatively small thermal capacity of the exchanger, and to the fact that the distribution of temperature is nearly independent of the flow, the conditions become steady to 0°·002 C. in a few minutes when the flow is changed. The accuracy attainable depends chiefly on the limit of accuracy in reading the thermometers.

The Platinum Thermometers.

The thermometers employed were of my usual pattern in glass tubes, with leads partly of silver and partly of platinum, insulated by mica discs, spaced at intervals of 2 cm. throughout the length of the tube by means of mica crosses. Spacing the discs by means of mica crosses appears preferable to spacing the discs by long thin tubes of biscuit porcelain, as commonly practised by many makers, because the porcelain tubes are more hygroscopic than the mica. They also make the compensation less sensitive by shielding the leads. The thermometer coils were of pure standard wire, 0·01 cm. diameter (0″·004), and the ends of the compensating leads were connected by fusing on a short piece of the same wire to eliminate any conduction effects which might exist. Thick platinum leads extended for a distance of 7 cm. from the coil, where they were fused to silver leads. The object of this is partly to avoid possible contamination* of the fine wire with silver and partly to diminish conduction along the tube near the bulb. The immersion of the thermometers in the apparatus was

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* From the first I have always adopted this method of construction in my own thermometers for accurate work at high temperatures. It seems likely that many of the small variations of zero and difference-coefficient, found by careful observers, are due to contamination of the fine wire with gold or silver solder at its junction with the copper or silver leads. HOLBORN and HENNING, in their recent paper (*loc. cit.*), attribute some of the small variations of their platinum thermometers to this cause.

15 cm. At the head of each thermometer the silver leads were soldered to flexible copper leads, 3 m. long, with amalgamated copper terminals fitting the mercury cups of the compensated box described in a previous paper (CALLENDAR, *loc. cit.*, p. 90). This was essential to permit of rapid interchange of the thermometers in taking readings.

The ice- and steam-points were observed on several occasions. The sulphur-point was also observed on one occasion, when the following readings were taken :—

Thermometer.	T_1.	T_2.	T_3.	T_4.
Steam at 100°·262 C.	1785·39	1783·70	1785·38	1782·39
Ice at 0° C.	1284·07	1282·84	1284·11	1281·85
Fundamental interval	500·03	499·57	499·98	499·25
Sulphur reading	3394·67	3391·26	3394·38	3389·10
pt_s deduced	422·09	422·05	422·07	422·08
t_s from barometer	445·22	445·19	445·21	445·21
$t_s - pt_s$	23·13	23·14	23·14	23·13
Difference-coefficient × 10^4 . . .	1·505	1·506	1·506	1·505

Readings at the fixed points were taken and corrected for box-temperature and coil-errors to one figure beyond that given in the above table (corresponding to 0°·0002 C.), but the last figure has been rejected as not being fully significant even at the fixed points, and as being beyond the limit of accuracy at the sulphur-point. The fundamental intervals of the thermometers were approximately 5 ohms each, or 500 cm. of the bridge-wire. Thermometers T_1 and T_3 had been made at the same time, by my assistant Mr. W. J. COLEBROOK, for use as a differential pair, and had been adjusted with special care so that their uncorrected readings agreed to 1 in 10,000 throughout the scale. T_2 and T_4 were precisely similar thermometers made at different times, with resistances adjusted to about 1 in 1,000. The readings at the sulphur-point were taken in succession on the same day, when the barometer was falling slightly, in the order T_1, T_3, T_4, T_2. The corresponding temperatures, t_s, on the gas-scale are calculated from the observed barometer readings by assuming the normal boiling-point to be 444°·53 C., and the pressure variation to be 0°·090 C. per mm., as found by CHREE. The results show that all four thermometers agreed in their temperature scales to 0°·01 C. at the sulphur-point, which is nearly the limit of error of the readings. An iron-tube apparatus was employed for boiling the sulphur and the thermometers were fitted with a single screen. Experience has shown that this apparatus gives consistently a temperature nearly 0°·10 C. lower than the glass-tube apparatus with two screens, as originally described. Allowing for this, the difference coefficients of all four thermometers would be within 1 in 1,500 of the standard value, $1·50 \times 10^{-4}$, for pure platinum when the S.B.P. is taken as 444°·53 C. In any case, this correction (from 1·506 to 1·500) would not affect the scale of the thermometers by so much as 0°·002 C. at 50° C. In my experience, platinum thermometers, when carefully constructed of suitable wire, always agree so closely with this scale that it is seldom worth while to make a special determination of the difference-coefficient by reference to the sulphur boiling-point. It was, however, considered desirable to make the test in the present instance because the apparent variation of the specific heat of water depends in a great measure on the thermometric scale employed. The thermometers were also compared differentially between 0° C. and 100° C. and were found to agree so closely that no differences in their scales could be detected.

Method of Reading the Thermometers.

The galvanometer employed was of the moving coil type, with a resistance of about 13 ohms. Readings were generally taken by the constant-current method which I first introduced in 1891. In this method the platinum thermometer is connected on the compensator side of the box in series with the box coils, and is balanced against a compensated resistance,* equal to, or greater than, the resistance of the thermometer at the highest point of the range it is desired to cover, in this case 17·84 ohms. With this arrangement the current through the thermometer is nearly the same at all temperatures, since the resistances on both sides of the bridge are kept nearly constant. The current through the thermometer was approximately 0·005 ampere, and was adjusted so that the deflection of the galvanometer was 1 mm. at 1 metre on reversal for a change of temperature of 0°·001 C. Readings were taken by setting the contact-point on the bridge-wire as exactly as possible with a lens to the nearest millimetre, and then observing the small deflection of the galvanometer on reversing the battery. The definition was so perfect that it was possible to read to 0·1 mm. of the scale, or 0°·0001 C., by the galvanometer deflection when the temperature was steady. But this was the case only at the fixed points. No attempt was made to read nearer than 0°·001 C. at other temperatures, but the provision of ample sensitiveness greatly facilitated quickness and certainty of reading. The constant-current arrangement of the measuring apparatus possessed special advantages for the continuous-mixture method, because it was necessary to read four

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* These compensated resistances are very useful in accurate resistance measurements or platinum thermometry. They are best constructed of platinum-silver, wound on mica and annealed *in situ* at a dull red heat, compensated by a small resistance of pure platinum, having an equal temperature increment, and connected in the opposite arm of the bridge (CALLENDAR, 'Brit. Patent,' No. 14,509, 1887). The two coils may conveniently be enclosed in a glass tube with compensated leads like a platinum thermometer, and the point of zero temperature-coefficient may easily be adjusted as near to 20° C. as desired. In this case the whole change of resistance of the combination between 0° C. and 40° C. is less than 1 in 100,000, and the change between 15° C. and 25° C. is only 1 in 2,000,000. The best specimens of manganin generally have a temperature-coefficient of 2 or 3 in 100,000 per 1° C. at 20° C., which is more than 100 times as great; but even if the point of zero-coefficient for manganin could be adjusted to 20° C., the changes in the neighbourhood of 20° C. would be more than 10 times as great as with the platinum-silver coil compensated with platinum. For a further discussion of this point see CALLENDAR, 'Phil. Trans.,' A, vol. 199, p. 89, 1902.

thermometers at different temperatures in rapid succession. It was important that the sensitiveness of the galvanometer should be the same for each, and it was desirable that the rise of temperature produced by the measuring current should be nearly the same for each thermometer. This last condition is approximately secured by keeping the current constant. CHAPPUIS and HARKER (' Phil. Trans.,' A, 1900, p. 62; CALLENDAR, *loc. cit.*, p. 93) proposed to do this by keeping the watts C^2R constant, adjusting the current C to suit the value of R. But the emissivity of the wire increases somewhat more rapidly than R, so that the rise of temperature due to C at different points of the scale is nearly proportional to C^2. The rise of temperature produced by a current of 0·005 ampere at 30° C. was measured and found to be 0°·0066 C. The rise at 100° C. was found to be 0°·0063 C. Assuming that the variation between these limits was regular, it was evident that it could not produce a systematic error of the temperature scale greater than 0°·0001 C. between the limits 0° C. and 100° C. In measuring the mean specific heat over a range of 30° C., a limit of accuracy of 0°·001 C. in the thermometric readings appeared to be ample, because this would amount to only 1 in 30,000 of the heat measured, and it was hardly to be expected that the external heat-loss could be determined with a much higher order of accuracy than 1 in 10,000.

Theory of the Continuous-Mixture Method.

If X is the external heat-loss in calories per second, and Q the water current in grammes per second, the equation connecting the mean specific heats $s_{1,2}$, $s_{4,3}$ over the ranges t_1 to t_2 and t_4 to t_3 for a single value of the flow Q is evidently

$$s_{1,2}(t_1-t_2) = s_{4,3}(t_4-t_3) + X/Q. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If the heat-loss X could be neglected by sufficiently increasing the flow, this equation would give the required ratio of the specific heats directly, being simply the inverse ratio of the temperature ranges. In any case, if X is small and Q large (say 10 to 20 gr./sec.), this would give a good first approximation, better than 1 in 1,000 if X is less than 1 in 1,000 of the whole heat exchange. Assuming that the temperature distribution in the exchanger, and consequently the heat-loss X, does not vary appreciably when the flow is changed within reasonable limits, a second approximation could easily be secured by employing the first approximation to evaluate the heat-loss for a small flow, say 1 gr./sec., and employing the value so obtained for the large flow; or the heat-loss X might be directly eliminated by subtracting one equation from the other if the temperature ranges were so nearly the same that the values of the mean specific heats could be assumed to be the same for the small flow without sensible error. This method of reduction would undoubtedly give good results if the losses were small. In practice, however, it is impossible to secure *exact* similarity in the temperature distribution for flows varying in the ratio of 10 to 1, and it is, therefore, preferable to adopt a method of reduction depending on some assumed variation of the total heat. This appears at first sight a less direct method, but is peculiarly appropriate when the primary object of the experiment is to verify formulæ already obtained by different methods.

Variation of the Total Heat.

The variation of the total heat is not so familiar as the variation of the specific heat, but since the change of total heat between given limits is the quantity actually measured in a calorimetric experiment, the total heat is generally the most useful quantity to tabulate for experimental purposes. The numerical value of the total heat h from 0° C. to t° C. in terms of a unit at 20° C. differs but little from t over the range 0° C. to 100° C. It is, therefore, convenient to write

$$h = t + dh, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where dh is the small excess of h over t at any temperature, which may appropriately be called "the variation of the total heat."

The value of dh given by Lüdin's formula (5) is

$$dh = 0{\cdot}84\,\frac{t}{100} - 3{\cdot}8656\left(\frac{t}{100}\right)^2 + 6{\cdot}588\left(\frac{t}{100}\right)^3 - 2{\cdot}929\left(\frac{t}{100}\right)^4, \quad . \quad . \quad . \quad (9)$$

whence the value at 100° C. is $0{\cdot}84 + 6{\cdot}588 - 3{\cdot}8656 - 2{\cdot}929 = +0{\cdot}633$.

The corresponding formula for dh deduced from my formula (6) representing the results of the continuous-electric method is

$$dh = 1{\cdot}1605 \log_{10}\frac{t+20}{20} - 1{\cdot}464\,\frac{t}{100} + 0{\cdot}42\left(\frac{t}{100}\right)^2 + 0{\cdot}30\left(\frac{t}{100}\right)^3, \quad . \quad . \quad (10)$$

whence the value at 100° C. is $0{\cdot}903 - 1{\cdot}464 + 0{\cdot}420 + 0{\cdot}300 = +0{\cdot}159$, differing from Lüdin's formula by nearly 0·5 per cent.

These two formulæ are represented by the curves in fig. 6. In order to save space,

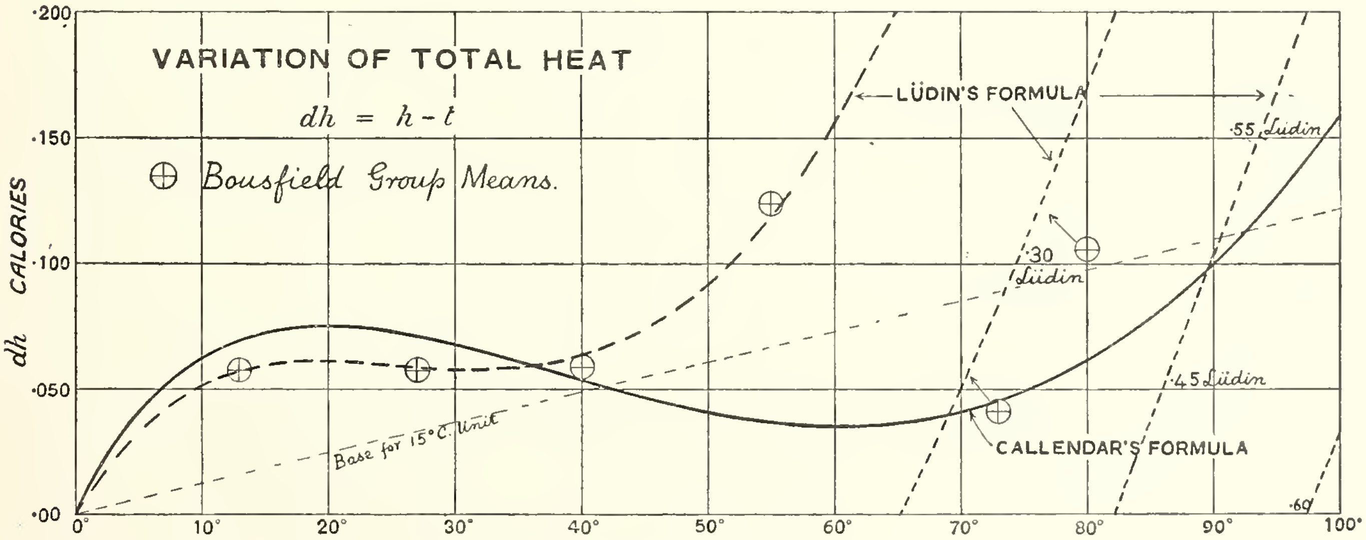

Fig. 6.

LÜDIN's curve from 65° C. to 100° C. is represented in three pieces, the curve being shifted downwards through 0·200 when it reaches the upper limit of the diagram. ROWLAND's observations on the mechanical equivalent from 5° C. to 35° C., if plotted on the same scale, would agree to 0·003 throughout his range with formula (10), the full curve. His experiments do not, as generally stated, afford any conclusive evidence of a minimum at 30° C. in the specific heat. ROWLAND himself considered that, owing to the increasing magnitude and uncertainty of the radiation correction beyond 30° C., "there might be a small error in the direction of making the mechanical equivalent too great at that point (30° C.), and the specific heat might keep on decreasing to even 40° C." The discrepancy from LÜDIN's curve in this region is less than 1 in 1,000 of the total heat, and is within the limits of error of LÜDIN's experiments. Formula (6) gives a minimum at 37°·63 C. LÜDIN's formula gives a minimum at 25°·22 C., which cannot be reconciled with ROWLAND's observations.

The point at which the specific heat in absolute units can be most accurately inferred from ROWLAND's experiments is 20° C., at the middle of his temperature range. The value at this point is probably within 1 in 2,000 of 4·180 joules per gr.-deg. C. on the scale defined by formula (1). ROWLAND himself gave the value 4·179 on the air scale; DAY's reduction of ROWLAND's thermometers gave 4·181 on the hydrogen scale. The results of REYNOLDS and MOORBY, when corrected to cover the range 0° C. to 100° C., give 4·184 joules for the mean calorie. Combining these two results we find 4·184/4·180, = 1·0010, for the ratio of the mean calorie to the calorie at 20° C. My formula (10) would make the ratio 1·0016, which is fairly good agreement. But LÜDIN's formula gives the ratio 1·0063, showing a discrepancy of 0·53 per cent., which would appear to be beyond the possible limits of error of REYNOLDS and MOORBY's experiments, since the extreme variations of their results did not exceed 0·36 per cent., and the mean would probably be correct to 1 in 1,000.

The evidence to be deduced from the observations of W. R. BOUSFIELD and W. E. BOUSFIELD (*loc. cit.*) with regard to the variation of the total heat rests on their "point-to-point" experiments over the following ranges:—

Range of temperature .	0–13° C.	13–27° C.	27–40° C.	40–55° C.	55–73° C.	55–80° C.
Mean value of J . . .	4·1937	4·1752	4·1756	4·1935	4·2024	4·2056
dh deduced	0·058	0·058	0·059	0·124	0·242	0·306
dh LÜDIN	0·057	0·059	0·064	0·119	0·285	0·371

The values of the variation *dh* at the points 13° C., 27° C., 40° C., 55° C., 73° C., and 80° C. are deduced from Messrs. BOUSFIELD's observations by taking their value 4·1752 for the unit at 20° C. and adding up their values of the total heat for the separate ranges. Up to 55° C. they agree very closely with LÜDIN's curve, as indicated by the crosses in fig. 6. Their values at 73° C. and 80° C. are somewhat lower than LÜDIN'S, but the discrepancy here is only from 0°·043 C. to 0°·065 C. They considered that the measurements could not be carried beyond this point with an open calorimeter owing to the rapidly increasing uncertainty of the heat-loss due to evaporation, "obturator" heating, &c. The general agreement with LÜDIN'S curve is so striking that it would seem at first sight as though it could hardly be due to chance. Their methods had no points in common, except that they both used mercury thermometers and open calorimeters.

Reduction of Observations by the Total-Heat Method.

The curves of variation of total-heat above described and explained, when plotted on a scale of 1 mm. to 0°·001 C. for dh, afforded the most accurate and expeditious method of reducing the observations by the continuous-mixture method, since it was easy to take exact account in this way of small differences of range with different flows. If h_1, h_2, h_3, h_4 are the total heats from 0° C. corresponding to the observed temperatures t_1, t_2, t_3, t_4, equation (7), when expressed in terms of the total heat, becomes

$$h_1 - h_2 = h_4 - h_3 + \mathrm{X}/\mathrm{Q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

Substituting $h = t + dh$, and writing Σt for the sum $t_1 - t_2 + t_3 - t_4$, and Σdh for the sum $dh_1 - dh_2 + dh_3 - dh_4$, this equation may be written

$$\mathrm{Q}\,(\Sigma t + \Sigma dh) = \mathrm{X}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

If the formula assumed for dh is correct, the values of the heat-loss X deduced from different flows should be nearly the same for the same temperature range, or should vary in relation to the mean excess-temperature of the calorimeter above its surroundings. If the formula employed for dh is incorrect, the calculated values of the heat-loss X will vary with the flow, and will bear no consistent relation to the external conditions.

As there was some delay in procuring the requisite sizes of solid-drawn copper tube for the high-pressure apparatus designed for work at temperatures up to 230° C., the apparatus was in the first instance constructed of ordinary brass tubing with solder joints for work below 100° C. The soft-solder joints would not stand high temperatures, but had the advantage that the apparatus could be taken to pieces readily and remade in different forms, to test the effect of variations in the external conditions on the heat-loss observed. Thus in order to test for possible errors due to conduction of heat along the thin tubes, 2 to 3 cm. long, 5 mm. bore, and 0·5 mm. thick, connecting the thermometer-pockets to the exchanger, the connecting tubes were replaced by short thick brass cylinders 1 cm. long by 2 cm. in diameter. This produced an appreciable effect on the thermometer readings only with the smallest flow of 1·25 gr./sec. It was inferred that the conduction error with the thin tubes actually employed would be inappreciable even with the smallest flow.

A possible source of error to be carefully avoided in the continuous-mixture method is leakage of fluid at any point of the circuit between the first and last thermometers. Precautions against this were taken in designing the apparatus by making the cooling coils and other inaccessible parts of the apparatus of continuous lengths of solid-drawn tubing, and arranging all joints and connections as far as possible so as to be easily accessible and at all times open to inspection.

In addition to this, a leakage test was regularly applied each day before starting observations, when the apparatus was at a nearly uniform temperature. The boiler was disconnected, and a glass tube of small bore was attached to the inflow at the top, to serve as an index. Any possible leaks were thus subjected to the full head of 15 feet. A special test was also made for leakage between the hot and cold tubes in the exchanger. A small continuous leak due to strain, amounting to about 1 c.c. per hour, was detected on one occasion, and immediately rectified. But, as a rule, the movements of the sensitive index were negligibly small, being due merely to slight changes of temperature, and more often positive than negative.

The apparatus was also tested with and without the jacket-tube J, figs. 4 and 5, between the exchanger and the regulator tank in which it was immersed. The loss from the thermometer-pockets, when unjacketed, was found to be from 1·2 to 1·4 calories per second, according to the conditions of the experiment, and to be nearly independent of the flow, since the mean excess-temperature of the thermometer-pockets above the regulator tank, namely $(t_1+t_2+t_4-3t_3)/4$, varied but slightly with the flow. The loss from the inner tubes of the exchanger itself, *when unjacketed*, was nearly 2 calories per second, but varied by nearly 20 per cent. of itself when the flow was changed in the ratio of 1 to 10. This could easily be foreseen, because the cold current was raised to a higher temperature when the flow was small. The actual distribution of temperature in the outer tube of the exchanger was observed by means of thermocouples, and found to correspond with theory and with the observed changes in the heat-loss with flow. The jacket-tube J was designed to intercept this variable heat-loss and reduce it to about a tenth for the smallest flow. The mean rise of temperature of the jacket-tube for the smallest flow was found to be of the order of 1° C. The mean difference of temperature between the jacket-tube and the regulator was always measured and allowed for in estimating the mean excess-temperature, but it was generally less than 0°·2 C. for the largest flow, corresponding to a heat-loss of about 1 in 10,000, which was about the limit of agreement of the temperature measurements. It was ultimately decided to do without jackets for the thermometer-pockets at temperatures below 100° C., because the heat-loss from the thermometer-pockets at these low temperatures was fairly small and nearly independent of the flow. The omission of these jackets considerably simplified the construction and connection of the apparatus. The main jacket J for the exchanger was employed in nearly all the experiments, because it made the heat-loss so nearly independent of the flow, and made the reduction of the observations comparatively simple and certain.

For regulating the temperature of the cold current, an electric temperature regulator was employed of the same type as that used in the continuous-electric method, which had been specially designed to prevent hunting. With a 32 c.p. lamp, and suitable adjustment of the cooling water, currents up to 20 gr./sec. could be kept steady to a few thousandths of 1° C. for considerable periods, over a range from 20° C. to 35° C. But this was not such an easy matter as might be imagined, owing to variations of temperature of the cooling water.

During the months of May, June, and July, 1911, upwards of 150 complete sets of readings were taken, each for a single flow. The upper limit of temperature was always nearly 100° C., but the lower limit was varied from 25° C. to 35° C. The flow was varied from 1 c.c./sec. to 20 c.c./sec. It is a great advantage of the method that it permits the flow to be so widely varied without introducing any serious experimental difficulties, but the largest flows were somewhat difficult to regulate, and there was no material gain in accuracy beyond about 10 c.c./sec., at which point the limit of accuracy of the thermometric readings corresponded with the limit of reading the total heat curves. Many variations were tried in the disposition of the apparatus, with corresponding variations in the heat-loss, which, even without jackets or lagging, seldom exceeded 1 per cent. of the heat-exchange for the largest flow. The results of all these experiments were so nearly similar that it will suffice to give one example of the detailed readings. The following readings were taken with the jacket-tube J surrounding the exchanger, but without lagging or jackets on the thermometer-pockets :—

OBSERVATIONS of July 3, 1911.

Flow gr./sec. Q . .	10·44	10·47	7·43	4·08	2·55	1·240
Thermometer t_1 . .	+99·980	99·972	99·901	99·702	99·451	98·762
" t_2 . .	−68·979	68·989	67·107	64·383	62·996	61·763
" t_3 . .	+25·442	25·445	25·466	25·524	25·548	25·587
" t_4 . .	−56·452	56·436	58·205	60·628	61·567	61·486
Sum Σt	− 0·009	− 0·008	+ 0·055	+ 0·215	+ 0·436	+ 1·100
Σdh from curve . .	+ 0·152	+ 0·152	+ 0·153	+ 0·154	+ 0·152	+ 0·148
Heat-loss X	1·49	1·50	1·54	1·51	1·50	1·55

The above table includes observations for five different values of the flow. Each flow was maintained steady for about half-an-hour, during which time two measurements of the flow were taken, and four sets of readings of the thermometers. The flows generally agreed to 1 in 500, and the thermometers seldom varied more than 0°·01 C. in half-an-hour. In the above example the readings for the maximum flow were continued for over an hour. Such changes in the thermometer readings as occurred during each flow were due partly to change in the barometer and partly to change in the temperature of the cooling water, which also made it necessary to reset the regulator between each flow, as indicated by the readings of the thermometer t_3.

It was found on reducing the above observations that insufficient time had been allowed for the conditions to become steady after changing the flow from 10·47 to 7·43 gr./sec. A change of 0°·016 C. occurred in t_3 after the first pair of readings at Q = 7·43. All the readings have been included in the mean, but, if the first pair had been rejected, the heat-loss would have been 1·50 for this flow. The signs attached to the temperatures are those taken in finding the sum Σt. The values of Σdh were taken from the curve given in fig. 6, representing my formula (10). The values of the heat-loss X deduced are nearly the same for all the flows. It should be observed that the heat-loss, 1·50 cal./sec., is less than 0·5 per cent. of the heat-exchange, 325 cal./sec., for the large flow, and that the flow could easily be varied in the ratio of 1 to 8. In the continuous-electric method with a vacuum-jacket, the heat-loss at 92° C. amounted to 4 per cent. of the maximum watts, or 10 per cent. of the difference between the flows, on which the result depends. In REYNOLDS and MOORBY'S experiments the heat-loss amounted to 5 or 10 per cent. (with or without lagging) of the difference of the loads in the heavy and light trials. In neither case could the flow be varied satisfactorily in a ratio greater than about 1 to 2. The continuous-mixture method is undoubtedly preferable to either in this respect, since it permits a wider range of variation of the flow, and a greater reduction in the heat-loss. The agreement of the values of the heat-loss deduced from the different flows by means of formula (10) is closer than might have been expected, because 1 in the last figure of the heat-loss corresponds to 0°·001 C., or 1 in 30,000 of the heat-exchange for the large flow. It may be said that formula (10) is verified to at least 1 in 5,000 for the ratio of the mean specific heat from 69° C. to 100° C., where it differs most widely from LÜDIN'S, to the mean specific heat from 25° C. to 56° C. Formula (10) gives 1·0050 for the ratio. LÜDIN'S formula gives 1·0104, differing by 0·54 per cent. If LÜDIN'S formula had been employed for the reduction, the heat-loss, instead of being nearly the same for the different flows, would have appeared to vary from 3·38 for the largest flow to 1·79 for the smallest flow. The heat-loss should, as a matter of fact, have been slightly less for the large flows than for the small, because the rise of temperature of the jacket J with the smallest flow was rather more than sufficient to compensate for the fall of mean temperature of the thermometer-pockets.

Seeing that the results of the continuous-electric method have now been so closely verified by the continuous-mixture method, which is independent of electrical energy measurements, it would appear to follow that the discrepancy of 1 per cent. at 80° C. between these methods and those of Messrs. BOUSFIELD and LÜDIN is to be attributed mainly to fundamental differences in the thermometric and calorimetric methods employed. In my continuous-flow methods the troublesome and uncertain corrections of mercurial thermometry at temperatures between 40° C. and 100° C. have been avoided, and a higher order of accuracy in the temperature measurements has been secured by the direct employment of platinum thermometers. Errors due to lag, or to uncertainty of the water-equivalent of the calorimeter and its variation with temperature, have been practically eliminated by keeping all the conditions steady, so that the observations could be pushed to the limit of accuracy of temperature measurement. Errors due to dissolved air and to evaporation, which are quite appreciable at 40° C., and begin to be serious at 50° C., with an open calorimeter, have been minimised by keeping the water free from air up to the moment of its passage into the calorimeter, where it is completely enclosed and protected from evaporation. Without presuming to criticise in detail the work of Messrs. BOUSFIELD, I maintain that these difficulties have not been adequately met in their investigations, and would inevitably give rise to constant errors, which could not be detected without fundamental variations in the conditions of experiment. While their method may undoubtedly be suitable for the purpose for which it was originally devised, namely, that of comparing the specific heats of similar solutions over the same range of temperature, I cannot admit that it affords any promise of exceptional accuracy in the determination of the variation of the specific heat *over different ranges* of temperature, which is a much more difficult problem. According to my own work and that of Dr. BARNES, the whole variation of the specific heat of water between 10° C. and 80° C. is less than one-half of 1 per cent., and demands the most accurate methods of investigation. The occurrence of so high a maximum as LÜDIN's experiments show in the neighbourhood of 80° C. is theoretically inadmissible, and cannot be reconciled with the work of REYNOLDS and MOORBY, or with the corrected results of REGNAULT, which are satisfactorily represented by my formula.

Variation of Specific Heat with Pressure.

The continuous-electric and continuous-mixture methods both compare the variations of the total heat of the fluid, $h = \mathrm{E}+pv$, under the condition of practically constant pressure, or give ratios of the values of the mean specific heat at constant pressure over different ranges of temperature. Below 100° C. the pressure is always atmospheric, and the variation of the specific heat with pressure does not exceed 1 in 10,000 per atmosphere. At higher pressures and temperatures it would be necessary to take account of the variation of the specific heat with pressure in comparing observations taken at different pressures, since the pressure in the apparatus must always exceed the saturation pressure at the highest temperature observed. This reduction can be effected with sufficient approximation by means of the thermodynamical relation,

$$(ds/dp)_\theta = -\theta\,(d^2v/d\theta^2)_p.$$

The variation amounts to nearly 2 in 10,000 per atmosphere at 200° C. The quantity of heat supplied to water in a boiler, maintained at constant pressure and temperature, per unit mass of water pumped into it at the same pressure but at a lower temperature, is the change of total heat at constant pressure, and is a quantity of the same kind as that measured in the continuous-mixture method. The work $(p-p_0)v_0$, which is generally included in tabulated values of the total heat, is supplied as work by the feed-pump, and not as heat in the boiler. It would amount to only 1 in 500 of the total heat at 200° C., and might be neglected except in the most accurate calorimetric work.

The quantity measured in REGNAULT's method was the change of total heat from boiler pressure and temperature down to the final temperature of the calorimeter at atmospheric pressure, which may be denoted by the expression $(\mathrm{E}+pv)-(\mathrm{E}_1+p_1v_1)$, where the suffix 1 denotes atmospheric pressure at the final temperature of the calorimeter. The differential of this is the rate of change of the total heat of water under saturation pressure, and exceeds the specific heat at a constant pressure equal to that of saturation by the expression $[v-\theta(dv/d\theta)_p](dp/d\theta)_{\mathrm{sat}}$, which amounts to nearly 0·3 per cent. at 200° C. The specific heat at constant pressure exceeds the so-called "saturation" specific heat at the same pressure and temperature by the expression $\theta(dv/d\theta)_p(dp/d\theta)_{\mathrm{sat}}$, which amounts to 0·6 per cent. at 200° C. The values of the total heat and the specific heat from 100° C. to 200° C. given in the following tables, in so far as they represent a reduction of REGNAULT's observations, must be taken as representing the total heat of water and its rate of variation under saturation pressure, and not under constant pressure; but the uncertainty of the reduction probably exceeds the difference in question.

The quantity measured by DIETERICI was the change of intrinsic energy E of water from saturation pressure and temperature in the heater to saturation pressure at 0° C., which may be denoted by $\mathrm{E}-\mathrm{E}_0$. Neglecting the small change of intrinsic energy due to 1 atmosphere at 0° C., the quantity measured by DIETERICI is less than that measured by REGNAULT by the expression $(pv-p_1v_0)$, which amounts to 0·43 calorie at 200° C., or 0·2 per cent. on the mean specific heat. His tabulated values of the mean specific heat at 200° C., when reduced to a unit at 20° C., are already 0·8 per cent. higher than my reduction of REGNAULT's observations, so that the discrepancy is increased to 1 per cent. at this point if allowance is made for the difference in the quantities measured. The actual specific heat at t tabulated by DIETERICI is the rate of increase of the intrinsic energy under saturation pressure, which is less than that of the total heat $\mathrm{E}+pv$ under the same conditions by the expression $[d(pv)/d\theta]_{\mathrm{sat}}$, which amounts to nearly 1 per cent. at 200° C. The specific heat tabulated by DIETERICI already exceeds that deduced from REGNAULT by 2 per cent. at 200° C., so that the discrepancy is increased to 3 per cent. in the value of the actual specific heat at this point. The discrepancy is of the same order as the whole variation of the specific heat, and is not unimportant from a theoretical standpoint. Accurate experiments at these temperatures are very difficult, but it is clear that further experiments are desirable, if any theory of the variation of specific heat is to be framed or tested.

Explanation of the Tables.

The most useful table in practice is that of the variation of the total heat, which also permits the mean specific heat between any limits to be readily calculated. The corresponding curve, representing the variation between 0° C. and 100° C., has been given in fig. 6, but the scale of fig. 6 does not permit the values to be read with sufficient accuracy from the curve as reproduced. It should be observed that it is important to tabulate the variation in terms of the specific heat at 20° C. taken as unity, and not in terms of the specific heat at 15° C., which is so often taken as the standard, because in the latter case the values of dh from 42° C. to 92° C. would all be negative, which would be inconvenient in using the table. If, on the other hand, the minimum value of s, or the value at 30° C., were taken as the standard, the values of dh would be inconveniently large.

The table gives the values of dh for each degree, and a column of differences is added to facilitate interpolation if desired, but the differences are so small for the greater part of the range 0° C. to 100° C. that this is seldom required. Above 100° C. the differences are larger, but the values are here so uncertain that it could seldom be worth while to interpolate. The method of using the table is fairly obvious, but the following examples may make it clearer.

To find the total heat h from 0° C. to any point t; add to the exact value of t, expressed to 0°·001 C., the corresponding value of dh for the nearest whole degree taken from the table, interpolating for fractions of a degree if great accuracy is required in a problem depending on small differences. Unless t is known to 0°·001 C., interpolation is unnecessary.

To find the change of total heat between t_1 and t_2; find from the table the corresponding values of dh, namely, dh_1 and dh_2, and add the difference $dh_2 - dh_1$ to the difference $t_2 - t_1$, with due regard to sign.

To find the mean specific heat from 0° C. to t; divide the corresponding value of dh by t and add unity.

To find the mean specific heat between t_1 and t_2; find the difference $dh_2 - dh_1$, divide by the difference $t_2 - t_1$, and add unity. Thus, if the given values are $t_1 = 25^\circ{\cdot}442$ C., $t_2 = 56^\circ{\cdot}452$ C., we find $dh_1 = 0{\cdot}073$, $dh_2 = 0{\cdot}037$, whence $dh_2 - dh_1 = -0{\cdot}036$, $s_{1,2} = 1 - 0{\cdot}036/31{\cdot}0 = 1 - 0{\cdot}00116 = 0{\cdot}99884$. The result will be correct to 1 in 10,000, if $t_2 - t_1$ is not less than 10° C. If the range is less than 10° C., the specific heat at the mean point of the range, taken from the table of specific heat at t, is a sufficiently close approximation in most cases.

The values of the entropy of water ϕ reckoned from 0° C. are sometimes required, and are generally given in steam-tables. Assuming that 0° C. is 273°·10 C. from the absolute zero, the formula for the entropy obtained by integrating from 0° C. to t formula (6) for the specific heat divided by $t + 273{\cdot}1$ is as follows:

$$\phi = 2{\cdot}36602 \log_{10} (t + 273{\cdot}1)/273{\cdot}1 + 0{\cdot}004586 \log_{10} (t + 20)/20 \\ - 0{\cdot}01618\,(t/100) + 0{\cdot}0045\,(t/100)^2.$$

TABLE of the Specific Heat of Water, $s = dh/dt$ at $t°$ C., for each degree from 0° C. to 200° C., in terms of the specific heat at 20° C. taken as unity, according to formula (6), p. 10, above, namely,

$$s = 0{\cdot}98536 + \frac{0{\cdot}504}{t+20} + 0{\cdot}0084\,\frac{t}{100} + 0{\cdot}0090\left(\frac{t}{100}\right)^2, \qquad (6)$$

referred to the standard scale of temperature t, deduced from the platinum scale pt by the difference formula (1), p. 1, above, namely,

$$t - pt = 1{\cdot}50\,t\,(t-100) \times 10^{-4}. \qquad (1)$$

t.	0° C.	1° C.	2° C.	3° C.	4° C.	5° C.	6° C.	7° C.	8° C.	9° C.	Differences.
° C.											
0	1·01056	1·00944	1·00844	1·00753	1·00671	1·00596	1·00528	1·00466	1·00410	1·00358	112 to 48
10	1·00310	1·00266	1·00225	1·00188	1·00154	1·00122	1·00093	1·00066	1·00042	1·00020	44 " 20
20	1·00000	0·99982	0·99964	0·99948	0·99934	0·99922	0·99911	0·99901	0·99892	0·99884	18 " 8
30	0·99877	0·99870	0·99865	0·99861	0·99858	0·99856	0·99855	0·99854	0·99854	0·99855	− 7 " +1
40	0·99856	0·99858	0·99861	0·99864	0·99867	0·99871	0·99875	0·99881	0·99887	0·99894	+ 2 " +7
50	0·99901	0·99909	0·99917	0·99925	0·99933	0·99942	0·99952	0·99962	0·99972	0·99983	8 to 11
60	0·99994	1·00005	1·00017	1·00029	1·00042	1·00055	1·00079	1·00083	1·00097	1·00111	11 " 14
70	1·00125	1·00140	1·00155	1·00170	1·00185	1·00201	1·00217	1·00234	1·00251	1·00269	15 " 18
80	1·00288	1·00306	1·00324	1·00342	1·00361	1·00380	1·00399	1·00419	1·00439	1·00459	18 " 20
90	1·00479	1·00499	1·00520	1·00541	1·00562	1·00583	1·00605	1·00627	1·00650	1·00673	20 " 23
100	1·00696	1·00719	1·00742	1·00766	1·00790	1·00814	1·00838	1·00862	1·00887	1·00912	23 to 25
110	1·00937	1·00962	1·00988	1·01014	1·01040	1·01066	1·01092	1·01119	1·01146	1·01173	26 " 27
120	1·01200	1·01228	1·01256	1·01284	1·01312	1·01340	1·01368	1·01397	1·01426	1·01455	28 " 29
130	1·01484	1·01514	1·01544	1·01574	1·01604	1·01634	1·01665	1·01696	1·01727	1·01758	30 " 31
140	1·01790	1·01822	1·01854	1·01886	1·01919	1·01952	1·01985	1·02018	1·02051	1·02084	32 " 34
150	1·02118	1·02152	1·02186	1·02220	1·02254	1·02289	1·02324	1·02359	1·02394	1·02429	34 to 35
160	1·02464	1·02500	1·02536	1·02572	1·02608	1·02645	1·02682	1·02719	1·02756	1·02793	36 " 37
170	1·02830	1·02868	1·02906	1·02944	1·02982	1·03021	1·03060	1·03099	1·03138	1·03177	38 " 39
180	1·03216	1·03256	1·03296	1·03336	1·03376	1·03416	1·03457	1·03498	1·03539	1·03580	40 " 41
190	1·03621	1·03663	1·03705	1·03747	1·03789	1·03831	1·03873	1·03916	1·03959	1·04002	42 " 43

200 1·04045 REGNAULT (uncorrected) 1·0440 at 200° C.

The values are calculated from the formula to the fifth place, which is useful for small differences, and as serving to fix the value in the fourth place. The Mechanical Equivalent J may be taken as equal to 4·180 s joules/gr.-deg. C.

VARIATION of the Total Heat of Water, $h = t + dh$, reckoned from 0° C. Table of Values of dh for each degree from 0° C. to 200° C., in terms of the specific heat at 20° C. taken as unity, according to formula (10), p. 21,

$$dh = 1{\cdot}1605 \log_{10} \frac{t+20}{20} - 1{\cdot}464 \frac{t}{100} + 0{\cdot}42 \left(\frac{t}{100}\right)^2 + 0{\cdot}30 \left(\frac{t}{100}\right)^3 . \quad \text{(10)}$$

referred to the standard scale of temperature t defined by the formula (1), p. 1, above, namely,

$$t - pt = 1{\cdot}50\, t\,(t-100) \times 10^{-4} . \quad \text{(1)}$$

t.	0° C.	1° C.	2° C.	3° C.	4° C.	5° C.	6° C.	7° C.	8° C.	9° C.	Difference per 1° C.
° C.											
0	0·000	0·010	0·019	0·027	0·034	0·040	0·046	0·051	0·055	0·059	10 to 4
10	0·062	0·065	0·068	0·070	0·071	0·072	0·073	0·074	0·075	0·075	3 ,, 0
20	0·075	0·075	0·075	0·075	0·074	0·073	0·073	0·072	0·071	0·069	0 ,, −1
30	0·068	0·067	0·066	0·064	0·063	0·062	0·060	0·058	0·057	0·056	−1
40	0·054	0·053	0·051	0·050	0·048	0·047	0·046	0·045	0·044	0·043	−1
50	0·042	0·041	0·040	0·039	0·038	0·038	0·037	0·037	0·037	0·036	−1 to 0
60	0·036	0·036	0·036	0·037	0·037	0·037	0·038	0·039	0·040	0·041	0 ,, +1
70	0·042	0·043	0·045	0·046	0·048	0·050	0·052	0·054	0·057	0·059	1 ,, 2
80	0·062	0·065	0·068	0·072	0·075	0·079	0·083	0·087	0·091	0·095	3 ,, 4
90	0·100	0·105	0·110	0·115	0·121	0·127	0·133	0·139	0·145	0·152	5 ,, 7
100	0·159	0·166	0·173	0·181	0·189	0·197	0·205	0·213	0·222	0·231	7 to 9
110	0·240	0·250	0·260	0·270	0·280	0·290	0·301	0·312	0·323	0·335	10 ,, 12
120	0·347	0·359	0·372	0·385	0·398	0·411	0·424	0·438	0·452	0·466	12 ,, 14
130	0·481	0·496	0·511	0·527	0·543	0·559	0·575	0·592	0·609	0·626	15 ,, 17
140	0·644	0·662	0·680	0·699	0·718	0·737	0·757	0·777	0·798	0·819	18 ,, 21
150	0·840	0·861	0·883	0·905	0·927	0·950	0·973	0·996	1·020	1·044	21 to 24
160	1·069	1·093	1·118	1·143	1·169	1·195	1·223	1·250	1·278	1·306	24 ,, 28
170	1·334	1·362	1·391	1·420	1·450	1·480	1·511	1·542	1·573	1·605	28 ,, 32
180	1·637	1·669	1·702	1·735	1·768	1·802	1·836	1·870	1·905	1·941	32 ,, 36
190	1·977	2·013	2·050	2·087	2·125	2·163	2·202	2·241	2·280	2·320	36 ,, 40

200 2·361 REGNAULT (uncorrected) h = 203·20 at 200° C.

If the specific heat were constant and equal to unity the value of ϕ would be

$$2{\cdot}30259 \log_{10} (t+273{\cdot}1)/273{\cdot}1.$$

The values of the specific heat, total heat, and entropy between 0° C. and 100° C. are for a constant pressure of 1 atmosphere. The values above 100° C. are for water under saturation pressure. The difference between saturation pressure and 1 atmosphere would not affect the values by 1 in 10,000 below 100° C.

In conclusion, my best thanks are due to Mr. W. J. Colebrook, Superintendent of the Physics Workshop of the Imperial College, and to other members of the staff under his direction, for the great care and skill displayed in making and adjusting the platinum thermometers and other apparatus required for this investigation.

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II. *A Critical Study of Spectral Series.—Part II. The p and s Sequences and the Atomic Volume Term.*

By W. M. Hicks, *Sc.D., F.R.S.*

Received January 24,—Read March 7, 1912.

Notation and Abbreviations.

Part I. refers to the First Communication on this Subject in the 'Phil. Trans.,' A, vol. 210, *p.* 57 (1910).

$n = 10^8/\lambda$ = wave number = number of waves per cm.
Adopted formula $n = \mathrm{A} - \mathrm{N}/(m+\mu+\alpha/m)^2$.
A is the limit of the series = n when $m = \infty$.
ν_1, ν_2 denote the first and second triplet separations.
Δ_1, Δ_2 denote the differences in μ which give rise to ν_1, ν_2.
w denotes the (atomic weight)/100.
v denotes the atomic volume.
Rydberg's notation for the series is adopted. Thus—
P denotes a principal series, S sharp, D diffuse, F the series in the ultra red whose limits depend on the first D sequence. K. and R. call the S the 2nd associated and D the 1st associated series. F is often referred to as Bergmann's series.
ZnS denotes the three sharp series of Zn.
$\mathrm{ZnS_2}$ the second S series of Zn.
$\mathrm{ZnS_1}$ (3) the 3rd line in the first S series of Zn.
$\mathrm{HgD_{21}}$ (3), $\mathrm{HgD_{22}}$ (3) denote respectively the chief line and the first satellite of the 3rd order in the second diffuse series of mercury.
$\mathrm{N}/(m+\mu+\alpha/m)^2$ in any series, say P, is referred to as VP (m), the V standing for variable part.

K.R. stands for Kayser and Runge.
E.H. stands for Exner and Haschek.

The present communication is in continuation of one presented to the Society in 1909. The greater part of the work was completed at that time, and it was hoped that it would be published shortly afterwards. Certain points, however, arose which the author was anxious to settle, and this led to a consideration of a number of spectra in which series of the ordinary type had not yet been recognised. He hopes to deal with some of the most interesting points which have come to light in the

Published separately, June 17, 1912.

course of that consideration, chiefly connected with the atomic weight term, and the constitution of certain spectra, in an ensuing paper. In the present one the constitutions of the sequences on which the Principal and Sharp series depend, and their relation to the atomic volume of the element, which were brought to light in Part I., are further considered in connection with the spectra of the second and third groups of elements. It was hoped to have included in the third group the high melting-point sub-group Sc, Y, La, Yb, and considerable progress had been made in reducing their spectra. They all show doublet series of S and D types, but their complete consideration would have taken so much time, better devoted to the general constitutional points which had arisen, that it was decided to postpone it. The evident importance, however, of the comparative study of all the elements in the same group of the periodic system made it seem desirable to give some attention to those elements which might possibly fill the gaps. It is generally acknowledged that these belong probably to elements associated with the rare earths, and their atomic weights give some indication of the places they should fill. Their spectra consist of a multitude of lines chiefly of medium or small intensity, and their complete discussion involves a great deal of time and close attention. All those, however, which the author has so far investigated show more or less analogous relationships, intimately connected, and irresistibly suggesting the *débris*, so to say, of strong lines. The connection is based on certain properties of the atomic weight term referred to above. The evidence of the spectrum of Eu leaves little doubt but that it fills the vacant space between Cd and Hg. Probably the gap between In and Tl is occupied by Gd. A superficial consideration of the spectrum of the latter shows a large number of doublets with a separation of 5000.* This number agrees with its atomic weight and its position between In (2212) and Tl (7792). As is well known, the spectrum of Ra is quite analogous to those of the Ca group, whilst possibly the gap between it and Ba may be filled by another radio-active substance. An attempt has been made to allot the S and D series of Eu and Ra and the result is given in Appendix I. In response to suggestions made to me in respect of Part I., I have ventured to give in a second appendix lists of the S and P series lines of the elements considered in the present communication.

The type of formula used here and in Part I. has been employed by MOGENDORFF in a still earlier paper read before the Royal Society of Amsterdam in November, 1906. He there showed that the formula reproduces the lines of Li, Na, Zn, and Tl in the different series with great exactness, and stated that he had also obtained corresponding formulæ for other elements.

The fact that the series depends in some way on the atomic volume of the element has been pointed out by REINGANUM.† He showed that if the atomic volumes of the 2nd group of elements be divided by 4, and those of the 3rd by 6, and if the

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* There are 53 within ·50 of 5000, or 76 within 1 A.U. of that value.

† 'Phys. Zeitsch.,' 5, p. 302.

logarithms of these modified atomic volumes and of the limits of the S series be plotted, then, with the exception of Zn and In, the corresponding points lie roughly on a straight line.

The p-sequence.—In determining the formulæ constants for the Sharp series, it immediately becomes evident that they are based on the P-sequence, viz., that which in the alkalies give the Principal series. It is impossible to get constants based on the S-sequence to reproduce the lines within considerable multiples of the possible errors. Not only does the P-sequence do so, but it will be found in correspondence that the Principal series are formed on the S-sequence, viz., that which in the alkalies gives the Sharp series. Confirmatory evidence is also afforded from the facts that the relationships between the constants are of a similar kind to those found in the alkalies and that the limit of the Principal series (S-sequence) is the same as the variable part of the first line of the Sharp whilst that of the Sharp is not rigorously the same as the variable part of the first line of the Principal. In other words, VP and VS denoting sequences, the limit of the Principal series is VP (1), whilst that for the Sharp series deviates considerably from VS (1). This fact renders the notation of the sequences introduced in Part I. confusing. The confusion may, however, to some extent be avoided if small letters are used to denote sequences and large letters the lines or series. Thus, in these elements $\mathrm{VP}(m) = s(m)$ and $\mathrm{VS}(m) = p(m)$.

The features of the p-sequence, as developed in Part I., are (1) $\mu = 1+f$ where f is a fraction (2) if the denominator be written in the form $1-\mathrm{W}(1-m^{-1})+\mu+\alpha m^{-1}$, where W is the atomic weight term, α is negative, α/μ is a constant (·215), μ is proportional to the atomic volume of the element, and $p(1) = \mathrm{S}(\infty)$. The s-sequence has (1) $\mu = f$, α negative, μ about ·5 less than the corresponding value for the principal and $s(1)$ is not $\mathrm{P}(\infty)$ but very nearly so, being always slightly less.

In the alkalies it was found necessary, if RYDBERG's relations between the limits of the S and P series were to be valid, that a very small term in m^{-2} had to be applied, although it was unnecessary, so far as reproducing the lines within observational error was concerned. In the present case, also, no term in m^{-2} is required for the Zn or Tl groups. In the alkaline earths themselves such a term βm^{-2} is required, β, however, being a small fraction of α.

The formulæ constants determined for the various elements are given in Table I. They are determined, as a rule, by taking the measures of the first three lines as having no observational errors, the limits of variation of constants due to these possible observational errors being given in brackets, as in Part I. It is found, however, that in the case of Zn, Cd, Hg, Sr it is necessary to allow for these errors if the subsequent lines are to come within observational limits. In these cases the constants have been slightly modified within permissible limits so as to bring all within, and the numbers attached to the constants in the tables are limits allowable on these modified constants. There is some uncertainty in the case of Ba. The series is ill defined. No lines were assigned by KAYSER and RUNGE to the S series—

TABLE I.

	S(∞).	μ.	α.	β.	ν, Δ.
Mg . . .	39752·83 (2·73) 39758·38 (1·12)	1·382492 (3605) 1·376746 (419)	− ·075952 (9336) − ·062211 (257)	·008307 (5890)	40·92, 19·87 ·000856, ·000413
Ca . . .	33983·45 (5·80) 33994·85 (1·10)	1·574562 (7058) 1·561400 (498)	− ·108386 (17663) − ·077202 (438)	·018813 (10986)	105·89, 52·09 ·002791, ·001368
Sr. . . .	31027·65 (4·00) 31037·27	1·643036 (5868) 1·631491	− ·111113 (14501) − ·083879	·016412 (8969)	394·38, 186·95 ·011836, ·005533
Ba . . .	28642·63	1·672500	− ·054144		878·21, 370·33 ·029328, ·011976
Ra . . .	22760·00	1·783424	− ·176286		2050·26, ? ·092658, ?
Zn . . .	42876·42 $\begin{pmatrix}+3{\cdot}34\\-1{\cdot}08\end{pmatrix}$	1·287059 $\begin{pmatrix}-1059\\+\ 461\end{pmatrix}$	− ·059160 $\begin{pmatrix}-1059\\+563\end{pmatrix}$		389·20, 190·21 ·007207, ·003475
Cd . . .	40710·60 $\begin{pmatrix}+2{\cdot}15\\-\ {\cdot}73\end{pmatrix}$	1·349486 $\begin{pmatrix}-846\\+294\end{pmatrix}$	− ·067133 $\begin{pmatrix}-738\\+264\end{pmatrix}$		1170·85, 542·02 ·023106, ·010370
Eu . . .	40364·08 40397·87	1·291603 1·267384	− ·047520 − ·010971		2630, 1004 ·051222, ·018327
Hg . . .	40139·55 $\begin{pmatrix}+5{\cdot}41\\-\ {\cdot}99\end{pmatrix}$	1·309577 $\begin{pmatrix}-1700\\+300\end{pmatrix}$	− ·068280 $\begin{pmatrix}-1438\\+\ 272\end{pmatrix}$		4630·46, 1767·01 ·087815, ·030002
Al . . .	48161·46 (2·49)	1·250525 (771)	− ·063349 (662)		112·15 ·001754
Ga . . .	46318·16 (?)	1·292185	− ·077314		826·10 ·013542
In. . . .	44454·76 (2·48)	1·287479 (870)	− ·069510 (769)		2212·38 ·037684
Gd . . .	?				5000
Tl. . . .	41470·23 (1·72)	1·264328 (534)	− ·070417 (456)		7792·39 ·134153

In the above table the two values given for Mg, Ca, Sr correspond respectively to the cases with βm^{-2}, and without the term in β. The last column gives in the first line the values of the doublet or triplet separations (ν_1 and ν_2), and in the second line the values of the Δ, *i.e.*, the quantities deducted in the denominator of $S_1(\infty)$ to give $S_2(\infty)$; in other words, they are the atomic weight terms on which ν_1, ν_2 directly depend.

in fact, they only observed the triplet S(2), $S_1(3)$, $S_2(3)$ of the next and $S_1(4)$—too few to give the series. The triplet S(1) was observed first by LEHMANN[*] (more accurately later by HERMANN[†]) and the series completed and arranged by SAUNDERS.[‡] The first three are only sufficient to determine the constants with a only; in the analogous cases of Mg, Ca, and Sr the limits so determined have all come out too large. Here it makes the calculated values of wave numbers for $S_1(4)$ and $S_1(5)$ differ from those assigned by SAUNDERS by amounts too large respectively by 71 and 159—in other words, the limits here, also, are much too large if his allocations are correct. If we use his allocation of $S_1(4)$ and attempt to find constants for βm^{-2} we get a formula quite out of line with the others. The first impression is to infer that SAUNDERS' allocation of the two last lines is quite wrong, but a closer acquaintance with other series gives more caution and suggests another way of meeting the difficulty. As a fact, it is difficult to represent all the P series, and especially the D series by any modification of the simple formulæ hitherto used. In the case of AlD it seems impossible to do so at all. Further, it will be shown in Part III. that the atomic weight term plays a very important part in producing new lines or displacing expected ones.

New lines are produced by the addition (or subtraction) of multiples of the atomic weight term to the denominators in the formulæ which irresistibly suggest modified molecular groupings. The full evidence for this can only come later when these lines are being discussed, but as bearing more especially on this part of the subject it will be convenient here to show how it enables us to explain why in the alkalies RYDBERG'S relations $S(\infty) = p(1)$ hold while the other $P(\infty) = s(1)$ does not. (F, G of Part I., pp. 75–76.)

If the first term of a series is modified by the addition of a number to the denominator, it may still be possible to represent the series by a formula containing am^{-1} only. If, however, the second be also changed in a similar way, it will in general not be possible to do so. We shall require a third term, βm^{-2}, so that the successive changes in the denominator produced by the two alterations may be represented. If a change be also made in the third line, it may still be possible to retain βm^{-2} only because it is an addition to a large number (m large), and it may still be possible so to apportion the four formulæ constants that the calculated results err by amounts less than the observational errors. In general, however, the limit will be considerably wrong. In Ca and Sr the limit with βm^{-2} is certainly very nearly the correct value. But, as above mentioned, βm^{-2} is not sufficient for Ba. Now we have before us the results of the discussion of the alkalies, where it was found that if RYDBERG'S relations (*i.e.*, F, G) are both to hold the p-sequence must have a small term βm^{-2} and the s-sequence a term βm^{-2}, in which β is of the same

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[*] 'Ann. der Phys.' (4), 8, p. 650 (1902).

[†] 'Ann. der Phys.' (4), 16, p. 698 (1905).

[‡] 'Astro. Phys. Jour.,' 28, p. 223.

order as the α. But the difficulty may be met as follows: If D denotes the denominator of $s(1)$ and D′ that of $P(\infty)$, the values of D−D′ instead of being zero are respectively (see Part I., p. 76)—

Na . . .	·002772±(8390);	Rb . . .	·010696+(16119), −(3210);
K . . .	·009150±(8716);	Cs . . .	·01672± ?

The values of 2W or Δ are given at the bottom of p. 80, viz.:

Na.	K.	Rb.	Cs.
·000744,	·002933,	·012887,	·032435,

whence*

$$\begin{aligned} 8W &= \cdot 002976 = \cdot 002772 + 1/41 \times \text{possible error for Na,} \\ 6W &= \cdot 008799 = \cdot 009151 - 1/25 \times \quad ,, \quad ,, \quad \text{K,} \\ 2W &= \cdot 012887 = \cdot 010696 + 1/8 \ \times \quad ,, \quad ,, \quad \text{Rb,} \\ W &= \cdot 016217 = \cdot 016712 - \ ? \quad ,, \quad ,, \quad \text{Cs.} \end{aligned}$$

It is thus possible to assert the truth of RYDBERG's relations if they are referred to the sequences—but not if referred to the series. The value of the first line of the S series is found by adding a multiple of the atomic weight term to the sequence term for that line, viz., 8W for Na, 6W for K, 2W for Rb, and W for Cs. The essential point now is that the term in βm^{-2} does not enter. In any case the multiple is to be obtained by first determining the real limit of the series and then the change in the denominator calculated for $m = 1$ to correct it to the observed value. This suggests a similar explanation for the appearance of the βm^{-2} terms in the Ca group, either an addition of an atomic multiple to the first term of the p-sequence, or the deduction of the same multiple from every term after the first, and this suspicion is intensified when we notice that the values of the β are themselves multiples of the atomic weight terms. If we compare the values of β and of Δ_2, given in Table I., this is at once clear. We find with extreme closeness

Mg.	Ca.	Sr.
$\beta = 20\Delta_2$,	$14\Delta_2$,	$3\Delta_2$.

To obtain the proper values for the limit it is found necessary to deduct from the observed denominators respectively $5\Delta_2$, $5\Delta_2$, Δ_2. Ba is too uncertain to get definite results from. If all SAUNDERS' lines belong to BaS and the modification depends on an addition to the first term only, it is necessary to deduct $12\Delta_2$ from the first and the μ and α become so large in comparison with the values for the other elements as to render the explanation very doubtful. It can, of course, be met by deducting multiples from the second line as well as the first, but we can have no certain grounds

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* Too much weight must not be given to these as the possible errors are so large.

to work upon until we can get some evidence as to what the limit really is. The constants determined for the three elements in this way are given in the following scheme. Values for Ba are also given on the supposition that Δ_2 is subtracted in the same way as for Sr.

For

Mg . . $n = 39754{\cdot}31 - \mathrm{N}/\{m+1{\cdot}379975-{\cdot}067249m^{-1}\}^2$ add $5\Delta_2$ for $m = 1$,
Ca . . $n = 33981{\cdot}96 - \mathrm{N}/\{m+1{\cdot}572477-{\cdot}094220m^{-1}\}^2$,, $5\Delta_2$,,
Sr . . $n = 31027{\cdot}58 - \mathrm{N}/\{m+1{\cdot}640373-{\cdot}097552m^{-1}\}^2$,, Δ_2 ,,
Ba . . $n = 28619{\cdot}23 - \mathrm{N}/\{m+1{\cdot}692912-{\cdot}084616m^{-1}\}^2$,, Δ_2 ,,

In the following Table II. a comparison of the calculated values with the observed is given. The first column under the element gives the maximum permissible error and the second the difference between calculated and observed. The third column, under Mg, Ca, Sr, gives the same difference when the lines are calculated from the formula in βm^{-2}. Under Eu no estimates of observational errors are available, and the two columns refer to the two series referred to in the text below and in Appendix I. In all cases the deviations are only given for the first lines of a doublet or triplet.

It will be seen that the only real deviations from observed values greater than the possible are for TlS (4) and CaS (5). In the case of TlS (4) the doublet separations given by the observed values is too small by 1·5, and the calculated value corrects this. The whole of the calculated values agree so closely with the observed as to make it certain that the error must be in the observed. The observed is 2665·67—a transcription error of 2665·76 would bring the two sets in agreement. As to the case of CaS (5) the line 3181·40 also gives an incorrect separation ν_1 which the calculated corrects. It has an observed accuracy of ·03 A.U., and the calculated differs by 15 times this amount. It should be noticed, however, that its intensity is higher than we should expect, viz., 4 as against 1 for S (5). Moreover it is an enhanced line and therefore does not belong to the S-series. It is probable, therefore, that it hides the true S line, which should be about 3181·00 and of less intensity.

A curious point is that in In the S_2 lines appear to be more persistent than the S_1. Kayser and Runge give a line 2200·0 as $\mathrm{S}_2(8)$, with possible error ·30. The calculated, however, deviates by more than 5 times this from the observed, and as the formula reproduces the other lines with good accuracy it is probable that 2200 is wrongly assigned to S, or should be 2201·6.

Connection of α *and* μ.—The study of the alkalies led to the result that the denominator of the *p*-sequence can be thrown into the form $m+1-\mathrm{W}(1-m^{-1})+\alpha(1-km^{-1})$, where W is the atomic weight term, and k is a constant which is about ·21520, the only exception was for Cs for which a slight modification was required. It is important to see whether a similar relationship holds for the analogous sequences in the elements now under consideration. In the alkalies W is one-half the difference

TABLE II.

	Mg.			Ca.			Sr.			Ba.		Zn.		Cd.		Eu.			Hg.		Al.		Ga.		In.		Tl.	
m.	O.	m^{-1}.	m^{-2}.	O.	m^{-1}.	m^{-2}.	O.	m^{-1}.	m^{-2}.	O.	m^{-1}.	O.	m^{-1}.	O.	m^{-1}.	O.	I.	II.	O.	m^{-1}.	O.	m^{-1}.	O.	m^{-1}.	O.	m^{-1}.	O	m^{-1}.
1	·03	·00	·00	·1	·00	·00	·12	·00	·00	?	·00	·03	·00	·05	·00		·00	·00	·05	·00	·03	·00	·10	·00	·10	·00	·03	·00
2	·03	+ ·02	·00	·05	·00	·00	·03	·00	·00	·05	·00	·03	·00	·05	− ·02		·00	·00	·05	·03	·03	·00	·05	·00	·05	·00	·03	·00
3	·03	− ·02	·00	·05	·00	·00		·00	·00	·05	·00	·05	− ·04	·03	·01		·00	·00	·10	− ·07	·05	·00	·05	·00	·05	·00	·05	·00
4	·03	·07	·02	·10	·33	·00	·10	·23	− ·05			·10	·01	·05	·02		·14	− ·01	·05	·03	·10	− ·02			·05	·04	·05	−1 ·21
5	·15	·15	·01	·03	1 ·15	·61	·30	·69	+ ·09			·15	·01	·10	·00		− ·36	− ·02		·02	·10	− ·02			·15	·13	·05	− ·02
6	·50	·10	− ·01	1 ·0	·46	− ·23						·25	− ·15	·30			?	− ·34		·00					·50	− ·12	·10	·00
7																	−1 ·12	+ ·20		− ·01					·30	·03	·15	·02
8																		− ·54		·04					?	1 ·8	·20	·12
9																				− ·03						·35	·20	− ·18
10																				·07							·30	− ·02
11																											·30	·03
12																				− ·10							·30	·12
13																				·19							·30	− ·19
14																												

(Δ) of the denominators which give the doublet separations. Here, however, triplets enter and two constants Δ_1 and Δ_2 appear. It is found that the Zn, Cd, Hg group follows the same rule if W is taken to be Δ_2, which is roughly one-half of Δ_1, but, as in the case of Cs, a modification is required for the high separations of Hg. Using the numbers given in Table I., it will be found that the following forms for the denominators hold:—

$$\begin{array}{llr}
\text{Zn} \ldots & m+1-\mathrm{W}(1-m^{-1})+\cdot290534(1-\cdot21558m^{-1}), & \begin{array}{r}-(762)\\+(606)\end{array}\\
\text{Cd} \ldots & m+1-\mathrm{W}(1-m^{-1})+\cdot359854(1-\cdot21537m^{-1}), & \begin{array}{r}+\ (55)\\-(160)\end{array}\\
\text{Eu} \ldots & m+1-\mathrm{W}(1-m^{-1})+\cdot309930(1-\cdot21246m^{-1}),^{*} & \\
\text{Hg} \ldots & m+1-\mathrm{W}/4 \qquad\qquad +\cdot317077(1-\cdot21534m^{-1}). &
\end{array}$$

The numbers in brackets after each formula give respectively the possible limits of variation of the k. It is clear that, as in the alkalies, k can easily be the same for all.

In Mg and the Ca sub-group we have the complication of the additional terms in βm^{-2}, or of the modified form of the sequence itself with am^{-1} only. In the first case β, as we have seen, is a multiple of Δ_2. The constant ratio k does not enter now unless we use β in place of Δ_2, in which case there results

$$\begin{array}{lll}
\text{Mg} \ldots & m+1-\ \beta(1-m^{-1})+\cdot382462(1-\cdot21533m^{-1})+\beta m^{-2}. & \beta = 20\Delta_2,\\
\text{Ca} \ldots & m+1-\ \beta(1-m^{-1})+\cdot574797(1-\cdot21572m^{-1})+\beta m^{-2}. & \beta = 14\Delta_2,\\
\text{S} \ldots & m+1-2\beta(1-m^{-1})+\cdot676156(1-\cdot21404m^{-1})+\beta m^{-2}. & \beta = \ 3\Delta_2,\\
\text{Ba} \ldots & ? &
\end{array}$$

The modified form does not so naturally fall into line. It is, of course, only a matter of calculation to put in a term $x(1-m^{-1})$ such that the ratio of a/μ left over is the same constant as in the other cases. If we confine ourselves to multiples of Δ_2 or of $\Delta = \Delta_1+\Delta_2 = 3\Delta_2$ roughly, and use multiples of these to give a/μ as nearly as possible constant, we get the following results:—

$$\begin{array}{ll}
\text{Mg} \ldots & m+1-15\Delta\ (1-m^{-1})+\cdot399010(1-\cdot21624m^{-1}),\\
 & m+1-45\Delta_2(1-m^{-1})+\cdot398605(1-\cdot21545m^{-1}),\\
\text{Ca} \ldots & m+1-\ 9\Delta\ (1-m^{-1})+\cdot609908(1-\cdot21585m^{-1}),\\
 & m+1-27\Delta_2(1-m^{-1})+\cdot609413(1-\cdot21522m^{-1}),\\
\text{Sr} \ldots & m+1-\ 3\Delta\ (1-m^{-1})+\cdot692393(1-\cdot21602m^{-1}),\\
 & m+1-\ 9\Delta_2(1-m^{-1})+\cdot690053(1-\cdot21336m^{-1}),\\
\text{Ba} \ldots & m+1-\ 2\Delta\ (1-m^{-1})+\cdot775746(1-\cdot21584m^{-1}),\\
 & m+1-\ 7\Delta_2(1-m^{-1})+\cdot776744(1-\cdot21685m^{-1}).
\end{array}$$

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* Might quite possibly be $\cdot215$, see Appendix I. [also note at end].

These last arrangements are, of course, no argument in favour of the constant ratio ·21520. They can only be regarded as suggestions of the way in which the $1-m^{-1}$ term may enter if we know that the constant ratio has a real existence, and that this modified sequence is the correct form. But in the present state of our knowledge nothing is to be gained by attempting a closer approximation. It may, however, be noted that the general agreement between the two arrangements Δ and Δ_2 is due to the fact that except for Ba Δ is roughly $3\Delta_2$. Also as affecting the argument in favour of the arrangement, it may be mentioned that a change of unity in the multiples of Δ or Δ_2 in the most favourable direction towards the value ·21520 affects that ratio in the two cases as follows, viz.:—

For Mg . . ·21380, ·21626; Ca . . ·21054, ·21697; Sr . . ·19588, ·21960;

and, of course, very much larger deviations for Ba.

A glance at Table I. shows that in Al and the Ga sub-group the α is always larger than $\cdot 215\mu$. In fact, the actual ratios of α/μ are

Al . . ·2528; Ga . . ·2641; In . . ·2419; Tl . . ·2664.

These cannot be the same within observation limits, and even in the Ga sub-group In is too far out to be due to mere errors of observation. It is clear, therefore, that no terms in $1-m^{-1}$ can occur in the same way as in the other cases.

In the discussion of the alkalies the term $W(1-m^{-1})$ was supposed to be based on the F-sequence, which was taken to be $m+1-2W(1-m^{-1})$. Here we have only two lines each in Al and Tl allocated to the F* series by RITZ, whilst those for the other elements of this group have not yet been observed. The limits of the F series are the values of VD (2). Using this, the denominators of the F series are found to be

$$\mathrm{Al} = m+1-\cdot 043761\,(1-m^{-1}),$$

$$[25\Delta = 50\mathrm{W} = \cdot 043850 \pm (24)],$$

$$\mathrm{Tl} = m+1-\cdot 037389\,(1-m^{-1}).$$

If now as before the p-sequence be supposed based on the F-sequence, but that the factor $1-m^{-1}$ does not now occur, the denominator for Al may be written

$$m+1-\cdot 043761+\cdot 294286\,(1-\cdot 21526m^{-1}).$$

Unfortunately we are not able to compare with the other elements of the Al sub-group (Sc, Y, La) to see if they follow an analogous rule; but the appearance of the

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* Called by some German writers BERGMANN'S series, as he discovered the analogous series in the alkalies.

constant ratio is at least suggestive. A similar arrangement does not hold for Tl, but we have been led not to expect it in the highest atomic weight of a group. If we define W as before, viz., $2W = \Delta$, we can write for the formulæ

$$\begin{aligned}
\text{Al} &= m+1-50W+\cdot 294286\,(1-\cdot 21526m^{-1}),\\
\text{Ga} &= m+1-10W+\cdot 359895\,(1-\cdot 21483m^{-1}),\\
\text{In} &= m+1-\ \ 2W+\cdot 325202\,(1-\cdot 21478m^{-1}),\\
\text{Tl} &= m+1-\quad W+\cdot 331405\,(1-\cdot 21248m^{-1}).
\end{aligned}$$

Ga and In may give ·21520 within observation limits.

The foregoing results, combined with those previously obtained for the alkalies, produce a strong conviction that the number ·21520 is an essential constant—possibly for all elements—but at the same time raise the question of the cause why they do not follow precisely the forms shown by the alkalies, the Zn group, and to some extent by the alkaline earths.

Atomic Volume Term.—In the spectra of the alkalies it was found that when the p-sequence was thrown into the form considered above the μ was very nearly proportional to the atomic volume, and still more nearly so if the denominators were written $m+\cdot 987\ldots+$, &c. Since the atomic weight term disappears when $m = 1$ the same result should hold for the denominator of $p(1)$, with the advantage that this can be determined much more precisely than μ. The value of the atomic volume of an element as calculated from its atomic weight and density must have some degree of indefiniteness, depending as it does on the temperature and physical state of the substance when its density is measured. Nevertheless there must be some physical property peculiar to each element of which the atomic volume as usually determined is a rough measure, and it is this which would occur in the spectral formulæ if the relation indicated in the alkalies is a reality. Probably the relation between this physical constant and the atomic volume would be exact if the latter were determined at absolute zero. Failing the possibility of doing this we might try to extrapolate downwards by using the coefficient of expansion determined at ordinary temperatures, or compare the substances in corresponding states, say at the melting-points. In this first survey, however, it is needless to attempt such refinement, and we shall confine ourselves to seeing what evidence there is that such relationships do enter, and try to get a rough idea of the way in which they do.

It will be better to discuss the relationship on the basis of the denominator of $p(1)$ rather than μ, the former being less dependent on errors of observation. In Part I. the quantities in question were considered as being proportional to the atomic volume, but as a result of the discussion below it will be found best to consider them as proportional to twice the atomic volume. The constant of the ratio for the alkalies was not determined; but the values of the denominators there given, combined with the values of the atomic volumes given by RICHARDS and BRINK,* lead to values of $D/2r$, given by the first line of figures in the following table:—

Na.	K.	Rb.	Cs.
·002466	·002578	·002615	·002541
·002761	·002732	·002740	·002640

the values for Cs being very uncertain. The values show first a gradual rise with atomic weight, and then a fall. The fall of melting-point, *i.e.*, increase of the measured atomic volume on nearing the melting-point, would explain a fall in the ratio shown by Cs. The first rise must be explained by another cause. Now, it was pointed out in Part I. that the proportionality (a/μ) was closer if the denominators were measured from about ·986 instead of 1, the number ·986 having appeared in quite another relation. In other words, a number about ·014 should be added to the fractional part of the denominator. If this be done, the results obtained are shown in the second line of figures in the above table. In this case, the exactness of the ratio is striking, the fall in Cs being probably due to error of formula as well as closeness of melting-point. We may take the ratios as very close to ·002740. This is for the alkali elements. It now remains to see whether any similar relationships hold for the elements here considered.

Taking first the Zn sub-group, the following values are obtained from Table I. for the values of the fractional parts of the denominators of $p(1)$, *i.e.*, of VS (1):—

Zn . . ·227900 ; Cd . . ·282353 ; Eu . . ·244083 ; Hg . . ·241297.

The densities at ordinary temperature, as given in LANDOLT and BÖRNSTEIN, are respectively

Zn . . 7·01 ; Cd . . 8·65 ; Eu . . ? ; Hg . . 13·55 ;

which give for the atomic volumes at ordinary temperatures

9·33, 13·00, ?, 14·76.

It is clear, at a glance, that the above denominators cannot be proportional to the atomic volumes, but it is easy to show that in Zn, Cd, and Hg they are respectively proportional to $9r$, $8r$, and $6r$. In fact, the ratios to these come out to

$$·002715 \times 9r, \quad ·002715 \times 8r, \quad ·002725 \times 6r.$$

The ratios show a remarkable agreement with themselves and also with those of the alkalies when referred to ·986. The practically exact equality of the above

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* 'Jour. Amer. Chem. Soc.,' 1907, p. 117.

numbers must be due to chance, for they would be altered by the slight alteration in density as measured in different physical conditions. We should be prepared to expect a considerable difference in the number for Hg, as it is so far above its melting-point. Without, however, giving any special weight to the exactness of the agreement, it yet affords strong evidence for the dependence of the p-sequence on the real atomic volume in the manner indicated. If Eu behaves in an analogous way we should expect it to be proportional to $7v$, *i.e.*, $\cdot 244083 = \cdot 002720 \times 7v$ or $v = 12\cdot 86$, whence, taking the atomic weight of Eu to be 152·03,* the density of Eu at ordinary temperatures should be about 11·86, *i.e.*, intermediate between those of Cd and Hg, as is to be expected.

In the case of the alkaline earths we have to consider the two forms of the sequence—(1) that involving βm^{-2}, and (2) that in which multiples of Δ_2 are added to give the first spectral line of the series. Also, in the first form the question arises whether the quantity to be discussed should be the denominator of VS (1) or with β left out. In fact, if the atomic volume term is the factor μ when the denominator is thrown into a form containing a term $\mu(1-\cdot 21520m^{-1})$, then the quantity to be considered would be the latter, assuming the results given in (p. 41). For comparison both cases are treated, 1 (*a*) and 1 (*b*), in the table below. The fourth line gives the numbers for Case (2). As in the Zn sub-group it will be found that multiples of v enter.

	Mg ($8v$).	Ca ($7v$).	Sr ($6v$).	Ba ($6v$).	Ra (xv).
Density . . .	1·72	1·57	2·54	3·77	1·02x
1 (*a*)	·002783	·002731	·002649	·002862	
1 (*b*)	·002710	·002625	·002570	?	
2	·002764	·002693	·002623	·002782	

The densities used in calculating are the means of those given by LANDOLT and BÖRNSTEIN; the values for Ca and Sr are not very accurate. In the case of Sr the density is given as between 2·50 and 2·58; the latter would alter the numbers above for Sr to ·002664 in Case (2) and ·002690 in Case 1 (*a*) The number for Ba is calculated on the doubtful basis of (p. 39), and it is necessary to take a multiple of $6v$. If SAUNDERS' allocation be correct the value of S (∞) is very much less, and the value of the denominator of VS (1) is close to 1·492765. In this case, if a multiple $5v$ is taken, the ratio is ·002705. Moreover, this ratio is in analogy with the others, and, so far, it adds weight to SAUNDERS' allocation. It is quite possible that the value of SrS (∞) is too high, which would result in too small a value for the ratio. The numbers, however, are sufficiently close for all these elements to afford additional

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* JANTSCH, 'C. R.,' 1908, vol. 146, p. 473.

evidence for the dependence on atomic volume.* In doing so, however, the best result is obtained by 1 (a), *i.e.*, by taking the values of the denominator of VS (1) without any modification, although (2) is nearly as good.

The density found for Ra, using as constant ·002740, is 1·02x, where x is a whole number. If the number for Ba is 6, *i.e.*, the same as for Sr, we might expect that 6 might be a limit and $x = 6$ for Ra. If for Ba the ratio is 5, then x might possibly be 5. If, however, the series runs down in regular order, then allowing for the gap between Ba and Ra, x would be 3, giving a density 3·06, *i.e.*, less than that of Ba. If $x = 5$ or 6, the densities calculated are 5·10 and 6·12; either are in fair order with the other elements of the group.

If the elements in the third group are treated in the same way, using the densities Al = 2·583, Ga = 5·95, In = 7·26,† Tl = 11·85, Al does not fall into step with the others. The results are

$$\begin{aligned} \text{Al} &= \cdot 002744 \times 6\cdot 5v, \\ \text{Ga} &= \cdot 002613 \times 7v, \\ \text{In} &= \cdot 002760 \times 5v, \\ ? &= \quad ? \\ \text{Tl} &= \cdot 002816 \times 4v. \end{aligned}$$

The agreement with the supposed law is very unsatisfactory, and in the case of Al is clear against it. Al is the case where, in order to produce the ·21520 constant, the μ had to be referred to the F-sequence (p. 42), which produced an addition to μ of ·043761. If this be done in this case also, the value of the denominator comes out to be ·002751 × 8v. This is so close to the law that it suggests the possibility of the elements of the third group behaving like the alkalies—themselves elements with doublet series. In that case it was found necessary to refer the quantities in question to ·986 + f, *i.e.*, add ·014 to the $\mu+\alpha$, where ·986 was a constant for the whole group. If so the result for Al would indicate that the constant for the third group should be ·956239, *i.e.*, (1 − ·043761), or that the quantity ·043761 should be added to the $\mu+\alpha$ as found. If this is done the following scheme results:—

Al.	Ga.	In.	Tl.
·002751 × 8v,	·002752 × 8v,	·002758 × 6v,	·002761 × 5v,

which recalls the close agreement found with the Zn group.

Probably the F-sequence depends on the group constant (·956) plus a multiple of the atomic weight term. For Al this is very small, so that the group constant would be somewhat smaller than ·9562 determined from the F. The difference would not appreciably affect the coefficients above. This would explain, however, the apparent

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* These results for the two groups were given in a paper read before Section A of the British Association at the Sheffield meeting (1910). 'Rep.,' p. 574.

† Mean of values given by LANDOLT and BÖRNSTEIN.

dependence of the value required on the F-sequence of Al, whilst the corresponding value from Tl is very different, viz., ·962661. For suppose the F-sequence takes the form $m+$ group constant $+\Delta(1-m^{-1})$ (see Part I.). The Δ for Al and Tl are respectively ·001754 and ·134153, whilst m is always 2 for the first line of the F series. Hence the difference of the values of the denominators of the F series of Al and Tl is $\frac{1}{2}(·134153-·001754) = ·06620$, whilst the values found are $·962611-·956239 = ·006372$, sufficiently close to show that the above explanation may be on the right lines. The fact that ·014 and ·0437 are in the ratio 1 : 3, *i.e.*, of the valencies of the Groups I. and III., may be a coincidence, but should be borne in mind for future testing. The results for these two groups suggest a similar kind of group constant for Zn and the Mg sub-groups of II., but if so no F series have yet been observed to determine them. It is at least to the point to notice that such a term would raise the coefficients of the Zn set (·002715) more to an equality with the values (·002755) of the Al set.

The evidence for the dependence of the p-sequence on the atomic volume is therefore strong from all the cases in combination. The actual value of the constant (·002740) cannot be accurately determined as yet, because we have no knowledge of the actual value for any element of the physical quantity we denote by "atomic volume"; but it is probably not far from ·002740. The results of the foregoing discussion therefore point to the p-sequence being of the form $a(1-km^{-1})sv$, where a and k are constants for all elements, not very different from $·002740/(1-k)$ and ·21520 respectively; v is the essential atomic volume of the element (possibly sphere of activity), and s is a whole number. How s depends on the position of the element in its group is a problem which it is to be hoped further knowledge may solve. Putting $k = ·21520$ makes a approximately $= ·003490$.

The values of s for the elements so far considered are as follows:—

Na 2	Mg 8	Zn 9	Al 8	Ga 8
K 2	Ca 7	Cd 8	Sc ?	In 6
Rb 2	Sr 6	Eu 7 ?	Y ?	?
Cs 2	Ba ? 5 or 6	Hg 6	La ?	Tl 5
	?		Yb ?	
	Ra ? 5 or 6			

The Term in $W(1-m^{-1})$.—This term does not affect the first line in the series, and its appearance would seem to indicate the possibility of some modification of the formula. In the course of some calculations connected with the Zn series, it was noticed that the lines could be reproduced when this term was absent provided the value of N was slightly altered for all terms beyond the first. It seemed worth while to test whether a similar connection held for other elements. The method adopted was to use the limit obtained by the earlier formulæ, calculate the denominator in VS (1), throw it into the form $\mu(1-·21520m^{-1})$ $(m=1)$, use this as the denominator for the succeeding terms and calculate the value of N required to reproduce the observed value. These were then corrected so that the separations of the S_1, S_2, and S_3 lines should have the constant value found for ν_1, ν_2. As an example, the case of Zn may be taken. The limit is 42876·42 and $D_m = m+1+{\cdot}290534\,(1-{\cdot}21520m^{-1})$. The results, with possible errors due to possible observational errors, are as follows :—

m.	
2	109790·5 ± 5·6
3	109783·8 ± 12·39
4	109817·7 ± 42·0
5	109836·7 ± 94·5
6	109618·0 ± 220

These numbers require correction to make the values of ν_1, ν_2 correct, viz., 389·19, 190·20. For $m = 2$ the observed values are 388·75, 190·09, *i.e.*, difference of −·44 and −·10. Least squares give as the most probable corrections −·33 to n_1, ·11 to n_2, and ·21 to n_3. This adds a correction of ·6 × possible variation, *i.e.*, 3·3 to the N, making N = 109793·8. Similarly for $m = 3$, ν_1 is ·46 too small and ν_2 is ·33 too small. Treated in the same way a correction of $\frac{10}{17}$ the possible must be added, making N = 109791·1. It is clear that the value of N can easily be constant and = 109790 ± 5 within limits of error. In fact, with this value the errors in λ are respectively about 0, $\frac{1}{2}$, $\frac{3}{5}$, $\frac{1}{2}$, $\frac{3}{4}$ the possible ones. The results are given in the following table :—

	N.	ξ.	μ.	δN.
Zn (5)	109792 (3)	0	·290534	117 (3)
Cd (4)	110022 (2)	0	·359856	346 (2)
Hg (9)	109607 (4)	0	·307463	− 68 (4)
Mg (5)	110457 (3)	− 1	·400856	782
Ca (5)	111406 (4)	− 1	·617130	1737
Sr (4)	111704 (2)	− ·6	·697845	2030
Ba (2)	113023 (3)	− 19	·789911	3348
Al (4)	109267 (4)	0	·238500	− 398
Ga (2)				
In (6)	109348 (6) 109400	0	·277705	− 332 − 175
Tl	109088 109200	0	·247083	− 577 − 475

The numbers after the chemical symbol (*e.g.*, Zn (5)) give the number of lines involved; ξ is a small alteration in the limit S (∞) as determined from the three first lines of a series. It is unnecessary to give α, as the formula for D_m is $m+1+\mu\,(1-{\cdot}21520m^{-1})$. The slight uncertainty in the last two digits of the number ·21520 will not appreciably modify the result. It is noticeable that the limits in the cases of the Mg group, in which a term m^{-2} was found to be necessary, are close to those found when the series is determined from the first three lines only, and consequently with the term in m^{-1} only. In Hg only nine lines out of the whole known were compared ($m = 2 \ldots 9$ and 12). In all there appear only four exceptions to the rule that the calculated values of N are constant in any one series after the first. They occur in Ca, Sr, In, and Tl. In Ca for $m = 3$ the number is $111458 \pm 8{\cdot}5$ instead of 111406 ± 4. In Sr for $m = 3$ the number is $111779 \pm$? This triplet is interesting as having been missed in K. and R.'s first list of the Sr spectrum and as having been calculated by RYDBERG. The other two exceptions are for In and Tl, in which the values appear to go in two steps, viz., for In 109348, 109348, $109390{\cdot}3 \pm 22{\cdot}6$, 109390, with the two last equal to either within limits of error. If ξ be taken to be -1 they may, however, all be brought to 109343 by allowing the maximum observational errors, but this is scarcely permissible. In Tl $m = 2, 3$ give 109088, $m = 5, 6$ 109200, $m = 6$ either value, whilst $m = 4$ gives 108671. The last is the case mentioned on p. 39, where there is a large error between calculated and observed, and in which a transcription error is suggested. If the value given by the original formula is used, the value for N becomes 109134. Here also, with a small change in the limit, the value of N may be made the same, but only at the expense of allowing maximum errors. It is probable the two last cases correspond to a real change. It is to be noted that, mercury excepted, all the elements of Group II. show a greater value than RYDBERG'S constant 109675, whilst those of Group III. show a less value. The generality of the rule is striking, but a further discussion must be postponed until the atomic weight terms are considered. It does not, of course, affect the question of the atomic volume terms considered above, as the reasoning there is based on the first terms of the series, in which N retains the normal value. It may be noted that this change of N gives the ratio $\alpha\mu^{-1} = {\cdot}21520$ for *all* the elements, and explains why the rule to deduct $W(1-m^{-1})$ always failed for the elements of large atomic weight.

The Principal Series.—No principal series were known in the 2nd and 3rd group of elements until PASCHEN[*] discovered those of Zn, Cd, Al, Tl and suggested certain lines in those of Mg, Ca, and Hg. Those for the first four were clear and definite, and little doubt could be felt as to the correctness of their identification as a whole. The same certainty cannot be felt as to those for Mg and Ca, and, in fact, I give below certain considerations which tend to throw doubt on some of them. The first definite observations of the HgP are due to MILNER,[†] who gave the lines of orders 5 to 16. For 5 to 8 he gave values for P_1 and P_2 but, as later work of PASCHEN has shown, he allocated the P_2 lines to the real P_1 and his P_1 lines do not come into the direct line of the series, although it is possible they may be collaterals. Since then PASCHEN[‡] has published a long list of lines observed by WIEDMANN, and has attempted

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[*] 'Zur Kenntnis ultraroter Linienspectra," 'Ann. der Phys.,' 29 (1909).

[†] "The Series Spectrum of Mercury," 'Phil. Mag.,' XX. (1910).

[‡] 'Ann. d. Phys.' (4), 35.

to complete the series. It is, however, difficult to be certain as to any identification proposed, as there is a maze of lines in this portion of the spectrum. Below I propose certain changes in his identification, for reasons which will be given.

If we now discuss the series for Zn, Cd, Al, and Tl we find that the limits of the series, as found from the lines as a whole, agree very closely with the values of VS (1), but the calculated values of VP (1) deviate very considerably from the values of S (∞). This is in agreement with the deduction already drawn that the S series depend on what was called the *p*-sequence in Part I., and the P series on the *s*-sequence. When, however, we attempt to find the constants μ and α in the usual way we get formulæ which reproduce the lines with fair accuracy in the case of Zn only. It is possible to modify the form so as to get good agreement within observational errors, but it seems preferable to proceed in another way and attempt to discover the connection between the P_1, P_2, and P_3 terms and the relationship which undoubtedly exists between the S and P series by direct comparison of their values. Such relationship will most probably show itself between the values of corresponding denominators. The values obtained, on the supposition of constant N, are given below. For comparative study the corresponding numbers are given for the alkalies.

As in previous cases figures in brackets after a number give the greatest possible variations in the last digits of the number, so far as the variation depends on errors of observations. Other systematic variations may enter by the possible changes in the limits P (∞) or S (∞). With the exception of the alkalies the values for S are calculated from the formulæ (see Table I.). Then VS (1) (or *p* (1)) is taken to be P (∞), and using this as the limit the denominators for the P lines are calculated direct from their observed values. This method, therefore, assumes the validity of the relation P (∞) = *p* (1) = VS (1). In the cases in question, as we have seen, this has always been found to be the case. In the case of the alkalies, however, one of the relations indicated does not hold unless we use the limit found directly from the series (see Table II., Part I.), and that accordingly has been done. Since, however, the top lines in the alkalies are so ill determined the value of P (∞) is used for VS (1). CsS (2) is so uncertain that the value from the formula is also inserted. RbS (2) is also from the formula, as BERGMANN'S observed value is very considerably in error. The difference between corresponding numbers are entered between them.

Arranged in this way a number of facts emerge at once. Regarding Zn, Cd, Al, and Tl, they all with one or two exceptions clearly indicate a general law that from $m = 2$ onwards the denominators for the different triplets or doublets in each element differ by the same amount, and that this amount is somewhere about ·7 to ·8 times the corresponding difference for $m = 1$, which gives the values of Δ_1, Δ_2, or the atomic weight terms. We may feel justified, therefore, in using this as a test to apply to PASCHEN'S allocation of the upper lines of the P series for Hg. The values

TABLE III.

Zn.

P_3	1·588669 (4)	2·748325 (36)	3·774784 (9)	4·784770 (30)	5·789948 (62)	6·792134 (570)
	3474	**2525**	**2414**	**2375**	**2283**	**2788**
P_2	1·592143 (3)	2·750850 (28)	3·777198 (9)	4·787145 (30)	5·792231 (62)	6·794922 (570)
	7209	**5355**	**5191**	**5154**	**5026**	**5343**
P_1	1·599352 (2)	2·756205 (19)	3·782389 (9)	4·792299 (30)	5·797257 (62)	6·800265 (570)
		528306	**524910**	**524960**	**524988**	**525038**
S_1		2·227899 (6)	3·257479 (83)	4·767339 (240)	5·272269	6·275227

P(∞) = 22096·29

Cd.

P_3	607869 (5)	784277 (25)	813109 (1137)	825854 (25)	831951 (57)	
	10368	**6980**	**6461**	**6407**	**6249**	
P_2	618237 (5)	791257 (25)	819570 (700)	832261 (28)	838200 (57)	
	23109	**17423**	**18269**	**17109**	**17160**	
P_1	641346 (4)	808680 (25)	837839 (222)	849370 (26)	855360 (57)	858125 (205)
		526358	**522077**	**522459**	**522874**	**522294**
S_1		282322 (0)	315762 (80)	326911 (120)	332486	335831

P(∞) = 21054·39

Hg.

P_3	535163	748179	764993	781676	793655	793650
	30002	**24779**	**23817**			
P_2	565165	772958	788810	**96518**	**96451**	**96760**
	87815	**71967**	**71364**			
P_1	652980	844925	860174	878194	890106	890410
		603628	**584737**	**591377**	**597599**	**594489**
S_1		241297	275437	286817	292507	295921

P(∞) = 21832·78

TABLE III. (continued).

			Al.			
P_2	507300	675177 (78)	701930 (23)	711820 (48)		
	1751	**1329**	**1377**	**1380**		
P_1	509051	676506 (78)	703307 (23)	713200 (48)	719220	
		489330	**484456**	**483791**	**484532**	
S_1		187176	218851	229409	234688	237855
			P(∞) = 22926·65			
			Tl.			
P_2	492090	694690	727011	739157	743478	759420
	134154	**94018**	**91195**	**90615**	**92157**	**85635**
P_1	626244	788708 (35)	818206 (15)	829811 (30)	835635	835780
		594887	**589176**	**589045**	**589001**	**585635**
S_1		193821	229030	240766	246634	250155
			P(∞) = 22786·01			
			Na.			
P_2	2·116161	3·132020				
	741	**770**				
P_1	2·116902	3·132790 (38)	4·138086 (200)	5·140442 (865)	6·142040 (1584)	
	490162	**490198**	**491053**	**491219**	**492503**	
S_1	1·626740	2·642592	3·647033	4·649223	5·650537	
			K.			
P_2	2·231690 (200)	3·262250 (28)	4·272653 (89)	5·277685 (200)	6·278840 (1174)	
	2939	**2975**	**2990**	**3167**	**2593**	
P_1	2·234629 (200)	3·265225 (28)	4·275643 (89)	5·280852 (200)	6·281433 (1174)	
	·464597	**·464325**	**·465725**	**·466967**	**·465168**	
S_1	1·770032	2·800900 (64)	3·809918 (267)	4·813885 (76)	5·816265 (475)	

			Rb.			
P_2	2·278956 (55)	3·316160 (28)	4·328553 (149)	5·334080 (314)	6·334350	7·339014
	12889	**12962**	**12995**	**13699**	**12415**	**12172**
P_1	2·291845 (55)	3·329122 (28)	4·341548 (149)	5·347779 (314)	6·346765	7·351186
	487501	**483147**	**485326**	**486337**	**482227**	
S_1	1·804344 (53)	2·845975 (?)	3·856222 (700)	4·861442 (270)	5·864538 (450)	
			Cs.			
P_2	2·328360 (30)	3·373705 (45)	4·389278 (236)	5·397220 (1090)		
	32492	**32104**	**32155**	**32025**		
P_1	2·360852 (30)	3·405809 (45)	4·421433 (236)	5·429245 (1090)	6·443220	
	491944	**490109**	**487789**	**489611**	**499599**	
S_1	1·868908	2·915700 (3390)	3·933644 (138)	4·939634	5·943621	
		2·921641				
		484168				
			Mg.			
P_3	1·659732					
	414					
P_2	1,660146					
	855					
P_1	1·661001	2·817586 (132)	3·847690 (864)	4·862890 (2616)	5·871649 (5523)	
		·502739	**·501097**	**·504792**	**·507626**	
S_1		2·314847 (6)	3·346593 (46)	4·358098 (125)	5·364023 (280)	
			P(∞) = 20467·39			
			Ca.			
P_3	1·792310	3·055350				
	1368	**963**				
P_2	1·793678	3·056313				
	2792	**1995**				
P_1	1·796470	3·058308 (65)	4·124116 (996)?			
		·573314	**·599043**			
S_1		2·484994	3·525073	4·540524		
			P(∞) = 16760·56			

of the denominators calculated for his lines, the first line being, of course, taken to be also the first of the S series, are as follows :—

P_3 . .	1·535163	?	3·764993	4·775856	5·780490	6·782813
	30002		**4944**	**18593**	**13165**	**10837**
P_2 . .	1·565165	2·734512	3·769937	4·794449	5·793655	6·793650
	87815		**9763**	**84538**	**96441**	**96760**
P_1 . .	1·652980	?	3·860174	4·878987	5·890106	6·890410

The numbers clearly do not follow the law. It is possible, however, to select a set which do so, but only by supposing that the P_2 lines from $m = 4$ and beyond do not occur. They are given in the table above, where the agreement with the law is evident. Paschen also suggests another set for $m = 2$, in which the separations are still more out of order, viz. :

2·734512
13667
2·748179
159052
2·907231

He supports this with a considerable list of combination terms, which, though striking, do not prove that the lines in question belong to the direct P series. In fact, there is evidence that some of these combinations are related to the D series. Further, I hope to show, in the next part, that his $P_1(2)$ here is a collateral of the singlet P series discovered by him and published in the same paper. A comparative list of the lines is given in Appendix II.

A similar rule is seen to hold (as was indeed known from the results of Part I.) in the case of the alkalies, except that here the difference of the P_1 and P_2 is the same for all orders. In this group, it will be remembered, the principal series is based on the p-sequence.

Another law also appears in the relation of the Sharp series to the Principal, viz., that the denominators for the Sharp series of any element are found by deducting a constant value from the corresponding denominator of the Principal series, except that the difference is a greater one for the first term, they are roughly as follows :—

Zn . . ·5283, ·5249 ; Cd . . ·5263, ·5224 ; Al . . ·4893, ·4844 ; Tl . . ·5949, ·5891 ;
Na . . ·4901 ; K . . ·4660 ; Rb . . ·4856 ; Cs . . ·4880 ;

a similar arrangement also is shown by the suggested allocation in Hg, viz., ·6036, ·59, an additional evidence in its favour. The differences between P and S in the list do not appear to be rigorously constant after $m = 2$. This can be easily explained by very small changes in the limits $P(\infty)$ or $S(\infty)$. In fact, as has been seen already, Rydberg's law does not appear to be quite rigorously exact. Paschen's

2·907231 would make the first number ·6659, and, therefore, quite out of analogy with the others. Again, in the alkalies the same law is seen, with just the same modification as in the previous case, viz., constant for each.

A closer inspection shows that the differences between the P terms cannot be exactly constant after $m = 2$. They seem to descend in two steps instead of one. The general law, however, seems so well established that the cause of the real variation is to be sought. It is possible it may be due to the properties of the atomic weight term. The second law, however, affecting S, P seems to be very closely followed. It should be noticed that the alkalies and Al give differences less than ·5, whereas the others give values greater than ·5. It suggests that the remainder of the Al sub-group, viz., Sc, Y, La, Yb, would also require values less than ·5. If such a rule held for the two sub-groups in each group of the periodic table, we should expect the Mg, Ca, &c., to require values less than ·5. The evidence, however (see below), is rather against this so far as any evidence is available.

In the alkalies the Principal series are formed on the p-sequence, and the subtraction of the respective constants by the second of the above laws gives the first term of the S series as hitherto recognised. The question naturally arises, what becomes of the term deduced in a similar way from the first term of the s-sequence, and do lines exist corresponding to these? If we attempt to calculate them we must know the value of the constant to be deducted. Is it the same as for $m = 2$, which is larger than that for the others, or is it a number larger still? If we use the rough values obtained for $m = 2$ in Table III. and apply them to $m = 1$, the following values of the denominator result:—

Zn . . 1·0710 ; Cd . . 1·1170 ; Hg . . 1·0494 ; Al . . 1·0203 ; Tl . . 1·0313 ;

corresponding to lines in the neighbourhood of

	Zn.	Cd.	Hg.	Al.	Tl.
S_3 . . .	1916	2198	1884		
S_2 . . .	1909	2173	1824	1752	1856
S_1 . . .	1896	2119	1682	1748	1622

We should expect such lines, if they exist, to be exceptionally strong. A number of weak lines are known in these regions, but the only strong ones that could possibly belong are the Cd lines—

Intensity.	λ.	n.	
1	2170·11	46066·38 ± 10·6	
			551·26 ± 14
$4r$	2144·45	46617·64 ± 4·3	
			1076·36 ± 15
$3n$. . . .	2096·1	47694·00 ± 11	

but the nature of the three lines are different and 1076 is about $\frac{9}{10}\nu_1$. The ν_2 should be 542 and the observed is within limits of error. Al has a weak doublet

1	1857·56	53816·42	
			100·66
3	1854·09	53917·08	

The separation is probably within error limits of $\nu = 112$, but is as it stands also about $\frac{9}{10}\nu$. The evidence is therefore against the existence of the terms in question, but the possibility of the lines splitting up into collaterals of smaller intensity, as is the case of HgP, should be borne in mind.

If the Cd triplet is correctly assigned, viz., $n = 47694$, the number to be deducted from the s-sequence should be ·5275 in place of ·5243. This is as much above ·5243 as that is above ·5222.

We may now proceed to consider Paschen's identification of lines for the MgP and CaP series in the light of the regularities discovered above. In applying them it is necessary to decide on the limits to employ, using, at least at first, Rydberg's law as to their connection. The limit calculated for MgS from the first three lines gives (see Table I.) 39758·18 ± 1·12, and from the first four (*i.e.*, term in m^{-2}) 39752·83 ± 2·73, from which Rydberg's law gives ($\mathrm{MgS}_1(1) = 19285{\cdot}44$) respectively 20472·74 and 20467·39. The value 39752 agrees best with the measurements of the higher orders, whilst 20464·43 is the actual limit calculated from the three first lines of Paschen. Taking then $\mathrm{S}(\infty) = 39752{\cdot}83$ and $\mathrm{P}(\infty) = 20467{\cdot}39$, the numbers for comparison are given in the table above, using for $\mathrm{P}_1(2)$ Paschen's bolometer reading (7655·3), as it gives the most favourable comparison. It will be seen that the differences are respectively 2739 (138), 1097 (900), 4792 (2741), 7626 (5803). These by rather forcing the limits of variation can be made to give typical differences of about, say, 2700, 2000. A closer agreement can, of course, be found by allowing Rydberg's law to be only approximate. The result of the discussion, therefore, does not contradict Paschen's identification.

In view, however, of the suspicion raised above that the difference for Mg and Ca might be expected to be less than ·5, it will be interesting to see if lines satisfying this can be found. Out of observed lines, however, I have only been able to find two which might fit in with this system, viz., $15768{\cdot}3 = \mathrm{P}_3(2)$, $15759{\cdot}1 = \mathrm{P}_2(2)$. These give values of the denominator of ·786281 and ·786645 with a difference 364, fitting in well with that of $\mathrm{P}_3(1)$ and $\mathrm{P}_2(1)$, but there is no appearance of a $\mathrm{P}_1(2)$, which should have a difference of about 4725 over the denominator of $\mathrm{S}(1)$.

For Ca Paschen gives for the first triplet 19856·9, 19935·8, 19946·8, and for the first of the next triplet 9546·8. Using limits on the same basis as for Mg it is found the $\mathrm{P}(\infty) = 16760{\cdot}56$, $\mathrm{S}(\infty) = 33983{\cdot}45$. The first S triplet, which Rydberg's law makes also the first of the P, gives separations 2792 and 1368. Paschen's first triplet gives 2600 and 359, which is not in order. If, however, the line 19917·5 observed also by him be taken for P_2, the separations become 1995, 963, and quite in order, being both about ·7 times the first set. In the table above I have, therefore, ventured to insert it in place of his selection, although it coincides with an undoubted D line. The denominator of this triplet is ·5733 above the corresponding one for S. His next is ·6510 above it, which is far out and cannot be made normal by any reasonable change in the limits. If the line 9694·5 be taken the difference becomes ·5990, which is better but still too large. This is the only other available line observed in the neighbourhood, so that it is probable that the first line of the next triplet has not been observed.

Summary.

1. The most important result of the discussion would seem to be the considerable weight of evidence, in addition to that afforded in Part I., that the series lines—at least the Principal and Sharp—depend in a very definite way on a certain physical quantity peculiar to each element which is approximately measured by what is generally understood as its atomic volume. The numerical evidence afforded from a study of the low melting-point elements of the first three groups of the Periodic Table is remarkably exact. The numerous lines of all these series are represented within limits of error, and as a rule with extreme closeness, by the formula adopted. The argument is based on the denominator of $p(1)$, and this is determinable with great exactness; in fact, any possible error in this due either to error of observation or error in the limit chosen for the series will exert practically no influence on the result.[*] A change in N might do so to some extent. Any uncertainty is due to uncertainty in the values used for the atomic volume, which might amount to as much as 1 per cent., *e.g.*, changing 2740 by 30. The high melting-point elements of Group II. do not show the law with such certainty, but there are clear indications of it. In these elements the type of formula has required a modification, and, in addition, the series are not well developed in the higher members Sr, Ba and Ra. Consequently the limits are not determined with such certainty as in the other cases. Nevertheless Mg and Ca quite fall into line with the others, and even in Ra it is possible to give some indications of the value of the density of the solid metal.

The fact that the terms depend on multiples of atomic volumes as ordinarily calculated may be interpreted in one of two ways. Either that the periods of the vibrating configurations do actually depend on multiples of the essential atomic volumes *or* that multiples do not enter here, but that the packing together of the configurations when they are aggregated into solid masses is closer or less close. *E.g.*, compare Zn with factor 9 and Hg with factor 6. The period of Zn may depend

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[*] An increase of ξ in the limit of Zn would alter the ratio by $(1 - \cdot 00022\xi)$, and ξ cannot be more than a few units. In the case of Ba only is ξ indeterminate to the extent of so much as 170, and for Ba the corresponding factor is $(1 - \cdot 00013\xi)$, large enough to require a change in the multiple of ν.

on 9 times its volume constant, and Hg on 6 times its corresponding volume constant. On the other hand, Zn and Hg may depend on their volume constants in the same way, but the centres of the Zn molecules be packed 9 times more closely together than in the normal case, and the centres of the Hg molecules 6 times. On the first view the multiples depend on the internal configuration of the atom, on the second on the configurations of the molecules in gross matter, in other words, on the value of the ratio atomic weight to density. If the first interpretation is correct, we might expect to find other series in an element depending on other multiples. I am not sure that I have not observed indications of such, but it will require further search before a definite reply can be given. On the second interpretation no such additional lines can be expected.

2. Additional evidence to that obtained in Part I. has been afforded of the existence of a universal constant, approximately ·21520, which gives the ratio of α/μ in the p-sequence $\mu+\alpha/m$, and also in the s-sequence if certain relations indicated between the s- and p-sequences are found to be exact. This constant must be a pure number[*] in contradistinction to N, which is of the dimension $(\text{length})^{-1}$.

3. A comparison of the denominators of $VP_1(m)$, $VP_2(m)$, $VP_3(m)$ has indicated that whilst in the alkalies they differ by the same amount in the same element for all orders, in the 2nd and 3rd groups the difference proceeds in two steps, viz., that after the first order the remaining differ by the same amount, and that this is about ·7 times the difference for $m = 1$. Further, a comparison of the above with $VS(m)$ shows that a similar law holds between the denominators of $VS(m)$ and $VP(m)$. These laws are applied as a criterion to the lines allotted by PASCHEN for HgP, MgP, and CaP, and, in consequence, certain modifications are suggested.

4. It is found in the 2nd and 3rd groups, in opposition to the rule in the first, that the S series follows the p-sequence and the P series the s-sequence.

5. An attempt is made to arrange the S and D series for Europium and Radium. Eu is found to fit the gap between Cd and Hg and a density 12·58 deduced for it. The density of Ra should be $1·02x$, where x is probably 5 or 6.

APPENDIX I.

The S and D Series of Europium.

The only published spectra of Europium are the arc and spark spectra of the ultra violet lines by EXNER and HASCHEK. CROOKES[†] has observed, but not published, its spectrum, but remarks that the Europium used by EXNER and HASCHEK must have contained several impurities. EXNER and HASCHEK'S list of arc lines contains over

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[*] $2/(3\pi) = ·21511$.

[†] "On Europium and its Ultra-Violet Spectrum," 'Roy. Soc. Proc.,' 74, p. 550 (1905).

500 lines shorter than 4698. A photograph of a portion of the longer wave-length, kindly given me by Sir W. CROOKES, contains a few faint lines above EXNER and HASCHEK'S limit, as well as a few others not given by the latter.

Scandium and its group, Yt, La, Yb, show doublet series.* On the contrary, Europium, with which they are associated, has a spectrum of triplets with separations 2632 and 1004. Moreover, when expressed as fractions of the square of the atomic weight (152·03),† these are found to be in correspondence with those for Cd and Hg, and therefore suggest that Eu is the member wanting in the Periodic Table between those elements; if so, we should expect to find the corresponding S and D series, which are well developed in Cd and Hg, as well as other peculiarities. Unfortunately, however, the first line $S_1(1)$ and $S_2(1)$ should come about 5400 if they are similar to Cd and Hg, and this region is outside the published lists.

It is possible, however, to allocate observed lines to fit the conditions for the S and D series. They are given in the following lists:—

SHARP SERIES.

	λ.	n.	ν.
$m = 1$	(5379·1)‡	(18585·5)	
			2632·5
	(4711·69)‡	(21218)	
			1004
	4498·81	22222·00	
$m = 2$	3322·01	30093·73	
			2629·42
	3055·07	32723·15	
			1001·38
	2964·35 spark	33724·53	
$m = 3$	2909·10	34365·08	
			2633·86
	2701·99	36998·94	
$m = 4$	2744·36	36427·75	
			2634·60
	2559·30	39062·35	
$m = 5$	2659·50	37590·17	
$m = 7$	2577·69	38783·00	

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* Discussion deferred to a later communication.

† JANTSCH, 'C. R.,' 1908.

[‡ See note at end.]

DIFFUSE SERIES.

	λ.		n.			ν.	
$m = 2$	3637·84	spark	27480·99	**2630·69**	30111·68	**1004·13**	31115·81
	3638·22		27478·27	**2633·41**			
	3629·94		27541·00	**2630·45**	30171·45		
	3619·97		27616·83				
	3320·03						
	3313·46						
	3212·89						
$m = 3$	3004·9	spark	33269·45	**2632·45**	35902·00	**1002·45**	36904·45
	3001·48		33307·36				
	2708·91	spark					
$m = 4$	(2787)		(35869·76)	**2632·5**	38502·26		
	(*2786*)		*35881·25*				
	2596·49	spark					
$m = 5$	2683·29	spark	37258·85	**2632·5**	(39891·35)		
	2682·72		37264·77				
	(2506)						
$m = 6$	(2624·72)		(38088·08)	**2632·5**	40720·59		
	(*2624·36*)		(*38093·38*)				
	2455·03						
$m = 7$	(2588·18)		(38625·87)	**2632·5**	41258·37		
	(*2587·96*)		(*38629·12*)				
	2423·03	spark					
$m = 8$	2564·27		38986·05	**2648·07**	41634·22		
	2401·15	spark					
$m = 9$	2387·41	spark			41873·94		

The first two λλ for S 5379·1 and 4711·69 are extrapolated from the observed faint line 4498 by taking $\nu_1 = 2632{\cdot}5$ and $\nu_2 = 1004$, which is about the mean value of the ν's. Several other alternatives might be taken, but this gives the best analogy with Cd and Hg. The first three lines give for the formula

$$n = 40364{\cdot}08 - \mathrm{N}/\{m + 1{\cdot}291603 - {\cdot}047520m^{-1}\}^2$$

with errors for $m = 4$, 5 of ·14 and ·36, probably within any observational error. The values of the Δ come out (with $\nu_1 = 2630{\cdot}5$ and $\nu_2 = 1004$) to

$$\Delta_1 = {\cdot}051222 = {\cdot}022162w^2,$$
$$\Delta_2 = {\cdot}018327 = {\cdot}007929w^2.$$

Δ_2 is intermediate to those for Cd and Hg, viz., $\cdot008208w^2$ and $\cdot007500w^2$ respectively, but for the latter Δ_1 are $\cdot018289w^2$ and $\cdot021953w^2$, so that Δ_1 for Eu is a slightly larger multiple of w^2 than for Hg, supposing that the atomic weight of Eu is correctly given as 152·03.

The ratio $(\alpha + \mathrm{W})/(\mu + \mathrm{W})$, which ought by analogy to be ·21520, is ·21246. But the uncertainty of the top line might account for this: *e.g.*, if this supposed line be taken 2·2 A.U. greater this ratio would be ·21520 with $\mu + \mathrm{W} = {\cdot}310572$.

There is some appearance of a satellite series for EuS., viz., the lines whose wave numbers are

$$\left.\begin{array}{ll} \mathrm{S}_{12}(1) & (18516{\cdot}60) \\ \mathrm{S}_{22}(1) & (21150) \end{array}\right\} \text{based on } 22155{\cdot}46,$$
$$\mathrm{S}_{12}(2) \quad 30090{\cdot}02 \quad \mathbf{2633{\cdot}13} \quad 32723{\cdot}15.$$

These give the formula

$$40361{\cdot}90 - \mathrm{N}/\{m + 1{\cdot}294528 - 053875m^{-1}\}^2,$$

in which the calculated values of λ for $m = 4$ and 5 differ from the observed by ·12, ·41. The limit is so close to the former that they may be taken as coincident, indicating, therefore, that the lines are satellites as ordinarily understood. There appear, also, to be series associated with these. For instance, writing the wave numbers, with separations,

S_1.	ν_1.	S_2.	ν_2.	S_3.
(18858)*	**2633**	21491·37 (1+)	**998**	22489·34 (1)
or (18856)*	**2630**	(21486)	**1003**	22489·34 (1)
30090·02 (3)	**2633·13**	32723·15 (4)	**1001·38**	33724·53 (1+) spark
34365·08 (3)	**2633·86**	36998·94 (4)		
36440·76 (2)				
37604·15 (1+)				
38325·24 (2) spark				
38789·61 (2)				
39128·98 (1) spark				

the numbers in brackets denoting intensities.

[* See note at end.]

With 18856 for the first line the first three give

$$n = 40397\cdot87-N/\{m+1\cdot267384-\cdot010971m^{-1}\}^2,$$

and the differences of λ from the observed for $m = 4, 5, 6, 7, 8$ are respectively $-\cdot01$, $-\cdot02$, $-\cdot34$, $+\cdot20$, $-\cdot54$. The last possibly does not belong to the series.

The agreement is good and the extrapolation is made on an observed pair S_2 and S_3, so that there is a temptation to take it as the real S series. The μ and the α are not, however, analogous to those of Cd and Hg, and the ratio $(\alpha+W)/(\mu+W)$ is about ·1 instead of ·215.

The following lines also give a parallel series :—

S_1.	ν_1.	S_2.	ν_2.	S_3.
(19913·0)	**2633·80**	22546·80 (1+)	**1004·39**	23551·19 (2)
30171·45 (2)				
31626·68 (5)	**2635·05**	39061·73 (1).		

The first is extrapolated as before by ν_1 only. The second has no observed lines for ν_1 or ν_2, the magnitudes seem in wrong order, and no other orders have been observed. Little weight can therefore be given to it. But the formula is

$$40440\cdot60-N\,\{(m+1\cdot379503-\cdot068050m^{-1}\}^2,$$

with a limit about half way between those of Cd and Hg, and with a ratio $(\alpha+W)/(\mu+W) = \cdot21703$. Moreover, the ν_1's associated with the three series show an increase with the limit, as should occur. For instance, $\Delta_1 = \cdot051160$ would give respectively 2629, 2631, 2635 for limits 40364, 40397, 40440. This is quite in accordance with the general constitution of spectra.* The abnormal intensities may be due to the kind of instability referred to above.

The D series has been filled up by using spark lines where arc were wanting. If, as we suppose, Eu is analogous to Hg, the spectrum taken from the salt on the carbon arc might be expected to partake somewhat of the nature of a spark spectrum. To get a spectrum analogous to the simple spectrum of Hg use should be made either of the arc *in vacuo*, or with the salt in a vacuum tube. In addition, it is reasonable to expect that the wanting elements throughout the horizontal row in the Periodic Table might show a greater amount of instability in the molecular groupings than the corresponding elements in the vertical groups. I hope to show in a future communication that there is direct evidence of such re-groupings in other spectra, and that we can obtain indications of their nature. If the grouping peculiar to a particular series is subject to an excessive disrupting force in the production of the spectrum, a few only will survive, and consequently the line observed will be faint,

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* "On the Dependence of the Spectrum of an Element on its Atomic Weight," 'Brit. Assoc. Reports,' 1911 [p. 342].

and others be observed displaced according to certain laws. The matter is far too large to deal with here and will require a paper to itself. I mention it here, however, in order that judgment may be suspended if any natural doubt is felt concerning the small intensities of the series, the mingling of the arc and spark lines, and the various lacunæ which appear. That lacunæ actually do occur in EXNER and HASCHEK'S list is shown by the absence of the line 4552·6 from the arc, its appearance as a weak line in the spark, whilst it is of considerable strength in CROOKES' photograph.

In the list of D lines those in brackets have not been observed. They are either D_{12} lines deduced from D_{21}, or D_{21} deduced from D_{12}. The lines in italics are those calculated from the formula for D_{11}. The values of D_{11} and D_{12} gradually converge, as they should do, their differences being

75·83, 37·91 ?, 11·49, 5·92, 5·30, 3·25.

There may be some doubt whether the series generally assigned to the diffuse for Zn, Cd, Hg are really diffuse. The α term is negative, and agreement within observational errors is obtained only by using $m-{\cdot}5$ instead of m, but they are clearly of the same type for all these elements. The formula for Eu was therefore taken of this form. The constants were determined by using the same limits as for S, viz., 40364·08, and only the *two* first lines. The result for D_{11} is

$$n = 40364{\cdot}08 - N/\{m + {\cdot}956046 - {\cdot}068460/(2m-1)\}^2.$$

D_{21} is determined from this by finding the difference between the μ's for the first line of D_{11} and D_{12}. This is practically the same as $\Delta_1/6$, and the altered μ is used for the calculation of the succeeding values. The table gives the difference between the observed and calculated values, on the supposition that ν_1 is 2632·5. The third column is the result if ν_1 be taken as 2633. As throughout the paper, * denotes a line used for calculation.

m.	D_{11}.	D_{21}.	D_{21}.
2	*	*	*
3	*	·53	
4		− ·29	− ·25
5	− ·02	− ·22	− ·18
6		− ·02	·00
7		− ·03	·00
8	·60	− ·52	− ·49
9		+ ·76	+ ·79

(The last two are probably not the real lines.)

In this note I am not going into the question of the constitution of the Europium spectrum in general. Indeed, the list of triplets with separations 2630 and 1004 is a very long one, and, in addition, there are the usual narrow triplets depending on the D satellites. As an example of a strong triplet the following set may be taken, all of intensity 50 on Exner and Haschek's scale:

λ.	n.	ν.
4435·74	22537·95	
		2630·30
3972·16	25168·25	
		1003·87
3819·80	26172·12	

The S *and* D *Lines of Radium.*

Judging from the falling off both in intensity and number of the S and D lines as we pass from Mg and Ca to Sr and Ba, it might be expected that the corresponding series for Ra—two places farther on in the Periodic Table—would be difficult to allocate even if they were present at all. The difficulty is increased the more because the only spectral measures published are those of the spark, in which these series are always weakened. Spark spectra, in general, show a greatly increased number of lines which are related to one another in quite definite ways and many related to series lines. This makes the search for doublets much more difficult, as there exist whole series of doublets with separations slightly different from one another. This necessitates a complete study of the whole spectrum in order to feel complete certainty in any allocation of lines to a series, unless such series is clearly marked by many terms. There is, therefore, some degree of uncertainty in the allocation proposed below, in spite of the evidence adduced in its favour.*

The most complete and reliable measurements of the spectrum are those of Runge and Precht,† between 6487 and 2709. Their plates were only sensitive up to 6500. In addition, Exner and Haschek publish tables both for the arc and spark, but their material can hardly have been pure. They give comparatively few lines, and probably not so reliable as their other lists.

Even in Runge and Precht's work it is probable that most of the lines which would be comparable with the weaker ones in the Ba lists have not been observed. The result is that it is not so easy to allocate the D series, as the separations result from a pair of lines the second of which is strong and the other is a not observed weak satellite of the first. In consequence we shall get separations less than the true ν_1 and ν_2, and this is exemplified in the list which follows. The wave-numbers only are given—the wave-lengths will be found in Appendix II.

$$\nu_1 = 2050·27, \qquad \nu_2 = 832·00\ ?$$

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* There is also some additional evidence drawn from their relation to other lines, of a similar nature to that referred to under Europium.

† 'Ann. der Phys.,' 14, p. 419.

The D Series.

$m = 3$	(16107·45)	**2050·27**	18157·72 (4)	**832·00**	18989·71 (6)
	12·31		12·31		
	(16119·76)	**2050·27**	18170·03 (8)		
	3·34				
	16123·10 (10)				
$m = 4$	(18510·67)	**2050·27**	20560·94 (2)		
	1·75				
	18512·42 (8)				
$m = 5$	19804·02 (1)				
$m = 6$	(20582·97) ($\lambda = 4857·05$) ? hidden by $\lambda = 4856·25$ (8)				
$m = 7$	21089·93 (2)				
$m = 8$	21438·12 Exner and Haschek's arc.				

The S Series.

$m = 3$	(14728·20)	**2050·26**	16778·46 (10)	**882·05**	17660·51 (10)
$m = 4$	17846·78 (8)	**2050·27**	19897·05 (1)		
	17879·71 (1)	**2043·50**	19923·21 (4)	**890·95**	20814·91 (2)
$m = 5$	(19440·00)	**2050·22**	21490·22 (1+)	Exner and Haschek's arc.	

In the above the figures in brackets after the wave-numbers represent intensities; the wave-numbers in brackets are those of unobserved lines, put in partly to illustrate the arrangement of satellites.

The lines 16107, 16119 ($\lambda\lambda = 6206·6$, $6201·9$) would be in the region where the photographic plates were insensitive; in fact, the measured lines here are of intensity 4 at least, whereas $\lambda = 6206·6$ would certainly be less (by analogy), but 6201·9 (by analogy) ought to have been seen if it existed, unless overshadowed by the very strong line 16123 ($\lambda = 6200·3$). 18510 would certainly be of small intensity, probably less than those actually measured, but the convergence (3·34) and (1·75) of the two satellites of the lines looks correct. If $D_{13}(3)$ is correctly allotted and $\nu_2 = 882$, there must be a satellite $D_{23} = 18107·66$. Its distance from $D_{22} = 50$, which lies in order with 12·31 and 3·34.

In the S 14728 ($\lambda = 6787·86$) is extrapolated. The next set ($m = 4$) appear to show satellites. It may be noted that an alteration of 7 in $S_2(4) = 19923$ brings both ν_1 and ν_2 into order. The strong line 17846 has been used in the calculation. Exner and Haschek give 21490·22 in the *arc* as a weak line and 19440·58 is extrapolated from this. The value calculated from this formula in m^{-1} is 19430·58, and from analogy with Ba and Sr the true value should be expected to be somewhat larger than this. It should be noted that it is outside EXNER and HASCHEK's region of observation; 21490 may possibly, therefore, be a correct identification for $D_{21}(5)$.

The first three D_{11} lines ($m = 3, 4, 5$) give the formula

$$n = 22760{\cdot}09 - N/\{m + 1{\cdot}130149 - {\cdot}195236m^{-1}\}^2.$$

This gives the following values of obs.−cal. of λ for the next three ($m = 6, 7, 8$), viz., −·78, −·11, −·17. The first is too large for an observational error, and the true line is possibly hidden by the strong line 4856, but there may possibly be another explanation which would at the same time make the others in still better agreement, and bring into relation with the series the strong lines 5041·52 (6), 4856·25 (8). As this depends on the relations of the atomic-weight terms to D series its discussion must be deferred. The object at present is to determine the limit, which cannot be far from 22760·09. This should also be the limit for the S series. Using this with the two first suggested lines* for S_1, *i.e.*, (14728·20) and 17846·78, the resulting formula for S_1 is

$$n = 22760{\cdot}00 - N/\{m + 1{\cdot}783424 - {\cdot}176286m^{-1}\}^2.$$

The separations $\nu_1 = 2050{\cdot}27$, $\nu_2 = 832{\cdot}00$ now give $\Delta_1 = {\cdot}092658$ and $\Delta_2 = {\cdot}034390$, but there is some doubt about ν_2. With this value of Δ_2 the denominator of the formula may be written

$$m + 1 - \Delta_2 + {\cdot}816780\,(1 - {\cdot}21582m^{-1}),$$

in very close analogy with the other cases.

APPENDIX II.

The S *and* P *Series Lines of the 2nd and 3rd Groups of the Periodic Table.*

Mg.			Ca.		
S_1.	S_2.	S_3.	S_1.	S_2.	S_3.
(2) 5183·84	5172·87	5167·55	(2) 6162·46	6122·46	6102·99
3336·83	3332·28	3330·08	3973·89	3957·23	3949·09
2942·21	2938·67	2936·99	3487·76	3474·98	3468·68
2781·53	2778·36	2776·80	3286·26	3274·88	3269·31
2698·44	2695·53	2693·97	3181·40	3170·23	3166·95
2649·30	2646·61	2645·22	3117·74	3107·96	3101·87
MgP 15028·3, 7656·6 ± 1, 6315·6, 5783·4			19856·9 CaP = 19917·5, 9694·5 ? 19946·8		

---

* This is the same as finding S_2 from the actually observed lines allocated to S_2.

Sr.			Ba.		
S_1.	S_2.	S_3.	S_1.	S_2.	S_3.
(2) 7070·7	6878·8	6791·4	(2) 7906·13	7392·83	7195·71
4438·22	4361·87	4326·60	4903·11	4700·64	4620·19
3865·59	3807·51	3780·58	4239·91	4087·53	4026·57
3628·62	3577·45	3553·7	3975·55		
3504·70	3456·78	3434·95	3841·72		

Ra.		
S_1.	S_2.	S_3.
(3)	5958·4	5660·81
(4) { 5601·72	5024·5	
5591·4	5017·9	4803·1
	? 4652·0	

Zn.					
S_1.	S_2.	S_3.	P_1.	P_2.	P_3.
(2) 4810·71	4722·26	4680·38	(2) 13054·89	13151·50	13197·79
3072·19	3035·93	3018·50	6928·58	6938·73	6943·47
2712·60	2684·29	2670·67	5772·22	5775·64	5777·24
2567·99	2542·53	2530·34	5308·71	5310·31	5311·04
2493·67	2469·72	2457·72	5068·71	5069·67	5070·16
2449·76	2427·05	2415·54			

Cd.					
S_1.	S_2.	S_3.	P_1.	P_2.	P_3.
(2) 5086·06	4800·09	4678·37	(2) 13979·22	14327·99	14474·62
3252·63	3133·29	3081·03	7346·10	7382·49	7396·58
2868·35	2775·09	2733·97	6099·31	6111·68	6116·35
2712·65	2629·15	2592·14	5599·11	5604·99	5607·09
2632·29	2553·61		5339·71		
2582·86	2507·93	2474·15			

Eu.

S₁.	S₂.	S₃.	The second series.		
(2) (? 5379·1)*	(4711·69)*	4498·81*	(5301·5)	4651·75	4445·33
3322·01	3055·07	2964·35	3322·42	3055·07	2964·35
2909·10	2701·99		2909·10	2701·99	
2744·36	2559·30		2743·38		
2659·50			2658·51		
			2608·47		
2577·69			2577·25		
			2554·90		

[* 5381·46, 4713·77, see note at end.]

Hg.

S_1.	S_2.	S_3.	P_1.	P_2.	P_3.
(2) 5460·97	4358·56	4046·78	(2) 12071·32	13208	13674·32
3341·70	2893·67	2752·91	6907·78	7044·27	7092·456
2925·51	2576·31	2464·15	5804·28	5838·99	5868·30
2759·83	2446·96	2345·41	5354·240		5384·901
2674·99	2380·06	2284·2	5120·830		5138·26
2625·24	2340·60		4981·00		4991·7
2593·43	2314·7	2224·7	4890·45		4897·1
2571·85	2284·2		4827·3		4832·4
2556·36	2284·2		4782·3		
2545·09	2275·5		4748·3		
(2536·36)			4723·0		
2529·47			4702·0		
2524·48			4685·5		
			4672·9		
			4662·6		
			4653·6		

Al.

S_1.	S_2.	P_1.	P_2.
(2) 3961·68	3944·16	(2) 13125·36	13151·65
2660·49	2652·56	6696·27	6698·94
2378·52	2372·21	5557·28	5558·17
2263·83	2258·27	5107·5	
2204·73	2199·71		

Ga.		In.	
S_1.	S_2.	S_1.	S_2.
(2) 4172·25	4033·19	(2) 4511·44	4101·87
2780·28	2718	2932·71	2753·97
2481·1		2601·84	2460·14
		2468·09	2340·30
		2399·33	2278·3
		2357·7*	2241·6
		2332·2	2218·3
			2200·0 ?
		* ? 8·7	2191·2

Tl.			
S_1.	S_2.	P_1.	P_2.
(2) 5350·65	3775·87	(2) 11513·22	13013·8
3229·88	2580·23	6549·99	6713·92
2826·27	2316·01	5528·118	5584·195
2665·67	2207·13	5109·65	5137·01
2585·68	2152·08	4891·3	4906·5
2538·27	2119·2	4760·8	4768·7
2508·03	2098·5	4678·3	
2487·57	2083·2	4617·4	
2472·65	2072·4	4574·8	
2462·01			
2453·87			
2447·59			
2442·24			

The lines for MgS and CaS were first allotted by RYDBERG* in his original memoir presented on November 13, 1889, to the Swedish Royal Academy. The values are the observations of KAYSER and RUNGE ('Ann. d. Phys.' (3), 43, p. 387, 1891). In the same paper KAYSER and RUNGE observed Sr (2, 4, 5), but they were arranged in the series by RYDBERG ('Ann. d. Phys.' (3), 50, p. 629), who pointed out that there ought to be a set 3865·39, 3807·37, 3780·47, and that they were probably hidden by strong Cyanogen bands. This was afterwards fully confirmed by K. and R. ('Ann. d. Phys.' (3), 52, p. 115). The first lines of the series were first observed by LEHMANN ('Ann. d. Phys.' (4), 8, p. 647, 1902), but the more accurate values of SAUNDERS ('Astro. Phys. Jour.,' 32, p. 170) are inserted in the list. In the case of Ba the second triplet and the first of the next two were observed by K. and R., but

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* 'Kongl. Svensk. Vetens. Akad. Hand.,' Bd. 23, No. 11. In this memoir, which laid the foundation of what is known as to series relationships, the material is chiefly due to the observations of THALÉN, of HARTLEY and ADENEY, and of LIVEING and DEWAR.

the series was first arranged by Saunders (‘Astro. Phys. Jour.,’ 28, p. 223), who completed the list by the addition of the three lines $S_{23}(3)$, $S_1(5)$. The highest triplet was observed as in Sr by Lehmann, but the numbers given in the list are those of Hermann (‘Ann. d. Phys.’ (4), 16, p. 698).

In ZnS the first three triplets were allocated by Rydberg (*loc. cit.*). The list was completed by K. and R., and their measures for the whole are inserted. We owe the discovery of ZnP to Paschen (‘Ann. d. Phys.’ (4), 29, p. 644).

In CdS, again, Rydberg gave the first two triplets, and the first two lines of the next, whilst K. and R. gave the remainder. They also gave 2521·74 for $S_3(5)$, but it must be wrong, for it gives a separation from $S_2(5)$ of 494·77 instead of 541·90. It is, therefore, 3 A.U. too small. $S_1(6) = 2582{\cdot}86$ makes $\nu_1 = 1156{\cdot}38$ instead of 1171·00. CdP is due to Paschen (*loc. cit.*), but the values inserted after the first are the later ones of Paschen and Wiedmann (‘Ann. d. Phys.’ (4), 35). For Eu see Appendix I.

In HgS Rydberg arranged the first three triplets, Kayser and Runge added the fourth and the first line of the fifth. The remaining lines, $m = 6$ to 13, of HgS were observed and arranged by Milner (‘Phil. Mag.’ (6), 20, p. 636). The lines $S_2(5, 6)$ observed by Stiles (‘Astro. Phys. Jour.,’ 30, p. 48), $S_3(5)$, $S_2(9, 10)$ observed by Huff (‘Astro. Phys. Jour.,’ 12, p. 103), $S_2(7)$ Exner and Haschek, $S_3(7)$ Eder and Valenta have been inserted by the writer. They give for the fifth triplet $\nu_1 = 4630{\cdot}80$, $\nu_2 = 1762{\cdot}59$. $S_2(6)$ gives $\nu_1 = 4630{\cdot}7$. The seventh triplet gives 4641·4 and 1747·0; a slight error in $\lambda = 2314{\cdot}7$ would put both these right. $S_2(9, 10)$ make respectively $\nu_1 = 4659{\cdot}1$, $4653{\cdot}3$, but the former is identical with $S_3(5)$. There may be some doubt about $S_2(7)$ and $S_3(7)$, as they are both spark lines, and $S_3(7)$ is rather too strong, but there can be little doubt about the others. For $S_1(5)$ the measurement of Stiles is inserted in place of that of K. and R., as it was observed under better conditions. For the HgP Paschen made an unsuccessful attempt to locate the first triplet in the same paper as that in which he published the results for the other P series, referred to in the text. The series was first determined as to its lower orders $m = 4$ to 15 by Milner (*loc. cit.*), then Paschen and Wiedmann observed the same set up to $m = 16$, and attempted to settle the position of the top lines. In the list above, the arrangement is given as modified in the text (p. 54).

In the third group of elements the P lines have been observed and allocated by Paschen (‘Ann. d. Phys.’ (4), 29). 5105, as observed by him, was the edge of a band, and, as pointed out by him, was too strong to be AlP (4), although it should be close to it. Since then Manning, working in my laboratory, has found a very faint line at 5107·5, which is doubtless the line in question. Rydberg in his original memoir gave the five doublets of the AlS series, and at the same time suggested four others. The S and D lines here, however, come so close together that with the inexact values at his disposal his arrangement of these last is now seen to be incorrect. As in other cases, we owe to Kayser and Runge (‘Ann. d. Phys.’ (3), 48, p. 143) more correct measures, which at the same time established RYDBERG'S selection of the first five.

Some doubt may be felt about the lines adopted for GaS. In his memoir RYDBERG used certain regularities he had noticed amongst other series to deduce what the Ga series ought to be—adopting the doublet 4172, 4033 for S_1 and S_2. He calculated 2747 and 2436 for the two next lines in S_1 and 2966, 2505 for the D lines. Since then EXNER and HASCHEK have published their spark and arc measurements. KAYSER in his 'Spectroscopie'—no doubt guided by RYDBERG'S calculations, as there was nothing else to go upon—allotted E. and H.'s spark line 2780·28 to RYDBERG'S supposed 2747, with 2719·76 (arc) as the second of the doublet ($\nu = 800$ instead of 826). RAMAGE gives ('Roy. Soc. Proc.,' 70, 1901) 2780, 2718, in place of E. and H.'s 2780·28, 2719·76. It might appear, therefore, that 2718 is really a distinct line which, with the former, gives $\nu = 823·65$ (within errors of 826), whilst 2719·28 is the first of another doublet with $\nu = 826·68$. He gave also 2943·77, 2874·35 for D in correspondence with RYDBERG'S supposed 2966 and 2894. In the foregoing paper I adopted the same allocation for S (1, 2), and with it have taken E. and H.'s spark line 2481 as S_1 (3). For this it may be said that the corresponding lines come well in order as lying between the corresponding ones of Al and In, and the resulting formulæ constants also fit in well as between those of Al and In. On the other hand, they do not occur in the arc spectrum, where they ought to be stronger. Moreover, in E. and H.'s list, lines occur with the proper doublet separation and of corresponding nature and order of intensity, which certainly look as if they belong to the series; but, unfortunately, there are not sufficient to settle the question. The lines in question are given in wave-numbers as follows:—

D SERIES.

$m = 1$	(5r) 33954·36	826·07	(10r) 34780·43
	6·00		
	(10r) 33960·35		
$m = 2$	(39975·17)	(826·00)	(2r) 40801·17
	(2r) 39983·85		

[39975, suggested for $D_{12}(2)$, has not been observed.]

S SERIES.

$m = 1$	(30r) 23961·41	826·00	(30r) 24787·44 (in both arrangements).
$m = 2$	(3) 36757·27	826·68	(2) 37583·95.

As against this allocation is the fact that they do not lie in corresponding positions between Al and In, as is seen at once from the values for the first two lines of the S_1 series, which are as follows :—

	Al.		Ga.		In.
S	3961	211	4172	339	4511
	2660	59	2719	213	2932

(The other allocation 2780 gives differences 120 and 152 for the second line, in closer ratio to those of the first.)

D	3092	2943	3258
	2575	2500	2714

They apparently belong to series of S and D type correlated to the typical ones. The limit is in the neighbourhood of 47600. If the real one is $47600+\xi$, the formulæ obtained for them give the following denominators, viz. :—

$$\text{For S } 1{\cdot}206859-{\cdot}0002477\xi-({\cdot}052878-{\cdot}0002022\xi)m^{-1},$$

$$\text{D } {\cdot}713106-{\cdot}0005393\xi+({\cdot}245010+{\cdot}0008706\xi)m^{-1},$$

and ξ may be as large as ± 250.

In the InS RYDBERG allocated the three first doublets and the first of the next. KAYSER and RUNGE brought the observed up to six, and the second lines of the next two S_2 (7, 8). This is curious, as the only example so far observed in which the second series appears stronger than the first. I find, however, that lines observed in the spark spectrum by HARTLEY and ADENEY ('Roy. Soc. Trans.,' 1884), viz., 2332·2 and 2191·2, occupy the places for S_1 (7) and S_2 (9). The other measures are K. and R.'s. Their value for 2357·7 is, however, clearly 1 A.U. too small. It gives an incorrect value for ν which the formula corrects.

In TlS RYDBERG gave the first four doublets and the five succeeding lines for TlS_2, indicating a similar result to that of In, viz., that the S_2 series are more persistent than the S_1. KAYSER and RUNGE extended the list by adding nine lines to the S_1 series, thus completing nine doublets and adding four extra lines to S_1. It is possible that even here the S_2 may be the more persistent, and that they have not been observed because they are situated much farther down in the ultra violet. The TlP series again are due to PASCHEN. The line $\lambda = 4678{\cdot}3$ is really a mean position for the doublet TlP_{12} (7), the components being too close for resolution.

[*May* 13, 1912.—Whilst the foregoing has been passing through the press more complete lists of spectral lines, including those in the visible region, have been published by EXNER and HASCHEK.* It is possible, therefore, to see how far the

---

* 'Die Spektren der Elemente bei normalen Druck,' FRANZ DEUTICKE, Leipzig u. Wien, 1911.

extrapolation in the text for the sharp series of Europium is justified. The suggested values for the lines were 5379·1 and 4711·69, with a probability that they should be about 2 A.U. higher, if the ratio $(\alpha+\Delta_2)/(\mu+\Delta_2)$ were to have the normal value ·2152. In E. and H.'s lists are found two doublets, 5381·46, 4713·77 ($\nu_1 = 2631\cdot39$) and 5377·13, 4709·95 ($\nu_1 = 2633\cdot63$). The former is the more probable as it gives the typical ratio α/μ more closely. The formulæ constants calculated from this are

$$40363\cdot19 - \mathrm{N}/\{m+1\cdot292265-\cdot048561m^{-1}\}^2,$$

giving $(\alpha+\Delta_2)/(\mu+\Delta_2) = \cdot21636$ in place of the former value ·21246, and, therefore, closer to the value as given by other elements. The alteration in the constants is so slight that other measures, as, for instance, the estimated density of Eu, are not affected.

The supposed satellite series to EuS is not confirmed. At least there is no observed line with a wave-number near 18516·60. In the long series given at the bottom of p. 61, the first lines for S_1 and S_2 were extrapolated to wave-numbers 18858, &c. The nearest triplet to this is 5291·48, 4644·44, 4438·12, with wave-numbers equal to 18893·12, 21525·20, 22525·87, giving $\nu_1 = 2632\cdot08$, $\nu_2 = 1000\cdot67$. It fits in well as the first line of the series there indicated.]

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BY

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SUPERINTENDENT OF KEW OBSERVATORY.

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By C. CHREE, *Sc.D., LL.D., F.R.S., Superintendent of Kew Observatory.*

Received March 30,—Read May 9, 1912.

CONTENTS.

§ 1. IT was discovered half a century ago by SABINE, LAMONT and WOLF that a relation exists between sunspots and the daily range of magnetic declination. If the regular diurnal inequality of declination be determined for the year as a whole, then it has been shown that corresponding to equal increments of sunspot frequency, as determined by WOLF and WOLFER, of Zurich, there are at least approximately equal increments in the range. In some instances the range taken has been not that of an inequality derived from all hours of the day, but one derived from daily measurements at two fixed hours, approaching more or less closely to the average times at which the needle has its extreme easterly and westerly positions. The range thus derived is unlikely to bear an absolutely invariable ratio to the range of the diurnal inequality, but for the present purpose the comparison may be regarded as made with the range of the diurnal inequality, but of minor accuracy.

Published separately, July 10, 1912.

The relation refers, it should be noticed, to corresponding data from the year as a whole. It may be expressed by the equation

$$R = a(1+mS), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where R denotes the range of the diurnal inequality of declination, S the sunspot frequency, while a and m are constants for the particular station concerned.

In several previous papers* I have dealt with this formula, showing that it applies equally to the other magnetic elements, though with different values of a and m, and that it may be applied—though with less close agreement between observation and calculation—to the individual months of the year, provided m as well as a be allotted different values in different months. The values obtained for m for different magnetic elements, and for the same element at different seasons of the year, varied largely. At all the European stations considered, m was larger for H (horizontal force) than for D (declination), and larger for winter than for summer.

§ 2. WOLF and WOLFER's frequency figures are not the only statistics published for sunspots. Measurements have been made at Greenwich for many years of the areas of the faculæ, whole sunspot areas and umbræ both as "projected," *i.e.*, as measured in photographs, and as "corrected" for foreshortening. In a paper† published in 1906 I took all the Greenwich measurements into account when discussing D and H data from Falmouth for the magnetically quiet days of the twelve years 1891 to 1902. It was found (*loc. cit.*, Table II., p. 168) that for the twelve years mentioned the variations from year to year in the four quantities—whole spots projected, whole spots corrected, umbræ projected and umbræ corrected—had followed so similar a course that it could make little difference which of the four one took to represent solar activity in any investigation relating to mean annual values. The corrected areas, for instance, for whole spots and umbræ stood very nearly in the ratio of 6 to 1.

The variation from year to year in WOLFER's sunspot frequencies differed distinctly but not largely from that of the Greenwich spot areas. A considerably greater divergence appeared in the case of the Greenwich measurements of faculæ.

Formulæ of the type (1) were assumed as existing between the range of the mean diurnal inequality for the year in D and H at Falmouth and each in turn of the five solar quantities—faculæ (corrected areas), umbræ (projected and corrected areas), whole spots (corrected areas), and WOLFER's sunspot frequencies. Values were found for the constants a and m in (1) by the method of least squares, and a comparison was made (*loc. cit.*, Tables XVIII. and XIX., pp. 190 and 191) between the observed and calculated values of the D and H ranges for the twelve years, in order to see in which of the five cases the agreement with observation was closest.

In both D and H the closest agreement was obtained for WOLFER's frequencies,

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* 'Phil. Trans.,' A, vol. 202, p. 415; vol. 203, p. 151; vol. 208, p. 245, &c.

† 'Cambridge Transactions,' vol. 20, p. 165.

but the difference between the agreement in their case and in that of whole sunspot areas was small. In the case of H, the umbræ corrected gave as good an agreement as the whole spots, and the umbræ projected were very little behind. In D, the umbræ gave a distinctly inferior agreement; and in both D and H the agreement in the case of the faculæ was very decidedly inferior to that from the other solar quantities.

The natural inference from these results—though in the absence of trial it can only claim to be a probability—is that in any attempt to investigate a numerical relationship between sunspots and terrestrial magnetism it is not likely to matter much whether we consider WOLFER'S frequencies or the Greenwich areas of whole spots or of umbræ; and, if we take Greenwich data, it would appear unlikely to make much difference whether projected or corrected areas are employed.

§ 3. The first attempt* which I made to investigate a relationship between sunspots and terrestrial magnetism on individual days employed WOLFER'S *provisional* frequencies, as published quarterly in the 'Meteorologische Zeitschrift.' When discussing the Kew "quiet" day diurnal inequalities of the eleven years 1890 to 1900, it occured to me that if any intimate relationship exists between sunspot activity and magnetic disturbance on the same day, we should expect sunspot frequency to be decidedly below its mean on the average magnetically "quiet" day. A comparison was accordingly made of the mean sunspot frequency derived from the "quiet" days selected by the Astronomer Royal, and that derived from all days of the year. The comparison was made for the eleven years 1890 to 1900 as a whole, and for two sub-groups of years, representative of sunspot maximum and minimum. It was also made, employing the whole eleven years, for three seasons of the year, winter (November to February), summer (May to August), and Equinox (remaining four months). In no single instance was there a difference between the mean sunspot frequencies from all days and from "quiet" days only, such as suggested any real relationship. The two mean frequencies derived from all months of the eleven years, viz., 41·22 for all days and 41·28 for "quiet" days, were practically identical.

§ 4. The next attempt† which calls for remark proceeded on different lines. It made use of the annual Greenwich tables, which give the daily values of projected sunspot areas—expressed in terms of the one millionth of the visible disc as unit—applying them to the 660 selected "quiet" days of the years 1890 to 1900, and to 209 days of the same eleven years selected for the large size of the magnetic disturbances shown. The days of each month were divided into three groups; the first and last of these groups in a month of 30 days contained respectively the 10 days of largest and the 10 days of smallest sunspot area. It was then investigated how the 660 "quiet" days and the 209 highly disturbed days distributed themselves between the

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[*] 'Phil. Trans.,' A, vol. 202, p. 433.

[†] 'Phil. Trans.,' A, vol. 208, p. 234.

three groups. The distribution expressed in percentages of the total number of days, whether 660 or 209, was as follows:—

	In group of days of—		
	Largest spot area.	Intermediate spot area.	Smallest spot area.
"Quiet" days	31·7	34·5	33·8
Highly disturbed days. . . .	35·6	34·0	30·4

Thus the group of days of largest spot area contained 2·1 per cent. fewer "quiet" days, and 5·2 per cent. more disturbed days than the group of days of smallest spot area.

§ 5. The fact that this second investigation gives at least a suggestion of the relationship sought for, while the first investigation gave a purely negative result, was at first very puzzling; but it began to dawn on me that the difference might have something to do with the fact that days of large spot area, and days of small spot area both tend to congregate in groups, and not to be isolated. Influenced partly by this idea, and partly by the desirability of testing a theory of ARRHENIUS, who suggested that the magnetic disturbance effects visible on the earth, are due to the discharge from the sun of electrified particles likely to take some 48 hours to travel to the earth, I next investigated (in the same paper) whether the association was not between magnetic phenomena on the earth and phenomena existing on the sun, 1, 2, 3, or 4 days previously. In one investigation the 10 days of each month were taken for which the *absolute* D range (*i.e.*, the excess of the daily maximum over the daily minimum declination) was greatest. Calling any one of these selected days n, the Greenwich projected sunspot area was put down in separate columns for the day n, and three previous days $n-1$, $n-2$, and $n-3$. This being done for each of the 10 days of largest D range in the month, we have 10 spot areas in each of the four columns headed n, $n-1$, $n-2$, and $n-3$. Summing up and taking means for each column, we get results representative of the spot area on a representative day, characterised by a large D range, and on each of the three previous days.

If ARRHENIUS's theory were true, then we should expect the mean spot area for day $n-2$ to be decidedly in excess of the means from the other three columns, and also in excess of the mean derived from all days of the month.

As a matter of fact, when all the months of the 11 years were treated in this way, and the results combined, the mean spot areas from the four columns were *all* in excess of the mean from all days, and the excess was largest for column $n-3$.

As complementary to this investigation, the 10 days of least D range in each month of the 11 years were got out, and the corresponding sunspot areas were put down for each of these and the three previous days. In this instance, there was a *deficiency* in the mean derived from each of the columns headed n, $n-1$, $n-2$, $n-3$ as compared to the average day of the 11 years, and the deficiency was greatest in column $n-3$.

The calculations were repeated, limiting the days of largest and of least D range each to 5 a month. The two groups of days thus represented more extreme conditions than in the previous investigation, and consistently with this the phenomena proved to be of the same general character as before, only more pronounced. In the investigation which employed 5-day groups there were in reality six columns headed $n+1$, n, $n-1$, $n-2$, $n-3$, and $n-4$, thus representing six successive days, extending from four days before to one day after the representative day of large (or small) D range.

§ 6. As another line of attack, the initial selection of days was based on the sunspot area,* the one group of days for any month consisting of the 10 days of largest area, the other of the 10 days of least area. The D ranges were put down for each day of either group, and for the three *subsequent* days in columns headed respectively n, $n+1$, $n+2$, and $n+3$. Taking again a mean from all months of the 11 years, the mean D ranges from the four columns for the group of days of large spot area were all above the mean derived from all days of the year, and the excess was greatest in column $n+3$.

In short, when the 11 years as a whole were combined, all the lines of investigation pointed to a relationship between the size of the absolute D range on individual days and sunspot areas on one or more preceding days. It appeared, however, that if ARRHENIUS's views were correct, the time requisite for the electrified particle to travel from the sun to the earth must vary from less than 1 to more than 3 days, and it seemed that 4 days must be a more common interval than 3, and 3 days a more common interval than 2. The phenomena were, however, at least as favourable to the view that magnetic conditions on any one day represent an integral to which a number of previous days contribute.

The similarity in the nature of the results derived by these different investigations from the 11 years as a whole, and the fact that the apparent sunspot influence indicated was far from infinitesimal, seemed to preclude the possibility of the phenomena being wholly accidental. There was, however, this remarkable fact, that when the years were treated individually, some of them, notably 1895, gave results which appeared to be of an opposite character to those derived from the whole 11 years, there being an apparent association of large D ranges with small, not large, spot areas. Further investigation thus appeared necessary, and it was clear that it ought to be of a much more comprehensive character, calling for a large expenditure of time. It is only within the last twelve months that a suitable opportunity has presented itself.

§ 7. The first question now to be considered is whether D is the best magnetic element on which to base the enquiry. The investigations which involved applications

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* National Physical Laboratory, 'Collected Researches,' vol. 5, 1908, p. 55.

of WOLF's formula (1) to diurnal inequality ranges showed that when Kew "quiet" days were considered—the information for other than "quiet" days at Kew is still lacking—inclination (I) was the element for which the constant m was largest, *i.e.*, for which the greatest percentage increase of range occurred for a given increase in sunspot frequency. Next to I came H.

Values of I are not recorded directly by the magnetographs, but have to be calculated from the recorded values of H and V (vertical force). Thus it would be a very difficult, if not practically impossible, task to find absolute daily ranges of I. Daily ranges of H, on the other hand, are as easily obtained as those of D, provided one neglects the corrections required to allow for the variation of temperature. At Kew such neglect seldom causes an error as large as 2γ ($1\gamma \equiv 1 \times 10^{-5}$ C.G.S.) in the absolute daily range, and often is without any effect, and for investigations such as the present the slight increase in the accuracy of individual daily ranges that might ensue from the application of temperature corrections would be immaterial.

In 1908 a grant was obtained from the Government Grant Committee for the measurement of all Kew H and V curves of the 11 years 1890 to 1900, and the work naturally included the determination of the absolute daily ranges, which thus became available for the present enquiry.

The increase of sensitiveness in the method expected from the substitution of H for D ranges was considerable, as will be seen by reference to Table I. Adopting the notation of (1), 100m represents the percentage increase in the range of the diurnal inequality answering to an increase in WOLFER's sunspot frequency from 0 to 100. The results to which the letter A is attached in Table I. were obtained by least squares, those to which the letter B is attached by what I have called the "method of groups."

TABLE I.—Values of 100m at Kew.

	Method.	D.	H.	H value ÷ D value.
From range of mean diurnal inequality for the year . .	A	0·71	1·07	1·51
	B	0·66	1·04	1·58
From inequality ranges of 12 months of the year individually considered	A	0·63	0·89	1·41
	B	0·68	1·00	1·47

If, then, the relation between absolute ranges on individual days and sunspots follows similar laws to those presented in the case of the range of the diurnal inequality, we should expect the differences disclosed by investigations such as those described in §§ 5 and 6 to be increased some 50 per cent. when D ranges are replaced by H ranges.

Absolute daily ranges, however, are affected by disturbance in a much greater degree than inequality ranges derived from all days of the year, so some direct confirmation was desirable. It was obtained as follows: The monthly groups of 10 days already employed in connection with the D ranges, were utilized for H ranges, for the 3 years 1892, 1893, and 1894, which were the years of largest sunspot frequency between 1890 and 1900. The investigation was limited to the representative day n of largest (or least) sunspot area, and the three immediately following days $n+1$, $n+2$, and $n+3$.

The results derived by meaning the several columns for the three years separately appear in Table II. Each entry, it will be understood, represents a mean derived from 10 × 12 or 120 days,

TABLE II.—Comparison of D and H results from 10-day Groups.

Element.	Year.	Days of large spot area.				Yearly mean from all days.	Days of small spot area.			
		n.	$n+1$.	$n+2$.	$n+3$.		n.	$n+1$.	$n+2$.	$n+3$.
D (unit 1′)	1892	16·96	17·96	18·75	19·74	17·70	16·23	15·96	16·01	15·96
	1893	15·37	15·91	16·32	16·35	15·62	15·39	15·28	15·17	15·33
	1894	17·73	18·05	18·11	18·19	16·50	15·06	14·58	14·88	15·14
Mean . .	—	16·69	17·31	17·73	18·09	16·61	15·56	15·27	15·35	15·48
H (unit 1γ)	1892	84·4	88·5	91·7	101·2	84·0	73·4	71·0	71·0	68·0
	1893	70·9	73·1	75·4	76·0	69·7	69·1	66·1	63·9	65·8
	1894	86·8	91·5	91·8	95·1	81·4	69·1	69·1	71·3	73·1
Mean . .	—	80·7	84·4	86·3	90·8	78·4	70·5	68·7	68·7	69·0

Expressing the algebraic excess of each of the 3-year means in the columns n, $n+1$, $n+2$, and $n+3$ over the corresponding means from all days of the year (viz., 16′·61 for D and 78·4γ for H) as percentages of the latter mean values, we obtain the results given in Table III.

TABLE III.—D and H results from 10-day Groups, as Percentages.

Element.	Group of days of large spot area.				Group of days of small spot area.			
	n.	$n+1$.	$n+2$.	$n+3$.	n.	$n+1$.	$n+2$.	$n+3$.
D	+0·5	+4·2	+ 6·7	+ 9·0	− 6·3	− 8·0	− 7·5	− 6·8
H	+3·0	+7·7	+10·1	+15·8	−10·0	−12·3	−12·3	−12·0

Taking the numerical sums of the percentage figures from the large and small spot area groups separately, we find

(H sums)/(D sums) = 1·79 from days of large spot area,
,, ,, = 1·63 ,, ,, ,, small ,, ,, .

This makes the phenomenon some 70 per cent. larger in H than in D, and so more than justifies our anticipations.

§ 8. In the majority of the earlier investigations use was made of 10-day groups selected by reference to the size of the absolute daily range. In the investigations now to be described it was decided to employ 5-day groups, and to make the Greenwich projected sunspot area the criterion for selection. It had become obvious that the number of days preceding and following the representative day must be largely increased, if one wished to ascertain the true nature of the phenomenon, and it was obvious that the arithmetical operations would thus become exceedingly heavy, even with 5-day groups. Experience had also shown that the 5 days of largest spot area in a month were not infrequently consecutive, while this was hardly ever the case for the 10 days of largest area. Thus 5 appeared a more natural number than 10, while the fact that the majority of the 5 days often occurred in a sequence led to a marked economy of time in entering the data in the several columns.

The main reason for preferring the spot area as the criterion for grouping the days was that it promised to facilitate the comparison of results from different stations, and the comparison of results from different elements at the same station. The numerical results for the sunspot areas for the groups of days of the present investigation will obviously serve for any similar investigation dealing with the same period of years.

One slight drawback to sunspot areas as the criterion of selection is the absence of spot areas for a few days in the Greenwich publications. In these cases the day for which information was lacking was disregarded when selecting the 5 days of large (or small) spot area; but when it occurred in any column (other, of course, than n) it had assigned to it the arithmetic mean of the areas for the two adjacent days.

There were a few days for which Kew H ranges were lacking. The gaps were filled up by reference to the Falmouth curves, with the exception of one occasion when the traces at both Kew and Falmouth got off the sheet. The range for that day was taken as if the curve stopped at the edge of the sheet. Judging by the appearance of the curves, the consequent underestimate of the range was not serious.

It was decided to take 15 days before and 15 after each selected day. Thus, calling the representative day n, there were 31 columns of figures extending from day $n-15$ to day $n+15$.

There was one month in 1890 and one in 1900 when the days showing measureable sunspot areas numbered less than 5. These two months were omitted, leaving in all 130. The investigation relating to the 5 days a month of largest spot area thus included the treatment of 130 × 31 × 5, or 20150, H ranges and as many sunspot areas.

Sunspot Areas.

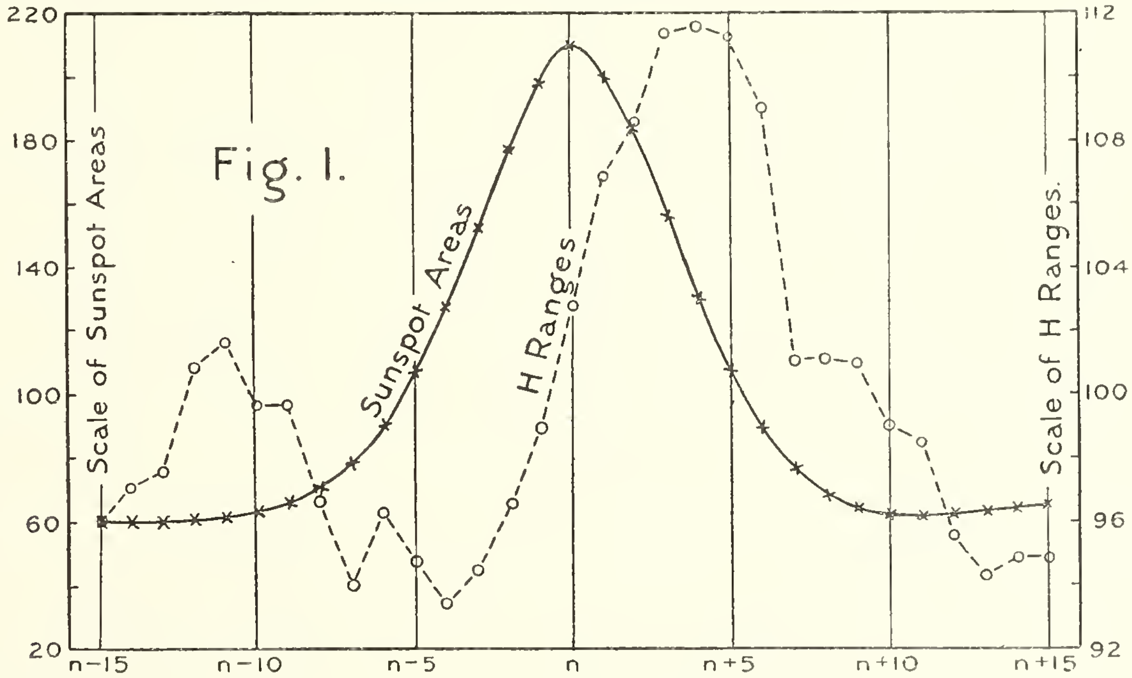
§ 9. In the subsequent comparisons of sunspot areas and magnetic phenomena use was made not merely of the whole 11 years 1890 to 1900, but also of the following groups of these years:—

1890, 1899, and 1900 representing sunspot minimum;
1891, 1895, and 1896 representing the most rapid portion of the rise of sunspot areas to the maximum and their subsequent decline, and also representing an exceptionally high average state of magnetic disturbance;
All the years (8) except those in the last-mentioned group;
1892, 1893, and 1894 representing sunspot maximum.

In the case of the 11 years, the three seasons winter, equinox, and summer, as defined in § 3, were also considered separately.

In the case of the sunspot maximum years there were two investigations, one based as in the other cases on the 5 days a month of largest spot area, the other on the 5 days a month of least spot area. The sunspot area data derived from these investigations appear in Table IV. Column n gives the characteristics of the representative of the selected 5 days a month. The columns $n-15$ to $n-1$ give the characteristics of the 15 days immediately preceding the representative day, columns $n+1$ to $n+15$ the characteristics of the 15 days immediately following the representative day. The figures in these 31 columns represent percentages of the mean spot area derived from the whole 31 columns.

The method aims at securing a pulse of high (or low) spot area centering at day n, and our immediate object is to ascertain the form of that pulse.



§ 10. The 11-year data in the first line of Table IV. are shown graphically in the full line curve of fig. 1. They represent an exceedingly smooth and nearly symmetrical

TABLE IV.—Sunspot Areas Expressed as Percentages of their Mean.

	$n-15$.	$n-14$.	$n-13$.	$n-12$.	$n-11$.	$n-10$.	$n-9$.	$n-8$.	$n-7$.	$n-6$.	$n-5$.	$n-4$.	$n-3$.	$n-2$.	$n-1$.	n.
Eleven years, all months . .	61	60	60	61	62	64	66	71	78	90	107	127	152	178	198	210
,, ,, Winter . . .	60	60	60	63	65	69	74	80	87	98	112	128	150	169	186	198
,, ,, Equinox . .	59	60	61	61	63	63	64	68	75	87	105	130	158	186	207	219
,, ,, Summer . .	64	61	59	58	58	59	61	65	73	86	101	123	150	178	200	212
1890, 1899, 1900	48	49	49	50	48	47	45	48	58	77	103	139	182	227	267	292
1891, 1895, 1896	53	54	57	61	66	70	75	80	86	95	108	124	145	169	188	202
Other 8 years	64	64	61	61	60	61	63	67	75	88	105	128	155	182	202	213
1892, 1893, 1894	71	69	65	64	63	64	67	72	80	91	105	124	147	169	188	198
1892, 1893, 1894, representative days of *minimum* spot area	136	137	137	136	132	127	122	114	105	93	81	69	57	46	38	33

	$n+1$.	$n+2$.	$n+3$.	$n+4$.	$n+5$.	$n+6$.	$n+7$.	$n+8$.	$n+9$.	$n+10$.	$n+11$.	$n+12$.	$n+13$.	$n+14$.	$n+15$.	Mean spot area.
Eleven years, all months . .	200	184	156	130	107	89	77	69	65	63	62	63	63	64	65	939
,, ,, Winter . . .	187	170	150	128	109	92	79	70	64	62	62	64	66	68	68	945
,, ,, Equinox . .	210	201	164	135	110	91	78	70	64	61	55	51	49	48	48	890
,, ,, Summer . .	202	181	155	127	103	86	74	67	65	65	68	71	74	76	78	983
1890, 1899, 1900	267	228	180	138	103	76	60	48	43	41	41	40	37	34	35	163
1891, 1895, 1896	195	176	151	125	103	86	74	68	65	65	66	70	72	75	76	1044
Other 8 years	202	187	158	132	109	91	78	69	64	62	60	59	59	60	61	900
1892, 1893, 1894	188	178	152	130	110	95	84	76	70	67	64	62	61	62	64	1786
1892, 1893, 1894, representative days of *minimum* spot area	39	49	63	77	92	104	115	122	127	130	130	127	123	120	119	1735

pulse, with its crest of course in column n. The differences between the figures in any corresponding pair of columns $n-s$ and $n+s$ are very small, but on the whole there is a tendency for the figure in column $n+s$ to be the larger of the two. From column $n-15$ to column $n-9$, and again from column $n+9$ to column $n+15$, the sunspot figure is nearly constant. The pulse is obviously of a favourable type for the investigation of the presence or absence of a corresponding pulse in any magnetic quantity.

The pulses in the case of all three seasons from the 11 years are fairly symmetrical with respect to column n for values of s up to 5 or more; but for values of s in excess of 9 or 10 there is considerable a-symmetry. The figures show a marked tendency to fall from column $n+11$ to column $n+15$ in the case of equinox, and a similar tendency to rise in the case of summer. These phenomena are presumably "accidents," and would disappear if a large number of 11-year periods were combined; but they merit attention, in view of their possible influence on the magnetic phenomena presently to be described.

Whether the more rounded character of the pulse in winter is wholly accidental is more open to doubt. If a natural phenomenon, characteristic of the season, it would seem to imply some direct action of the earth on sunspots, and so far as I am aware astronomers have not succeeded in establishing any such action.

The difference between the sunspot maximum and minimum years is marked, the pulse being much more rounded and less accentuated in the former. This may have been a peculiarity of the particular sunspot cycle, but it seems not unlikely to be fairly representative of sunspot maximum and minimum. Towards minimum there are usually a number of days without visible sunspots, and any finite number, however small, is infinite when compared to zero.

Omitting the last line of Table IV., which represents the exact antithesis of the conditions represented by the first eight lines, it will be seen that the sunspot area even on the fourth day after the representative day of largest area is still some 30 per cent. above the mean for the period. It would thus be quite in harmony with the hypothesis of a direct instantaneous action of sunspots upon the earth, if the range of the magnetic elements were decidedly above the mean for at least 4 days after the day of largest area. But, on this hypothesis, the excess above the average range on the fourth day after the day of largest area should be only some 30 per cent. or less of the excess on the actual day of largest area.

If the effect on the absolute magnetic range in individual days followed a similar law to that exhibited by the range of the mean diurnal inequality for the year, its absolute size would depend on the absolute difference in the sunspot area. For instance, if we compare the results in Table IV. for the groups of years of sunspot minimum and maximum, the total range of sunspot area in the former case—being the excess at day n over day $n+14$—would be in Greenwich units

$$(292-34)\times 163/100 = 420,$$

while in the latter case it would be

$$(198-61)\times 1786/100 = 2447.$$

Thus, on the above hypothesis, the difference between the greatest and least representative daily magnetic ranges—got out from the days included in Table IV.—should be about 5·8 times as large in the sunspot maximum as in the sunspot minimum group of years.

The rise to the crest of the pulse in Table IV. and the subsequent fall practically take place between days $n-7$ and $n+7$, *i.e.*, the pulse extends over about 15 days. There would obviously be advantages in making the pulse narrower. This could be done, to a certain extent, by reducing the monthly number of selected days. But even if we took only the one day of largest spot area of the month, the pulse would remain far from wall sided, because the days adjacent to that of largest spot area have almost always themselves areas much above the average of the month. On the other hand, if one took only 1 or 2 days a month, the number of years would probably have to be largely increased to get as smooth a progression as that shown in the first line of Table IV.

The last line of Table IV., dealing with the representative days of *least* spot area of the years of sunspot maximum, gives of course a trough instead of a crest at day n. The symmetry with respect to column n is not quite so good as in the case of the representative days of largest spot area from the same group of years, but still is very fair.

§ 11. Table V. gives the results for H ranges corresponding to the sunspot data in Table IV. The values of the ranges in columns $n-15$ to $n+15$ are expressed as percentages of the mean range derived from these 31 columns. These absolute mean ranges appear in the last column of the table.

If there were no relation between sunspots and magnetic phenomena on individual days, then we should expect the departures from 100 in the figures in the first 31 columns of Table V. to be small and irregular. There is certainly less smoothness in the progression of the figures than in Table IV., and the percentage variations shown are much smaller; but there are features which it is impossible to ascribe to accident.

Let us first consider the data from the 11 years in the first four lines of Table V. Accidental features are obviously not entirely eliminated, but there cannot be two opinions as to the existence of a marked pulse, the crest occurring some days after that of sunspot areas. In every case there is a marked depression or trough some days in advance of the day n which represents the maximum of sunspot areas. In the first line of Table V., representing all months of the year—represented graphically in the broken-line curve of fig. 1—the trough occurs about 4 days in advance, and the range is still below its mean on the day before sunspot maximum, *i.e.*, at a time when, as appears from Table IV., sunspot area is almost double its mean. The rise from the trough to the crest is regular, and the crest itself

TABLE V.—Horizontal Force Ranges Expressed as Percentages of their Mean.

	$n-15$.	$n-14$.	$n-13$.	$n-12$.	$n-11$.	$n-10$.	$n-9$.	$n-8$.	$n-7$.	$n-6$.	$n-5$.	$n-4$.	$n-3$.	$n-2$.	$n-1$.	n.
Eleven years, all months . .	96	97	98	101	102	100	100	97	94	96	95	94	95	97	99	103
,, ,, Winter . . .	96	94	93	97	99	96	94	91	90	95	96	98	97	97	103	103
,, ,, Equinox . .	99	102	100	103	102	97	97	96	94	93	95	94	96	100	102	109
,, ,, Summer . .	94	95	99	102	104	105	106	102	97	100	94	90	92	94	94	96
1890, 1899, 1900	97	100	100	102	102	99	97	93	92	94	93	95	95	96	101	103
1891, 1895, 1896	100	100	102	104	103	105	111	105	101	103	101	95	95	93	91	93
Other 8 years	95	96	96	100	101	97	95	93	91	94	92	93	94	98	103	107
1892, 1893, 1894	96	96	96	101	102	96	91	90	88	90 .	86	86	86	91	97	110
1892, 1893, 1894, representative days of *minimum* spot area	106	107	109	114	106	108	108	103	105	106	102	106	103	96	94	88

	$n+1$.	$n+2$.	$n+3$.	$n+4$.	$n+5$.	$n+6$.	$n+7$.	$n+8$.	$n+9$.	$n+10$.	$n+11$.	$n+12$.	$n+13$.	$n+14$.	$n+15$.	Mean H range.
																γ
Eleven years, all months . .	107	108	111	112	111	109	101	101	101	99	98	96	94	95	95	61·3
,, ,, Winter . . .	103	101	111	114	115	114	99	104	107	104	107	100	95	93	94	49·8
,, ,, Equinox . .	113	114	113	110	106	101	98	98	98	96	94	94	96	97	97	64·5
,, ,, Summer . .	105	109	110	111	113	113	106	103	100	98	96	94	93	94	94	69·5
1890, 1899, 1900	107	109	113	112	108	106	98	101	103	100	98	95	95	97	97	44·4
1891, 1895, 1896	92	94	99	104	101	100	97	97	97	100	104	105	103	103	101	65·1
Other 8 years	113	114	116	115	115	112	103	103	102	98	96	92	91	92	93	59·9
1892, 1893, 1894	114	119	124	122	126	123	109	107	105	101	97	89	87	87	88	79·3
1892, 1893, 1894, representative days of *minimum* spot area	86	89	90	92	91	94	96	96	99	102	103	100	98	103	100	77·4

rounded, the ranges in columns $n+3$ to $n+5$ being almost equal. The crest value is 12 per cent. above the mean range, and the preceding trough value 6 per cent. below. Thus the amplitude of the wave from trough to crest represents 18 per cent. of the average H range.

The figures for the three seasons in Table V. are less regular. The number of years would presumably have to be trebled to get results as smooth as in the first line of the table. All the seasons, however, show the same general features as the year as a whole. In winter and equinox an excess above the mean range appears at an earlier day than in the case of the year. In summer, on the other hand, the range does not attain its mean value until the sunspot maximum has passed. The differences, however, that exist between the seasonal data for sunspots in Table IV. may be responsible for some of the differences between the seasonal data in Table V.

The crest occurring after the day of sunspot maximum is not the only one visible in Table V. The results for the year and the three seasons all show a secondary pulse, whose crest occurs about 11 days before the day of largest spot area, *i.e.*, about 15 days before the crest of the principal pulse in the H ranges.

Coming to the separate groups of years, each, it will be seen, shows the above two pulses, the crest of the one about 4 days after, the crest of the other about 11 days before, the crest of sunspot areas. The group of years in which the phenomena are most prominent and regular is that including the three years of sunspot maximum. In this case the difference between the principal crest and the preceding trough represents 40 per cent. of the mean daily range, or about 32γ.

The sunspot minimum years give very similar results to the sunspot maximum years, but the difference between the principal crest and trough is only 20 per cent. of the mean daily range, or about 9γ. The group of years 1891, 1895, 1896 exhibits special features. This group includes the years in which the earlier investigation, referred to above, found large sunspot areas associated with small D ranges, and conversely. The same conclusion would have followed from the present investigation if it had been limited to the day of largest spot area and three following days. The fundamental phenomenon apparently was an exceptional development of what in the other years is a secondary pulse, with a postponement of the trough preceding the day of largest spot area until day $n-1$. As in other years, however, there is a marked rise from this trough; but the trough itself is unusually deep, and the crest of what in other years is the principal pulse does not much overtop the average value. Thus in some ways the depression in the H ranges some days in advance of the sunspot pulse appears a more persistent feature than the excess in the H ranges some days after the crest of that pulse.

§ 12. The last line in Table V., answering to the selected days of *least* spot area, dealt with in the last line of Table IV., shows a marked depression in the H ranges, extending from 2 days before to 8 or 9 days after the day n of least sunspot area. The actually lowest figure is on day $n+1$, but from day n to day $n+5$ the value is nearly constant. In this case the sunspot area was below its mean from 6 days before to 5 days after day n, so that here again there seems a lag of about 4 days. The incidence of the pulse which has its crest about day $n-12$ in the last line of Table V. is sufficiently accounted for by the high values of sunspot area in the last line of Table IV. for days prior to $n-11$. The difference between this crest and the subsequent trough represents 28 per cent. of the corresponding mean absolute daily range of H, or about $21 \cdot 7\gamma$. This is about two-thirds of the corresponding amplitude in the line above, answering to the days of largest spot area. The ranges of the sunspot values in the last and second last lines of Table IV. were respectively about 1804 and 2447 of the Greenwich units of area, so the H range and sunspot area ratios in the two cases are fairly similar.

§ 13. While Table V. seems to prove to demonstration that in the average year there is a clear association of H ranges with sunspot area some days previously, the relation is either of a somewhat complex character, or else is liable to be much overshadowed in individual years by other influences. It is obviously desirable that details enabling an independent judgment to be formed should be at the disposal of all interested in the subject. It is hoped that Table VI. will suffice for this purpose.

The figures in Table VI. are the mean absolute H ranges, in terms of 1γ as unit, from the representative 31 days $n-15$ to $n+15$ of the individual 11 years. Values which exceed the mean derived from the whole 31 days are in heavy type, so that one can see at a glance how far each year conforms to or departs from the general features of the 11 years combined, as exhibited in the first line of Table V. No single feature, it will be seen, is clearly exhibited by all the years. Three of them have the figure in column $n+4$ below the average, though the deficiencies are all trifling; and four of them have the figure in column $n-4$ above the average.

§ 14. One aspect of the case which suggests itself when individual H ranges are scrutinised calls for consideration. The number of days contributing to the mean value for a single year of one of the 31 columns of Table VI. is normally 60. Now there are a few days the H range of which is altogether outstanding. Thus in February, 1892, two successive days had ranges of 720γ and 650γ. The range of the average day of 1892, though larger than that of any other year, was only 84γ. This will explain how the presence of even one outstanding range in a column sensibly affects the mean value, and if any "accident" should bring two or three such days into the same column for a single year the result might be to simulate a marked influence which had no real existence.

It is obvious *à priori* that, so far as the present research is concerned, a range of 720γ must be regarded as largely an "accident." There are no outstanding daily values of sunspot area in the whole 11 years which overtop their neighbours in the way the larger magnetic ranges do. The recognition of this fact suggested the next mode of attack. It follows lines which were suggested by the procedure followed now

TABLE VI.—Horizontal Force Ranges (unit 1γ) for 31 Consecutive Days, including Representative Day n, of Large Sunspot Area.

Year.	$n-15$.	$n-14$.	$n-13$.	$n-12$.	$n-11$.	$n-10$.	$n-9$.	$n-8$.	$n-7$.	$n-6$.	$n-5$.	$n-4$.	$n-3$.	$n-2$.	$n-1$.	n.
1890	**46·7**	**47·7**	**47·6**	**45·9**	44·0	43·2	42·4	40·2	41·8	42·3	41·2	41·4	41·1	40·6	42·8	40·9
1891	57·7	58·0	57·4	61·1	59·1	**62·9**	**67·3**	**67·5**	**70·3**	**72·7**	**70·3**	**66·2**	**67·0**	**63·7**	60·6	58·6
1892	**86·2**	**87·6**	**92·6**	**94·3**	**90·1**	80·0	75·5	69·8	67·8	74·3	64·1	63·4	64·4	72·8	80·0	**90·5**
1893	64·4	61·3	61·2	66·4	68·6	**71·0**	68·0	67·3	63·8	62·5	59·2	57·2	59·4	61·9	**64·6**	**71·3**
1894	78·5	79·3	75·3	79·8	**84·8**	77·5	72·8	77·5	77·5	77·0	80·5	**83·7**	81·6	80·9	**85·9**	**90·8**
1895	**78·2**	**76·7**	**80·3**	**76·9**	**71·2**	69·4	**74·1**	67·1	64·2	64·7	61·4	59·4	60·1	58·8	59·0	62·1
1896	59·0	61·3	61·5	**64·9**	**71·5**	**73·2**	**75·3**	**70·0**	61·9	**63·0**	**65·7**	60·1	59·6	59·8	57·0	61·0
1897	46·5	48·1	47·8	48·8	50·4	51·4	**54·9**	**54·9**	52·0	**53·8**	**57·1**	**56·1**	**57·6**	**57·1**	**56·8**	53·1
1898	49·5	49·0	48·6	52·1	53·7	55·0	55·5	53·7	54·2	**56·3**	**56·8**	**57·1**	**60·5**	**69·1**	**69·3**	**68·4**
1899	42·6	47·0	**50·7**	**54·7**	**56·3**	**53·3**	**51·2**	48·0	46·8	48·4	46·8	49·2	49·0	47·7	50·1	**51·2**
1900	**39·9**	38·2	34·7	35·4	36·1	34·8	35·6	35·3	33·7	34·4	36·2	36·4	36·3	**39·0**	**41·6**	**44·7**
11 years mean . .	59·0	59·5	59·8	**61·8**	**62·3**	61·1	61·1	59·2	57·6	59·0	58·1	57·3	57·9	59·2	60·7	**63·0**

Year.	$n+1$.	$n+2$.	$n+3$.	$n+4$.	$n+5$.	$n+6$.	$n+7$.	$n+8$.	$n+9$.	$n+10$.	$n+11$.	$n+12$.	$n+13$.	$n+14$.	$n+15$.	Mean.
1890	42·1	41·4	43·2	44·1	**44·3**	42·5	43·4	**47·5**	**49·1**	**47·3**	**46·9**	**46·3**	**46·1**	**49·6**	**48·8**	44·2
1891	54·8	51·4	53·7	**62·2**	59·5	61·6	57·7	56·3	59·3	61·6	**66·4**	**67·7**	**62·7**	61·4	59·4	61·8
1892	**94·8**	**100·7**	**117·1**	**116·8**	**109·7**	**102·3**	**92·6**	**94·4**	**88·0**	83·6	79·5	70·1	68·1	70·9	73·2	84·4
1893	**75·1**	**74·0**	**81·1**	**78·5**	**78·5**	**80·1**	**79·9**	**82·5**	**78·8**	**76·4**	**74·8**	**72·5**	**70·2**	**70·2**	**71·7**	70·1
1894	**102·6**	**108·0**	**96·9**	**95·8**	**110·7**	**109·1**	**87·0**	78·1	82·1	79·6	77·6	70·4	68·4	**66·7**	64·2	83·2
1895	**64·4**	64·8	69·4	69·8	70·2	70·6	**73·0**	**75·7**	**75·3**	**75·3**	**77·3**	**79·2**	**80·7**	**81·9**	**78·3**	70·6
1896	60·5	**67·4**	**70·2**	**71·0**	**66·4**	**63·3**	58·4	57·6	55·7	58·8	60·0	57·6	57·5	57·4	59·8	62·8
1897	49·7	46·6	47·3	48·6	51·5	**54·9**	**56·6**	**56·3**	**54·3**	50·6	48·3	50·6	50·7	51·7	**52·4**	52·1
1898	**75·7**	**74·1**	**64·3**	**61·0**	**59·8**	51·8	46·1	**46·8**	49·5	48·4	50·2	50·4	51·0	51·6	52·0	56·2
1899	**54·3**	**57·4**	**59·7**	**54·6**	49·6	**51·4**	48·2	49·6	49·7	49·4	46·4	45·8	47·1	47·5	48·2	50·1
1900	**46·0**	**45·7**	**48·4**	**50·4**	**49·9**	**47·3**	**39·5**	37·6	**38·9**	36·7	37·2	34·3	33·3	31·6	32·4	38·8
11 years mean . .	**65·5**	**66·5**	**68·3**	**68·4**	**68·2**	**66·8**	**62·0**	**62·0**	**61·9**	60·7	60·4	58·6	57·8	58·2	58·2	61·3

for some years at de Bilt in presenting the results obtained by international co-operation for the “ magnetic character ” of individual days.

Each co-operating station assigns a “ character ” figure “ 0,” “ 1,” or “ 2 ” to each day, according as it is quiet, moderately disturbed, or highly disturbed. The character figures assigned by the co-operating stations are summed at de Bilt, as if they were ordinary numerical quantities, and the final order assigned to the days in the scale of disturbance is based on these sums (or their arithmetic means). If, for instance, 30 stations send in results, and all assign character “ 2 ” to one particular day, while half the stations assign “ 2,” and half assign “ 1 ” to a second day, the total character sums obtained at de Bilt for the two days would be respectively 60 and 45, giving as the mean estimates 2 and 1·5.

The principles followed in assigning character figures at different stations vary, and the fact that the scale of values is so narrow necessitates grouping together at any one station days which differ widely in disturbance. It is also very difficult to maintain even a roughly uniform standard throughout a series of years. One naturally wishes to discriminate between the days of each year, and if one adopts a standard which gives fairly similar numbers of days of characters “ 0,” “ 1,” and “ 2 ” in a highly disturbed year, one has in a quiet year hardly any “ 2's,” and a wholly extravagant number of “ 0's.” The natural consequence is a tendency to lower the standard for a “ 1 ” or a “ 2 ” in a quiet year, and to raise it in a disturbed year. This renders character figures a somewhat uncertain basis for the comparison of one year or one group of years with another, but it militates only slightly against their use when comparing days of the same month, or even days of different months of the same year, unless the year is much more disturbed in some months than others.

The international scheme came into operation in 1906, and since that time character figures at Kew have always been assigned by myself, so that I have had considerable practice. The choice at Kew has been based not so much on the absolute size of the changes shown as on the more or less oscillatory nature of the curves.

§ 15. The second line of attack differs from the first only in substituting the character figures of individual days for their H ranges. As the period to be considered preceded the introduction of the international scheme, it was first necessary to assign character figures to the days of the 11 years. This was not so formidable a task as might appear at first sight. A single glance at the curves usually enables one to assign the character figure to about half the days of a month. My own practice is to consider the D and H curves of the month separately in the first instance, assigning to each character figures $\underline{0}$, 0, $\overline{0}$; $\underline{1}$, 1, $\overline{1}$; $\underline{2}$, 2, and $\overline{2}$. By “ $\underline{0}$ ” is meant a very quiet curve, by “ $\overline{0}$ ” a curve one inclines to assign “ 0 ” to but hesitates, regarding the assignment of “ 1 ” as at least a possibility, and so on. At Kew V (vertical force) curves need hardly be considered, as the element is so much less disturbed than D and H. If the D and H curves for the same day both get a “ $\underline{0}$ ” or a “ 0,” then usually character “ 0 ” is assigned without further enquiry. If both get “ $\overline{0}$,” or one a “ $\overline{0}$ ” and the other a "1," they are considered side by side, before a decision is reached. This will explain the general method. There are, of course, not a few days when the giving a "0" or a "1," or a "1" or a "2" is very much a toss up. If the choice made one day were to be made independently even the next week, there would be no doubt an appreciable number of alterations in the figure ascribed, and the longer the interval between the two choices the more would this tend to be the case.

In view of this fact, in the present enquiry, the days of each year were dealt with, so far as practicable, in immediate succession. While the standard remained, I think, fairly uniform throughout the days of any one year, it not improbably varied sensibly as between different years, for the time that elapsed between the consideration of the first and last of the years was naturally considerable.

In assigning the character figures the appearance of the curves was alone considered, and the lists of the daily ranges were never consulted, so that the two lines of investigation are at least absolutely independent. A distinction to be borne in mind is that the character figure is a measure only of disturbance, whereas the daily range is usually dependent both on disturbance and on the regular diurnal variation.

The data resulting from the use of the character figures appear in Table VII., results being given for the 11 years combined and for the same groups of years as in Tables IV. and V. The results in the 31 columns $n-15$ to $n+15$ are expressed as percentages of their mean; and the absolute values of these means are given in the last column of the table. In the last line of Table VII., as in the corresponding lines of Tables IV. and V., the column n contains the representative days of *smallest* spot area.

§ 16. The progression of the figures in Table VII. is less smooth than in Table V., but the conclusions indicated are very similar. In each of the first five lines, where the selected days were those of largest spot area, there is a conspicuous trough a few days before the representative day n, followed by a considerable rise to a crest, which occurs usually on day $n+4$. This crest markedly overtops the average mean, except for the group of years 1891, 1895, and 1896, which exhibits the same peculiarity as in Table V. In addition to this pulse there is a second pulse, as in Table V., with its crest about 11 days before the day of largest sunspot area. The chief departure from the phenomena seen in Table V. is that this earlier pulse has become decidedly more prominent. This fact, and the further fact that the earlier, or secondary, pulse is in both tables especially conspicuous in the case of the highly disturbed years 1891, 1895, and 1896, suggests that the phenomenon is largely a pure disturbance effect. At the same time, the years of sunspot minimum 1890, 1899, and 1900, show a more prominent crest at day $n-12$ than do the years of sunspot maximum, which were much more disturbed.

An explanation of the secondary pulse which may suggest itself is that a reduction of sunspot area below the mean for the year is itself a cause of disturbance. If, however, this were the true explanation, the last line in Tables V. and VII. should exhibit a crest about day $n+4$ much more prominent than the crests in any of the other lines at day $n-11$. This it will be seen is far from the case.

Table VII.—Character Figures Expressed as Percentages of their Mean.

	$n-15$.	$n-14$.	$n-13$.	$n-12$.	$n-11$.	$n-10$.	$n-9$.	$n-8$.	$n-7$.	$n-6$.	$n-5$.	$n-4$.	$n-3$.	$n-2$.	$n-1$.	n.
Eleven years	95	96	99	106	105	107	102	100	92	92	93	90	91	91	95	98
1890, 1899, 1900	92	98	101	111	111	104	94	92	87	91	83	88	94	90	102	103
1891, 1895, 1896	97	103	107	117	115	119	119	111	98	99	99	95	91	87	82	81
Other 8 years	94	93	94	101	100	100	94	94	88	89	89	88	92	93	101	106
1892, 1893, 1894	97	97	100	103	102	100	92	93	87	82	79	73	70	75	87	99
1892, 1893, 1894, representative days of *minimum* spot area	93	99	104	109	111	108	108	108	108	110	106	112	108	111	108	94

	$n+1$.	$n+2$.	$n+3$.	$n+4$.	$n+5$.	$n+6$.	$n+7$.	$n+8$.	$n+9$.	$n+10$.	$n+11$.	$n+12$.	$n+13$.	$n+14$.	$n+15$.	Mean character figure.
Eleven years	101	102	106	109	108	108	103	104	104	103	103	100	98	100	99	0·70
1890, 1899, 1900	111	112	117	118	113	115	105	102	104	106	92	89	85	94	96	0·47
1891, 1895, 1896	79	85	91	101	100	95	93	96	97	98	108	111	108	110	108	0·86
Other 8 years	111	111	114	113	112	114	109	109	107	106	101	94	93	96	95	0·64
1892, 1893, 1894	112	117	120	118	120	120	115	114	113	111	112	100	100	99	95	0·78
1892, 1893, 1894, representative days of *minimum* spot area	88	91	97	92	94	95	97	91	93	99	95	91	94	93	90	0·80

TABLE VIII.—Character Figures for 31 Consecutive Days, including Representative Day n, of Large Sunspot Area.

Year.	$n-15$.	$n-14$.	$n-13$.	$n-12$.	$n-11$.	$n-10$.	$n-9$.	$n-8$.	$n-7$.	$n-6$.	$n-5$.	$n-4$.	$n-3$.	$n-2$.	$n-1$.	n.
1890	**0·55**	**0·64**	**0·64**	**0·62**	**0·58**	**0·55**	**0·47**	0·47	0·51	**0·58**	0·51	0·45	0·42	0·42	0·47	0·42
1891	0·70	0·73	0·67	0·77	**0·82**	**0·88**	**0·87**	**0·92**	**0·90**	**0·95**	**0·92**	**0·88**	**0·92**	**0·82**	0·72	0·63
1892	**0·85**	**0·87**	**0·92**	**0·83**	0·77	0·72	0·72	0·72	0·70	0·63	0·58	0·50	0·45	0·55	0·68	0·77
1893	0·58	0·58	0·58	**0·70**	**0·73**	**0·78**	0·68	0·67	0·57	0·43	0·37	0·33	0·38	0·45	0·57	**0·70**
1894	0·83	0·82	0·85	0·87	**0·88**	0·85	0·75	0·78	0·78	0·85	**0·90**	**0·88**	0·82	0·75	0·78	0·85
1895	**1·10**	**1·15**	**1·25**	**1·27**	**1·13**	**1·12**	**1·12**	**1·03**	0·85	0·80	0·77	0·77	0·70	0·75	0·77	0·78
1896	0·70	0·78	**0·83**	**0·97**	1·02	**1·07**	**1·07**	**0·92**	0·78	0·80	**0·87**	0·78	0·73	0·66	0·62	0·67
1897	0·65	0·62	0·58	0·58	0·60	0·65	0·70	0·67	0·62	0·68	**0·78**	**0·85**	**0·88**	**0·85**	**0·85**	**0·75**
1898	0·60	0·48	0·50	0·62	0·60	0·68	0·67	**0·70**	0·63	0·67	**0·78**	**0·73**	**0·85**	**0·92**	**0·88**	**0·93**
1899	0·40	0·45	**0·62**	**0·70**	**0·77**	**0·68**	0·60	0·60	0·58	0·58	0·48	0·57	**0·67**	**0·62**	**0·65**	**0·70**
1900	**0·36**	**0·31**	0·18	0·27	0·24	0·25	0·27	0·25	0·13	0·13	0·18	0·24	0·25	0·25	**0·33**	**0·35**
11 years' mean . .	0·67	0·68	0·69	**0·75**	**0·74**	**0·75**	**0·72**	0·70	0·64	0·65	0·65	0·63	0·64	0·64	0·67	0·69

Year.	$n+1$.	$n+2$.	$n+3$.	$n+4$.	$n+5$.	$n+6$.	$n+7$.	$n+8$.	$n+9$.	$n+10$.	$n+11$.	$n+12$.	$n+13$.	$n+14$.	$n+15$.
1890	0·51	0·45	0·51	**0·53**	0·47	0·49	0·47	0·49	**0·55**	**0·58**	**0·53**	0·51	0·51	**0·56**	**0·55**
1891	0·57	0·52	0·53	**0·78**	0·77	0·73	0·70	0·68	0·68	0·73	**0·82**	**0·90**	**0·85**	**0·82**	0·77
1892	**0·88**	**0·90**	**0·90**	**0·93**	**1·03**	**1·00**	**0·88**	**0·87**	**0·82**	0·73	0·77	0·70	0·73	**0·78**	0·73
1893	**0·83**	**0·85**	**0·95**	**0·85**	**0·87**	**0·87**	**0·87**	**0·85**	**0·87**	**0·83**	**0·83**	0·70	0·73	0·70	0·75
1894	**0·90**	**0·98**	**0·95**	**0·97**	**0·92**	**0·93**	**0·93**	**0·95**	**0·97**	**1·03**	**1·02**	**0·93**	0·87	0·83	0·73
1895	0·80	0·87	0·92	0·92	0·93	0·90	**1·00**	**1·07**	**1·08**	**1·08**	**1·20**	**1·20**	**1·22**	**1·25**	**1·18**
1896	0·67	0·80	**0·88**	**0·90**	**0·87**	0·82	0·68	0·72	0·73	0·72	0·75	0·77	0·72	0·77	**0·83**
1897	0·65	0·57	0·58	0·58	0·67	**0·77**	**0·85**	**0·87**	**0·78**	**0·75**	0·63	0·65	0·63	**0·72**	**0·73**
1898	**0·88**	**0·80**	**0·80**	**0·78**	**0·70**	0·65	0·57	0·62	0·58	0·58	0·65	0·62	0·62	0·57	0·58
1899	**0·72**	**0·78**	**0·78**	**0·75**	**0·70**	**0·70**	**0·63**	**0·62**	0·58	0·57	0·48	0·47	0·52	0·55	0·57
1900	**0·35**	**0·36**	**0·36**	**0·40**	**0·44**	**0·45**	**0·40**	**0·35**	**0·35**	**0·36**	**0·31**	0·29	0·18	0·22	0·25
11 years' mean . .	**0·71**	**0·72**	**0·74**	**0·76**	**0·76**	**0·76**	**0·73**	**0·74**	**0·73**	**0·72**	**0·73**	0·70	0·69	**0·71**	0·70

§ 17. Table VIII. gives for comparison with Table VI. the character data for individual years from which Table VII. was derived. The entries are the arithmetic means of the character figures, heavy type being used when the mean value for the year derived from the whole 31 columns is exceeded.

If entries in Tables VI. and VIII., which exceed the yearly mean, be regarded as affected by a positive sign, and those which fall short of the mean as affected by a negative sign, the parallelism between the two tables can be roughly gauged by comparing the number of agreements and differences in the signs of the corresponding entries. There are in all 11×31, or 341 entries in each table. One of these—the entry in column $n+6$ of Table VI. for year 1895—exactly equals the mean value. Omitting this, there are no fewer than 286 agreements in sign as against 54 differences. Many of the differences of sign occur in cases where the departure from the mean value is trifling. The natural inference is that disturbance plays a large part in the phenomena exhibited even by the H ranges.

Of the 99 entries in the columns headed $n-9$ to $n-1$ only 32 are above the mean in Table VI., and only 31 in Table VIII.; whereas of the 99 entries in the columns headed $n+1$ to $n+9$, those above the mean number 59 in Table VI. and 62 in Table VIII.

§ 18. The difference between the days which follow and which precede the representative day n of large sunspot area is brought out, perhaps even more clearly, by considering the algebraical excess of the percentage value for day $n+s$ over that for day $n-s$, for the values 1 to 15 of s included in Tables IV., V., and VII. Table IX. gives the results thus obtained for the 11 years combined. It was derived from data going one decimal place beyond the data given in Tables IV., V., and VII.

TABLE IX.—Excess of Percentage Figure for Day $n+s$ over that for Day $n-s$ in Tables IV., V., and VII.

s.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.
Spot area . . .	+2	+ 6	+ 4	+ 3	+ 1	− 1	− 1	−2	−2	−1	0	+2	+3	+4	+4
H ranges . . .	+8	+12	+17	+18	+16	+13	+ 7	+4	+1	−1	−3	−5	−3	−2	−1
Character figures .	+6	+11	+14	+18	+15	+15	+12	+4	+1	−3	−2	−5	0	+4	+4

The first line shows how trifling the *a*-symmetry was in the sunspot areas, considering how greatly the area on day n exceeded the mean.

The differences appearing in the last two lines of Table IX. for values of s exceeding 9 are presumably dependent in part on sunspot phenomena prior to day $n-15$. The fact that the data from H ranges and character figures accord so closely, not merely in sign but in absolute size, must be regarded as largely fortuitous, because the scale of the character figures is a wholly arbitrary one.

§ 19. The application of the method of Table IX. to the data for the group of years

1892, 1893, and 1894, led to some very striking results, which are given in Table X. Use was made in the calculations of figures going one decimal place beyond the figures in Tables V. and VII.

Data in Table X., in the lines to which the letter A is attached, answer to the case where n is the representative day of largest sunspot area; those in the lines to which B is attached answer to the case where n is the representative day of smallest spot area. By A−B is meant the algebraic excess of the A figures over the corresponding B figures.

Table X.—Excess of Percentage Figure for Day $n+s$ over that for Day $n-s$ for Years 1892 to 1894 in Tables V. and VII.

s.		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.
H ranges	A. .	+18	+28	+38	+36	+40	+33	+21	+17	+14	+5	−5	−12	−10	−9	−8
	B. .	−8	−8	−12	−14	−11	−12	−9	−8	−9	−6	−3	−14	−11	−5	−6
	A−B. .	+26	+36	+50	+50	+51	+45	+30	+25	+23	+11	−2	+2	+1	−4	−2
Character figures	A. .	+25	+42	+49	+44	+41	+38	+27	+21	+21	+11	+10	−3	−1	+2	−2
	B. .	−20	−20	−11	−19	−13	−15	−11	−17	−15	−10	−16	−18	−11	−6	−3
	A−B. .	+45	+62	+60	+63	+54	+53	+38	+38	+36	+21	+26	+15	+10	+8	+1

Every B figure in Table X. is negative. For values of s up to 9 this may reasonably be ascribed to the passage of the pulse of low sunspot area centering at day $s = 0$. But for higher values of s it seems to arise from a pulse of high values in both range and character figures having its crest about day $n-12$ or $n-11$. This presumably is a more or less distinct phenomenon.

The spot area at the crest of the pulse of large spot area for the years 1892 to 1894, now under consideration, was 98 per cent. in excess of the mean for the 31 days, while the spot area at the trough of the pulse of small spot area showed a deficiency of only 67 per cent. from the 31-day mean. One would thus have expected the A figures in Table X. to exceed the B figures numerically, but the excess shown is larger than would have been anticipated. Thus, in this instance, a deficiency of sunspots below the mean seems to have exerted a smaller influence than a corresponding excess.

The large size of the percentage excesses in Table X., and the regularity in the figures for values of s up to 10, are phenomena of so striking a character that a warning seems desirable against attaching undue significance to them. From 1892 to 1894 there must have been a very close parallelism between the variations of sunspot areas and H ranges, pulses in the latter quantity tending to follow those of the former after an interval averaging about 4 days; but in view of the differences between the phenomena of different years shown in Tables VI. and VIII., it is clear that other important influences have to be considered.

These other influences would appear to have sometimes opposed the influence in virtue of which a sunspot pulse is followed by a magnetic pulse, and so long as the nature of the other influences and the various inter-relationships are unknown, it would be unsafe to assume that years of sunspot maximum always behave in the same way as 1892 to 1894.

§ 20. One of the possibilities suggested by Tables V. and VII. was that there might be a periodic fluctuation in magnetic properties, which was in phase with sunspot variations to a much greater extent in some years than in others. Various such periods have in fact been advanced by earlier investigators. A 26-day period has been suggested by several magneticians, including HORNSTEIN and BROUN. Dr. AD. SCHMIDT, of Potsdam, claims to have discovered that a large proportion of magnetic storms of the very largest kind are separated by intervals which are multiples of 29·97 days. In 1904–5, Mr. E. W. MAUNDER,[*] in two important papers, discussing the magnetic storms recorded at Greenwich from 1848 to 1903, claimed to have discovered a period of 27·275 days, corresponding to the time of rotation of the sunspot zones on the sun. The validity of Mr. MAUNDER'S claim to have established a period was supported by the present Astronomer Royal[†] amongst others, on arguments based on the mathematical theory of probability.

I had myself[‡] occasion, at the instance of the Editor of 'Terrestrial Magnetism,' to read carefully and criticise the first of Mr. MAUNDER'S papers, dealing with magnetic storms from 1888 to 1903. The result left me undecided whether Mr. MAUNDER had established his case. One important point in favour of his contention was that practically the same periodic time had been deduced from a study of magnetic storms at Toronto by Mr. ARTHUR HARVEY,[§] he and Mr. MAUNDER being ignorant of each other's work. A second fact in its favour was that a list of 125 magnetic storms at Kew between 1890 and 1900, got out by myself in an absolutely unprejudiced way, gave 21 intervals of from 25 to 28 days, while intervals of from 21 to 24 days and 29 to 32 days numbered respectively only 7 and 9. I experienced, however, a difficulty as to the proper mathematical basis for applying a probability calculation. As it so happened, the standard of disturbance accepted as defining a magnetic storm was such that the *average* interval between successive Greenwich storms from 1888 to 1903 was 29 days, and that between successive Kew storms from 1890 to 1900 was 28 days, both being intervals undesirably close to the supposed period. Another difficulty was that the times of commencement of the storms, from which Mr. MAUNDER derived his intervals, had an extraordinarily marked diurnal period, showing that they were

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[*] Royal Astronomical Society's 'Notices,' vol. 65, pp. 2 and 538.

[†] 'The Observatory,' vol. 28, 1905, p. 176.

[‡] 'Terrestrial Magnetism,' vol. 10, 1905, p. 9.

[§] 'Trans. Can. Inst.,' 1898–99, p. 345, &c.

largely influenced by something essentially local. The conclusion which I ultimately expressed* was that "whilst in the opinion of the writer further investigation is required to justify the final acceptance of any of Mr. MAUNDER's views, his paper is a most important one."

Several other criticisms of Mr. MAUNDER's work were published at the time. One which influenced me to some extent in undertaking the investigation now to be described, was made by Prof. H. H. TURNER† on behalf of Prof. SCHUSTER, in the discussion of Mr. MAUNDER's paper before the Royal Astronomical Society. Prof. SCHUSTER apparently considered the data to raise a presumption, rather than afford a demonstration, of the existence of *a* period, and after applying his periodogram methods he seemed to think there was more to be said for a 13·64 than a 27·28-day period. As a final summary of his views it is stated (*loc. cit.*, p. 84):—

"We have in fact a choice between two interpretations—

"1. Magnetic storms are apt to occur at times which, starting from a certain point, are multiples of 13·64 days. During some years the odd multiples and during other years the even intervals are principally concerned.

"2. Magnetic storms often recur after several successive intervals which are equal to some lapse of time sufficiently near 27·28 days to fall within the limits of rotation of sunspot zones."

§ 21. If we look at Tables V. and VII. we see that the interval between the crests of the principal and secondary pulses is somewhere about 15 days, but the crests are so rounded that the interval might well be a day or more short of this. The fact reminded me of Prof. SCHUSTER's remark about a 13·64-day period; it also suggested that we might have to do with the half of Dr. SCHMIDT's period. It thus appeared desirable to ascertain definitely whether the magnetic data employed in the previous investigations did or did not show a period. This was investigated in the following way:—

The 5 days of largest H range in each month were selected, and the magnetic character figures put down in successive columns for each of these and the 35 subsequent days. The columns were numbered n to $n+35$, the column n including the representative days of largest H range. A year or two's data sufficed to show that something was to emerge, so the enquiry was applied to the whole 11 years, and the investigation was extended so as to include 5 days (columns $n-5$ to $n-1$) preceding the selected days in column n.

The method may appear of somewhat a hybrid character. Naturally one would have preferred to base the enquiry entirely on the H ranges, or else entirely on the character figures. The objection to the former course was that a range is a 3 or 4 figure result. The research entailed dealing with $60 \times 41 \times 11$, or over 27,000 entries, and having for these character figures instead of ranges meant a great economy of

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* *Loc. cit.*, p. 14.

† 'Observatory,' Jan. 13, 1905, p. 80.

effort. The selection of the original 5 days a month from consideration of the H ranges was due to its greater simplicity. If there had been in each month 5 and only 5 days of magnetic character "2," one would naturally have preferred to take them. But some months had no days of character "2" at all, while others had considerably over 5, and there was no obvious simple way of selecting 5 days from each month as the most disturbed. One might, of course, have selected every day of character "2," but this would have given enormously more weight to the highly disturbed than to the quiet years.

Before discussing the results of the enquiry it is desirable to consider the nature of the data. In a large disturbance, or what is usually called a "magnetic storm," all the elements are as a rule so disturbed that one unhesitatingly assigns a "2" on inspection of the trace of any one of the elements, whether D, H, or even V. But there are many days to which I have assigned a "2" which would get only a "1" if the record of the most disturbed element—whether D or H—were left out of account. In the present investigation, as explained above, the selection of days depended entirely on the H range. It was thus certain *à priori* that in some months one or more of the selected days would only have a character figure "1," while days not selected would have character "2." Still it was abundantly clear that the character figure of the representative day n would be much above the average in every month, and that when a large number of months were included, the mean character figure from column n would be much larger than any other. The method was thus certain to give a well-marked pulse with its crest in column n.

Again, there is a tendency for disturbed days (or days of large H range) to occur in groups of 2 or more rather than singly. Suppose we have 3 consecutive days of character "2" amongst the 5 selected for one month, all the other days in their neighbourhood being of character "1" or "0." Obviously the character figures from these 3 days will occur in each of the 5 columns headed $n-2$ to $n+2$. Thus the pulse will not be a wall-sided one confined to day n, but will extend to adjacent days. The tendency to occur in groups is however less marked in the case of high character figures than in that of large spot areas. Thus we know in advance that we are certain to have a pulse, with crest at day n, somewhat resembling that of sunspot areas in Table IV., but probably less wide. Five or six days after the crest we may expect the pulse to die out, and thereafter, if no period exists shorter than 35 days, we may expect the mean character figures derived from the successive columns to show only irregular accidental departures from a dead-level value. If a period of m days exists, then we may expect a second pulse with its crest in column $n+m$, the height of the crest above the surrounding level being small unless the period is a well-marked one.

§ 22. The results of the investigation appear in Table XI. It includes data from the whole eleven years, and from three specified sub-groups of years. The figures in the columns headed $n-5$ to $n+35$ represent the corresponding mean values of the character figure, the days contributing to each mean being 660 for the 11-year and

180 for the 3-year groups. To assist the eye, vertical lines divide the columns into blocks of five. The last column gives the mean value of the character figure from all days of the year dealt with. These annual means are nearly, but not quite, the same as the means that would be derived by combining the figures from the 41 previous columns. Entries in the table which exceed the annual means are in heavy type.

Considering first the 11-year data, we have the primary pulse anticipated, with its crest at day n, the value for this day being more than double the mean from all days of the period. The 11-year mean is exceeded in the six columns $n-2$ to $n+3$, and columns $n-3$, $n+4$, and $n+5$ are also obviously affected by the pulse. From columns $n+6$ to $n+23$ inclusive we have a practically dead-level value, with only such fluctuations as would naturally arise accidentally. In column $n+24$ there begins a well-marked pulse, covering columns $n+24$ to $n+33$. The seven columns $n+25$ to $n+31$ give values above the 11-year mean, and the crest comes between columns $n+27$ and $n+28$. The values in these two columns are respectively 34 and 21 per cent. above the 11-year mean.

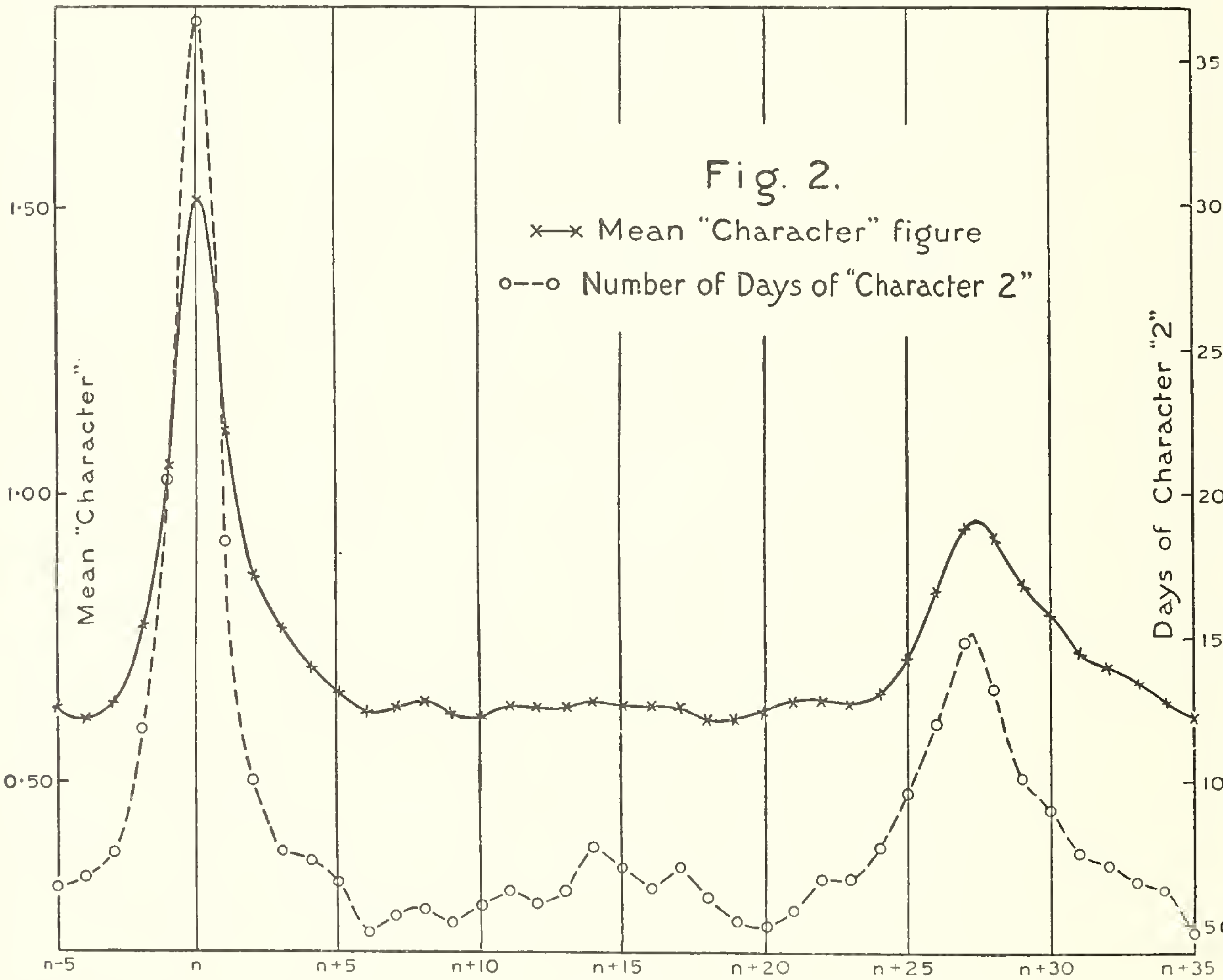
Fig. 2.

A consideration of the numerical results in the first line of Table XI, or their graphical representation in fig. 2, will probably remove the doubt which has I think

Table XI.—Mean Character Figures on 41 Consecutive Days, including the Representative Day n, of Large H Range.

	$n-5$.	$n-4$.	$n-3$.	$n-2$.	$n-1$.	n.	$n+1$.	$n+2$.	$n+3$.	$n+4$.	$n+5$.
Eleven years	0·63	0·61	0·64	**0·77**	**1·05**	**1·51**	**1·11**	**0·86**	**0·77**	0·70	0·66
1890, 1899, 1900 . .	0·43	0·41	0·41	**0·57**	**0·77**	**1·17**	**0·82**	**0·59**	**0·51**	0·43	0·48
1891, 1895, 1896 . .	0·70	0·68	0·77	**0·94**	**1·22**	**1·73**	**1·32**	**1·06**	**0·96**	**0·87**	0·76
1892, 1893, 1894 . .	0·82	0·73	0·72	**0·81**	**1·13**	**1·59**	**1·21**	**0·93**	**0·86**	0·77	0·74

	$n+6$.	$n+7$.	$n+8$.	$n+9$.	$n+10$.	$n+11$.	$n+12$.	$n+13$.	$n+14$.	$n+15$.	$n+16$.	$n+17$.	$n+18$.	$n+19$.	$n+20$.
Eleven years	0·62	0·63	0·64	0·62	0·61	0·63	0·63	0·63	0·64	0·63	0·63	0·63	0·61	0·61	0·62
1890, 1899, 1900 . .	0·43	0·44	0·43	0·43	0·43	0·38	0·39	0·44	0·42	0·43	0·41	0·38	0·37	0·40	0·42
1891, 1895, 1896 . .	0·68	0·73	0·74	0·73	0·70	0·75	0·75	0·81	0·84	0·80	0·82	0·78	0·70	0·74	0·77
1892, 1893, 1894 . .	0·74	0·74	0·74	0·69	0·64	0·72	0·76	0·71	0·73	0·71	0·71	0·77	0·71	0·69	0·66

	$n+21$.	$n+22$.	$n+23$.	$n+24$.	$n+25$.	$n+26$.	$n+27$.	$n+28$.	$n+29$.	$n+30$.	$n+31$.	$n+32$.	$n+33$.	$n+34$.	$n+35$.	Mean from all days.
Eleven years	0·64	0·64	0·63	0·65	**0·71**	**0·83**	**0·94**	**0·92**	**0·84**	**0·79**	**0·72**	0·70	0·67	0·64	0·61	0·70
1890, 1899, 1900 . .	0·39	0·37	0·37	0·34	0·47	**0·63**	**0·71**	**0·68**	**0·57**	**0·52**	**0·56**	**0·53**	**0·51**	0·44	0·41	0·47
1891, 1895, 1896 . .	0·74	0·78	0·76	0·84	**0·87**	**0·98**	**1·13**	**1·15**	**1·02**	**0·94**	0·82	0·79	0·73	0·72	0·66	0·84
1892, 1893, 1894 . .	0·78	**0·81**	0·75	0·76	**0·79**	**0·81**	**0·94**	**0·91**	**0·93**	**0·88**	**0·79**	**0·82**	0·78	0·74	0·72	0·78

hitherto prevailed amongst magneticians as to the reality of a 27–28-day period of a kind. There is undoubtedly a period, in the sense that a day which follows 27 or 28 days after a disturbed day is more likely to be itself distubed than is the average day. But whether there is a period in the sense in which the term is applied to solar and lunar phenomena, which go through a regular cycle in a fixed period of time, and continually persist in doing so, is of course an entirely different matter. The present investigation does not throw, and was not intended to throw, light on this further question.

§ 23. Data which relate to so long a period as 24-hours are not naturally very well adapted for determining the length of a period with any high precision. For such a purpose one wants data relating to a much shorter interval of time. Such data could be obtained in the present case by following the recent example of Prof. BIDLINGMAIER,[*] of Wilhelmshaven Observatory, in assigning character figures to individual hours of the day. It might prove possible in this way to estimate the period to a fraction of an hour, and investigate whether it is the same in all years, or depends in any way on the solar latitude of the greatest sunspot distribution, which is known to vary throughout the sunspot cycle. In this way light might be thrown on the cause of the phenomenon, whether of solar, lunar, or terrestrial origin.

Though we can hardly expect to make a very exact estimate of the length of the period shown by the 11-year figures in Table XI., it may be worth recording the results of several rough estimates which are fairly accordant. It will be best to employ not the actual data in Table XI., but the sums of the character figures for the 660 days from which these data were derived. These sums contain each three significant figures. They had the following values for the columns specified :—

Column . . .	$n+24$.	$n+25$.	$n+26$.	$n+27$.	$n+28$.	$n+29$.	$n+30$.	$n+31$.	$n+32$.	$n+33$.
Sum	430	467	545	620	607	556	523	476	464	440

Calculations were made on the following lines :—

$$\text{Basis (i)}\begin{cases}\text{From day } n+26 \text{ to day } n+27 \text{ rise of } 75 \text{ per diem,}\\ \quad ,, \quad n+28 \quad ,, \quad n+29 \text{ fall } ,, \ 51 \quad ,, \quad .\end{cases}$$

$$\text{Basis (ii)}\begin{cases}\text{From day } n+25 \text{ to day } n+27 \text{ mean rise of } 76{\cdot}5 \text{ per diem,}\\ \quad ,, \quad n+28 \quad ,, \quad n+31 \quad ,, \text{ fall } ,, \ 43{\cdot}6 \quad ,, \quad .\end{cases}$$

If we assume the rates of change between day $n+27$ and the summit, and between the summit and day $n+28$, to be first as in (i), second as in (ii), we find for the period—

On basis (i) 27·30 days,
,, (ii) 27·25 ,, .

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[*] 'Veröffentlichungen des k. Observatoriums in Wilhelmshaven,' Blatt 1–4, 1910, 1911.

The rise to the crest was clearly more rapid than the subsequent fall, the secondary pulse resembling closely in this respect the primary, for which successive character totals ran as follows :—

Column . .	$n-3$.	$n-2$.	$n-1$.	n.	$n+1$.	$n+2$.	$n+3$.	$n+4$.	$n+5$.
Sum . . .	423	510	690	996	731	570	511	463	438

Assuming a uniform progression between days $n-3$ and $n-4$, and again between days $n+4$ and $n+5$, we find

Value 430 occurring at $n-2{\cdot}92$ as well as at $n+24$,
,, 440 ,, $n+4{\cdot}92$,, ,, $n+33$.

These two values come near the beginning and end of both pulses, and we may thus regard 7·84 days in the primary pulse as represented by the somewhat increased width of 9 days in the secondary pulse. If now we assume the widening exhibited by the secondary pulse to be contributed to in like proportion from the parts which precede and follow the crest, and take $27+x$ as the time of the crest, we have

$$(3+x)\div\{5+(1-x)\} = 2{\cdot}92/4{\cdot}92,$$

whence $x = 0{\cdot}35$, and so period $= 27{\cdot}35$ days.

From these and other similarly rough calculations I should assign to the period as indicated by the 11-year data the duration 27·3 ± 0·1 days. Of any period shorter than this there seems not even a suggestion in the 11-year figures.

§ 24. Let us now return to a consideration of the results from the three shorter groups of years in Table XI. The figures are naturally less smooth than those in the first line, but all the groups show the 27–28-day period. Analogous figures were really got out for each half-year separately, and of these 22 sets of data there was not one that did not show enlarged values in the immediate neighbourhood of days $n+27$ and $n+28$. In every instance the mean from columns $n+26$ to $n+30$ exceeded the mean from columns $n+20$ to $n+25$, and in 14 of the half-years the largest value in any column subsequent to $n+5$—*i.e.*, subsequent to columns clearly affected by the preliminary pulse—occurred in one or other of the columns $n+27$ and $n+28$. There was only one whole year, 1894, in which the figures in columns $n+27$ and $n+28$ were both exceeded by the figure in any other column subsequent to $n+5$.

If we take the ratio borne by the larger of the two figures in columns $n+27$ and $n+28$ to the figure in column n as a measure of the prominence of the 27–28-day period, we find 0·62 for the whole 11 years, 0·59 for the sunspot maximum period, and 0·67 for the group composed of 1891, 1895, and 1896. The 27–28-day period was thus considerably most in evidence in the group of years which gave the faintest indication of the magnetic pulse following 4 days after the sunspot area pulse, and it was least in evidence in the sunspot maximum group of years, which gave the most prominent indication of the above pulse. The prominence of the 27–28-day period in the sunspot minimum groups of years, which contained comparatively few magnetic storms, would alone suffice to show that the phenomenon, whatever its nature, is not confined to outstanding disturbances such as those chronicled by Mr. MAUNDER.

A special feature in the results for 1891, 1895, and 1896 is a faint indication of a shorter period of about 14 days. The figures for this group of years in columns $n+13$ to $n+16$ all exceed the figure in any other column between $n+5$ and $n+23$. This seems hardly likely to be pure accident, and it may represent Prof. SCHUSTER'S 13·64 days' period.

§ 25. In view of the interest attaching to the reality of a 27–28-day period, a similar investigation to the preceding was carried out for the two years 1894 and 1895, employing the H ranges instead of the character figures.

These two years were selected because, when character figures were employed, the one, 1895, showed the 27–28-day period specially clearly, while the other, 1894, showed it less clearly than perhaps any other year. The investigation based on H ranges took account only of the 5 representive days a month and the 35 following days. The results are given in Table XII., accompanied by the corresponding results previously obtained from the character figures. To facilitate comparison, both sets of figures are expressed as percentages of the arithmetic mean value derived from the 36 columns.

In the case of 1894 two sets of H range figures are given. The former and the character figures given depend on all the 60 selected days of the year. In obtaining the second set of H range figures, all ranges were omitted which exceeded 200γ, and a mean was taken from the remaining figures in each column. The object was to see the effect of omitting a few of the larger magnetic storms—all, in fact, which gave H ranges in excess of the largest range of 1895.

The data from 1895, though naturally not as smooth as the 3-year and 11-year data in Table XI., show the 27–28-day period quite as clearly. It is as unmistakable in the range as in the character figures. Again both range and character figures afford distinct indications of a 13–14-day period, which it will be remembered appeared in Table XI. only in the group of years containing 1895.

In 1894 the character figures and the range figures (i) both show not a peak at day $n+27$ or $n+28$, but a high plateau extending from about day $n+25$ to day $n+34$. The range figures, in fact, would seem to favour a Schmidt, or 30-day period, rather than a 27–28-day period. The reason of this is clear on examining the range (ii) figures. The high values in the range (i) figures in column $n+29$ and subsequent columns were mainly due to the fact that two outstanding ranges, respectively 637γ and 660γ, "happened" to fall one or both in these columns.

§ 26. The investigation embodied in Tables XI. and XII., though leading to somewhat unexpected results possessed of intrinsic interest, does not afford an immediate explanation of the phenomenon for which an explanation was being sought, viz., the

TABLE XII.—Percentage Values from Character Figures and H Ranges on 36 Consecutive Days, including the Representative Day n, of Large H range.

Year.	Data.	n.	$n+1$.	$n+2$.	$n+3$.	$n+4$.	$n+5$.	$n+6$.	$n+7$.	$n+8$.	$n+9$.	$n+10$.	$n+11$.	$n+12$.	$n+13$.	$n+14$.	$n+15$.
1895	Character figures	179	141	121	121	107	97	86	91	81	76	72	93	95	103	114	103
	H ranges	169	123	108	97	92	90	90	88	86	87	92	92	104	107	105	101
1894	Character figures	183	146	118	106	103	93	95	99	101	91	77	84	78	78	86	80
	H ranges (i)	215	144	119	97	100	102	82	91	99	87	81	84	80	83	80	77
	„ (ii)	174	121	106	98	102	96	92	93	100	92	91	94	89	94	90	86

Year.	Data.	$n+16$.	$n+17$.	$n+18$.	$n+19$.	$n+20$.	$n+21$.	$n+22$.	$n+23$.	$n+24$.	$n+25$.
1895	Character figures	98	97	76	86	81	81	76	81	98	93
	H ranges	102	91	83	87	88	88	82	89	100	108
1894	Character figures	73	88	84	90	78	101	101	78	90	112
	H ranges (i)	77	87	98	86	82	92	100	87	89	108
	„ (ii)	86	98	96	89	92	98	108	93	90	102

Year.	Data.	$n+26$.	$n+27$.	$n+28$.	$n+29$.	$n+30$.	$n+31$.	$n+32$.	$n+33$.	$n+34$.	$n+35$.
1895	Character figures	114	133	131	110	110	98	98	84	86	86
	H ranges	114	128	119	114	104	97	98	93	91	93
1894	Character figures	119	108	106	114	112	105	106	101	106	108
	H ranges (i)	107	103	105	111	125	121	104	105	101	91
	„ (ii)	114	112	105	103	103	100	101	96	103	93

TABLE XIII.—Incidence of Different Magnetic Characters in 31 Consecutive Days, including the Representative Day n of Large Sunspot Area.

	$n-15$.	$n-14$.	$n-13$.	$n-12$.	$n-11$.	$n-10$.	$n-9$.	$n-8$.	$n-7$.	$n-6$.	$n-5$.	$n-4$.	$n-3$.	$n-2$.	$n-1$.	n.
Character "2" days . .	76	82	89	94	96	94	87	81	67	73	78	72	67	71	73	78
" "1" " . .	288	282	279	303	296	306	300	301	290	281	273	275	290	280	293	297
Disturbed days	364	364	368	397	392	400	387	382	357	354	351	347	357	351	366	375
Quiet "	296	296	292	263	268	260	273	278	303	306	309	313	303	309	294	285

	$n+1$.	$n+2$.	$n+3$.	$n+4$.	$n+5$.	$n+6$.	$n+7$.	$n+8$.	$n+9$.	$n+10$.	$n+11$.	$n+12$.	$n+13$.	$n+14$.	$n+15$.	Mean from 31 columns.
Character "2" days . .	82	89	85	86	88	89	80	86	83	82	89	87	80	81	75	81·9
" "1" " . .	302	295	321	332	325	320	319	312	314	315	301	290	295	304	311	299·7
Disturbed days	384	384	406	418	413	409	399	398	397	397	390	377	375	385	386	381·6
Quiet "	276	276	254	242	247	251	261	262	263	263	270	283	285	275	274	278·4

inconspicuousness of the crest in column $n+4$ of Tables V. and VII. in the case of the group of years 1891, 1895, 1896, and the great development of the crest occurring 14 or 15 days earlier. There is, it is true, in Table XI. and XII. some indication of a period of about 14 days for the years 1891, 1895, and 1896, which is not apparent in the other groups of years, and this would help to explain an increased prominence in the crest about column $n-11$ in Tables V. and VII., if the crest in column $n+4$ had its usual prominence. But it cannot by itself account for the earlier and presumably secondary pulse being more prominent than the later.

Table XIII. aims at throwing further light on the phenomena of Tables V. and VII. A given mean H range, or a given mean character figure, may arise in many different ways. Of two collections of equal numbers of days which have the same mean range or character figure, one will contain a larger number of days of character "2" than the other. It appeared desirable to ascertain whether increase in a mean character figure in Table VII. arose from similar increases in the number of days of character "1" and "2," or whether it denoted a special development of highly disturbed days.

Each mean value in Table VII. for the 11-year period was derived from 660 days. Table XIII. shows how many of these were of character "2," and how many were of character "1." The days of character "2" and "1" combined give the total of disturbed days, and the difference between this total and 660 gives the number of days of character "0," *i.e.*, quiet days. The last column in Table XIII. gives the mean of the corresponding entries in columns $n-15$ to $n+15$, showing that on the average out of the 660 days in each column 82 were of character "2," 300 of character "1," and 278 of character "0." Figures which exceed the means in the last column are in heavy type.

Table XIII. makes it clear that the secondary pulse in Table VII., with crest about column $n-11$, is due almost entirely to an excess of days of character "2," while the primary pulse, with crest about column $n+4$, is mainly due to an excess of days of character "1." The number of days of character "2" in columns $n-12$, $n-11$, and $n-10$ notably exceeds that in any other column.

Quiet days are markedly in excess of the mean from 7 to 1 day previous to the day of largest spot area, and they are even in slight excess on the representative day itself. They are also decidedly in excess in columns $n-15$ to $n-13$, though their excess in column $n-13$ is neutralised by the co-existing excess in the number of days of character "2."

On the whole, it may be said that the primary pulse is due rather to the absence of quiet conditions than to the presence of large disturbance.

§ 27. Table XIV. serves the same purpose relative to Table XI. that Table XIII. served relative to Table VII. It proceeds, however, on a slightly different plan, and gives some data for the 3-year periods in addition to those for the whole 11 years. The first four lines give the total number of days of character "2." Consider, for example,

TABLE XIV.—Incidence of Magnetic Character in 41 Consecutive Days, including the Representative Day n of Large H Range.

	$n-5$.	$n-4$.	$n-3$.	$n-2$.	$n-1$.	n.	$n+1$.	$n+2$.	$n+3$.	$n+4$.	$n+5$.	$n+6$.	$n+7$.	$n+8$.	$n+9$.	$n+10$.
1890, 1899, 1900, number of "2's" .	10	11	12	19	29	54	26	12	9	12	11	5	3	5	9	9
1891, 1895, 1896, ,, "2's" .	22	19	30	55	79	132	73	49	35	25	22	15	22	23	24	24
1892, 1893, 1894, ,, "2's" .	23	20	17	25	57	108	54	23	19	19	19	17	16	14	10	13
Eleven years, ,, "2's" .	63	66	75	**118**	**205**	**365**	**184**	**101**	76	73	65	47	53	55	51	57
,, ,, ,, "1's" .	293	271	273	274	280	266	**363**	**368**	**359**	**317**	**308**	**316**	**309**	**314**	**310**	288
,, ,, disturbed days . . .	356	337	348	**392**	**485**	**631**	**547**	**469**	**435**	**390**	373	363	362	369	361	345
,, ,, quiet days	**304**	**323**	**312**	268	175	29	113	191	225	270	**287**	**297**	**298**	**291**	**299**	**315**

	$n+11$.	$n+12$.	$n+13$.	$n+14$.	$n+15$.	$n+16$.	$n+17$.	$n+18$.	$n+19$.	$n+20$.	$n+21$.	$n+22$.	$n+23$.	$n+24$.	$n+25$.
1890, 1899, 1900, number of "2's" .	10	7	6	11	11	9	6	3	3	7	5	5	8	11	16
1891, 1895, 1896, ,, "2's" .	27	30	33	39	36	32	26	21	24	22	18	24	25	33	42
1892, 1893, 1894, ,, "2's" .	14	14	14	15	16	16	24	18	15	9	20	26	19	16	21
Eleven years, ,, "2's" .	62	58	62	77	70	63	70	60	52	50	55	66	66	77	**96**
,, ,, ,, "1's" .	292	298	294	269	275	289	277	282	301	**310**	**311**	292	284	276	275
,, ,, disturbed days . . .	354	356	356	346	345	352	347	342	353	360	366	358	350	353	371
,, ,, quiet days	**306**	**304**	**304**	**314**	**315**	**308**	**313**	**318**	**307**	**300**	**294**	**302**	**310**	**307**	**289**

	$n+26$.	$n+27$.	$n+28$.	$n+29$.	$n+30$.	$n+31$.	$n+32$.	$n+33$.	$n+34$.	$n+35$.	Mean values.
1890, 1899, 1900, number of "2's" .	21	22	19	13	13	12	12	11	7	5	10
1891, 1895, 1896, ,, "2's" .	48	65	65	45	34	23	21	19	24	17	33
1892, 1893, 1894, ,, "2's" .	24	32	26	28	22	25	28	24	17	12	21
Eleven years, ,, "2's" .	**120**	**148**	**132**	**101**	**90**	75	71	65	62	47	79
,, ,, ,, "1's" .	**305**	**324**	**343**	**354**	**343**	**326**	**322**	**310**	300	**312**	302
,, ,, disturbed days . . .	**425**	**472**	**475**	**455**	**433**	**401**	**393**	375	362	359	381
,, ,, quiet days	235	188	185	205	227	259	267	**285**	**298**	**301**	279

the column headed n. This relates to the 5 days of largest H range in each month. These days total 180 in each of the 3-year periods, and 660 in the eleven years. Of the 180 selected days in the first 3-year group only 54 attained character "2." The corresponding numbers in the second and third 3-year groups were respectively 132 and 108, and of the 660 days selected from the 11 years 365 reached character "2."

The three last lines in Table XIV. all relate to the whole 11 years. Still considering column n, we learn that 266 of the 660 days had character "1." Combining these with the 365 days of character "2," we have in all 631 disturbed days, leaving 29 days of character "0." Nearly all these 29 quiet days came from the last months of 1900, when days of character "2" were non-existent, and days of character "1" were rare.

The data in columns $n-5$ to $n-1$, to $n+1$ to $n+35$, have an exactly similar significance. They refer, as in Table XI., to the 5 days before and the 35 days after the selected days of largest H range. The last column in the table shows what numbers we should have got from average days of the years concerned. Eleven-year data in columns $n-5$ to $n+35$ which exceed the corresponding figures in the last column are in heavy type.

The results relating to the character "2" figures from the 11 years are shown graphically in the broken line curve of fig. 2, p. 100.

The number of days of character "1" in the 11 years is very notably in excess of the mean in columns $n+27$ to $n+32$, but it is the great development of character "2" figures that is mainly responsible for the prominence of the 27–28-day period in Table XI. Taking the 11-year data, the number of days of character "2" is above the mean only in columns $n-2$ to $n+2$ and $n+25$ to $n+30$. The rise to the crest and the subsequent subsidence in the primary pulse of character "2" figures are exceedingly rapid, and the same is true to only a slightly less extent of the secondary pulse. The numbers of days "2" in columns $n+27$ and $n+28$ exceed those in columns $n-2$ and $n+2$, and simply tower over the numbers in columns $n+3$ to $n+24$. The relative prominence of the character "2" figures in columns $n+27$ and $n+28$ is even greater for the two first 3-year periods in Table XIV. than for the 11-year period. In the third or sunspot maximum group of years this prominence is less.

The number of days of character "1" is much less variable in Table XIV. than the number of days of character "2." When, however, there are a large number of the latter days there are so many the fewer available for other character figures. Thus the number of days of character "1" is perhaps less instructive than the number of disturbed days as a whole. This latter number subsides much less rapidly than it rises in both the primary and secondary pulses. This presumably is a direct consequence of the known fact that while a highly disturbed day often immediately follows a quiet day, the converse is rare.

The fewness of quiet days in columns $n+26$ to $n+30$ presents the 27–28-day period in perhaps as striking a light as any.

The standard of disturbance qualifying for "2" in the present investigation is low compared to that adopted by Mr. MAUNDER as denoting a "magnetic storm." During the 11 years as a whole nearly 1 day in 8 was allotted "2," while Mr. MAUNDER on the average had only about one storm—lasting some 30 hours—in 28 days.

With the standard adopted here, the chance of the magnetic disturbance attaining character "2" is about twice as great for a day which follows either 27 or 28 days after a day of character "2" as it is for the average day of the year.

§ 28. Table XV. gives for each year of the eleven WOLFER'S mean sunspot frequency, the number of days of character "0," "1," and "2," and the corresponding character figure for the average day, and finally the mean values of the absolute daily H and D ranges. The D ranges are expressed in terms of force, on the basis that a 1′ change of declination corresponded to a force of 5·32γ acting perpendicular to the magnetic meridian.

TABLE XV.—Results for Individual Years.

Year.	WOLFER'S sunspot frequency.	Number of days of character.			Mean character figure.	Absolute daily range (unit 1γ).	
		0.	1.	2.		H.	D.
1890	7·1	193	155	17	0·51	44·8	56·8
1891	35·6	147	159	59	0·76	60·8	73·2
1892	73·0	129	189	48	0·78	84·0	94·2
1893	84·9	140	191	34	0·71	69·7	83·1
1894	78·0	98	220	47	0·86	81·4	87·8
1895	64·0	97	194	74	0·94	67·9	82·9
1896	41·8	132	168	66	0·82	64·5	77·2
1897	26·2	152	167	46	0·71	51·8	64·6
1898	26·7	161	158	46	0·68	56·0	65·4
1899	12·1	176	152	37	0·62	49·6	60·3
1900	9·5	274	82	9	0·27	37·3	48·8
Means . . .	41·7	154	167	44	0·70	60·7	72·2

As already remarked, it is difficult to avoid sensible fluctuations in the standard of character figures, but the range figures support the character figures in representing 1893—the year of largest sunspot frequency—as very decidedly less disturbed than the two adjacent years. Again, all the criteria agree in representing 1900 as decidedly the quietest year, though 1890 had fewer sunspots.

The range of the regular diurnal inequality was largest in the year of sunspot maximum. Other things being the same, the absolute range would naturally increase with that of the diurnal inequality. There is thus nothing surprising in the fact that the D and H absolute ranges in 1891, 1895, and 1896 are exceeded by those of 1893, though the character figure obtained for the latter year is less. Whether the character figure for 1892 ought really to be less than that for 1896, and whether the character figure of 1895 should be the largest of all, are results more open to doubt. The mean of the absolute daily ranges in 1892 and 1894, whether in H or D, decidedly exceeded that of any other year; but this was at least partly due to the incidence in these two years of an altogether outstanding proportion of the largest magnetic storms of the 11 years.

The H and D figures in Table XV. place the 11 years in exactly the same order as regards amplitude of range. In 1891, 1893, 1895, 1896, and 1897, the ratio borne by the mean D range to the mean H range lies between 1·19 and 1·22. The extreme values of the ratio are 1·08 in 1894 and 1·31 in 1900.

§ 29. Table XVI. distributes the total number of days of character "0," "1," and "2" under the twelve months to which they belong, and gives the corresponding mean value of the character figure. It also gives for comparison the corresponding mean absolute daily ranges in H and D, the latter expressed in terms of force as in the previous table.

TABLE XVI.—Results for the 12 Months. Totals and Means (11 Years 1890 to 1900).

Month.	Number of days of character.			Mean character figure.	Absolute daily range (unit 1γ).	
	0.	1.	2.		H.	D.
January	151	150	40	0·67	46·5	59·4
February	109	145	56	0·83	60·1	72·8
March	113	163	65	0·86	66·7	84·7
April	133	157	40	0·72	67·6	79·8
May	150	155	36	0·67	68·8	79·3
June	154	148	28	0·62	66·9	72·6
July	159	144	38	0·64	70·6	75·2
August	151	166	24	0·63	68·0	75·7
September	129	161	40	0·73	66·4	77·5
October	124	165	52	0·79	59·7	74·9
November	155	141	34	0·63	47·6	62·3
December	171	140	30	0·59	39·8	52·1

The more or less disturbed character of a month may be regarded as indicated either by the mean value of the character figure, or by the fewness of the days of character "0" as compared to the total. On either criterion, March was the most disturbed month, followed at no great interval by February and October. March was also the month of largest D range, but the H range in March was slightly exceeded in each of the five months April to August.

December had the fewest days of disturbance, the smallest mean magnetic character,

Table XVII.—Percentage Values of H Ranges (ordinary type) and Character Figures (heavy type).

	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Year.
1890	76 **81**	72 **73**	59 **53**	68 **51**	59 **68**	71 **59**	72 **70**	77 **87**	84 **96**	91 **110**	88 **95**	79 **44**	75 **74**
1891	75 **57**	79 **94**	100 **131**	110 **148**	110 **136**	90 **86**	87 **75**	102 **118**	112 **137**	120 **119**	106 **89**	108 **99**	100 **107**
1892	121 **91**	188 **137**	171 **131**	124 **93**	133 **102**	124 **86**	166 **140**	141 **93**	106 **114**	125 **110**	115 **95**	134 **143**	137 **111**
1893	119 **115**	98 **90**	101 **90**	115 **65**	95 **73**	128 **108**	118 **100**	130 **113**	120 **128**	120 **114**	127 **142**	108 **88**	115 **102**
1894	132 **101**	164 **115**	117 **83**	117 **102**	120 **121**	142 **162**	151 **155**	140 **113**	133 **132**	120 **119**	156 **174**	116 **126**	134 **125**
1895	102 **120**	110 **128**	113 **128**	120 **139**	111 **121**	123 **156**	114 **145**	85 **98**	94 **110**	123 **164**	135 **163**	117 **143**	112 **135**
1896	137 **172**	113 **150**	103 **128**	110 **121**	114 **116**	90 **97**	96 **125**	111 **144**	116 **91**	97 **90**	91 **79**	98 **94**	106 **117**
1897	86 **76**	70 **94**	78 **105**	115 **158**	100 **111**	83 **108**	76 **70**	75 **98**	73 **78**	85 **102**	79 **105**	111 **116**	86 **102**
1898	85 **101**	81 **73**	110 **94**	77 **84**	94 **97**	93 **108**	85 **110**	91 **113**	116 **105**	92 **90**	84 **89**	95 **126**	92 **99**
1899	84 **96**	70 **107**	76 **83**	83 **97**	94 **111**	90 **97**	78 **85**	84 **93**	90 **91**	70 **57**	71 **53**	88 **99**	82 **89**
1900	84 **91**	56 **39**	72 **75**	61 **42**	71 **44**	65 **32**	57 **25**	63 **31**	54 **18**	58 **25**	48 **16**	46 **22**	61 **39**

and decidedly the smallest daily range in both H and D. August and June, however, had a smaller number of days of character "2."

On the average of the 12 months, the D range is about 20 per cent. greater than the H range; but the proportional excess is notably less in June, July, and August than in the midwinter months.

§ 30. Table XVII. represents an attempt to reach comparative results for the 132 months of the 11 years. The figures in ordinary type were obtained from the mean values of the absolute daily H ranges in individual months. The value for each of the 11 Januarys was expressed as a percentage of the mean of the 11 January values, and the same was done for the other months of the year. This was intended to eliminate the annual variation in the amplitude of the daily range. The figures in heavy type were derived from the character figures, the value for each month being again expressed as a percentage of the arithmetic mean character figure for the 11 months of the same name. The data in the two columns headed "year" represent arithmetic means of the corresponding 12 percentage values in the monthly columns.

The difficulty of maintaining a uniform standard of magnetic character in different years should be remembered, as it introduces greater uncertainty in the character data of Table XVII. than in those of any previous table. Consider, for example, what would happen if the standard for characters "1" and "2" were lower for 1896 than other years. In January 1896 the character figure was remarkably large, as compared to that of the other months of the year. The consequence of the hypothetical low standard would be not merely to unduly exalt the character figure for January 1896 in Table XVII., but also to depress the character figures in all the other Januarys.

The data in the second last column of Table XVII. put the years in the same order as the corresponding data in Table XV.

The daily range remains very considerable in the quietest times when character figures are nearly all "0." Thus the range figures in Table XVII. naturally fluctuate within narrower limits than the character figures. The extreme smallness of the latter towards the end of 1900 is particularly striking.

While there are many marked differences in the order in which the two sets of figures place the months, a conspicuously high value in the one set of figures is nearly always associated with a high value in the other. January, 1896, March, 1892, June, 1894, November, 1894, and December, 1892, stand first in both lists for months of the same name; while February, 1892, July, 1894, September, 1894, October, 1895, November, 1895, and December, 1895, stand either first or second in both lists.

If we take a mean between the two sets of figures, November, 1894, was relatively the most disturbed, and November, 1900, was relatively the quietest month of all. February, 1892, from the same standpoint, only just fell short of November, 1894, and was followed after a slight interval by January, 1896, July, 1892, July, 1894, and June, 1894.

§ 31. An attempt was made to utilise the figures of Table XVII. in a similar way to that adopted earlier in the paper with daily magnetic values. Use was made of WOLFER's frequencies instead of the Greenwich sunspot areas, because mean values of the former were available for all months of the 11 years.

The three months of highest sunspot frequency in each year were entered in column n, the three months immediately preceding in column $n-1$, and the three months immediately subsequent in column $n+1$. The months having been thus arranged in three columns, corresponding lists were made of WOLFER's frequencies, and of the two sets of percentage figures in Table XVII. Exactly the same operations were then gone through, taking as basis the three months of least sunspot frequency in each year.

The mean results thus found from the eleven years are given in Table XVIII.

TABLE XVIII.—Data from Three Months of Largest and Three Months of Least Sunspot Frequency in each Year, 1890 to 1900.

	Sunspot frequencies.			H ranges, percentages.			Character figures, percentages.		
	$n-1$.	n.	$n+1$.	$n-1$.	n.	$n+1$.	$n-1$.	n.	$n+1$.
Months of largest frequency	43·4	54·7	43·6	103·0	104·5	102·4	110·9	104·1	102·6
Months of least frequency .	40·8	28·8	40·0	100·1	96·3	94·1	97·7	98·9	94·8
Excess of first group . . .	2·6	25·9	3·6	2·9	8·2	8·3	13·2	5·2	7·8

The number of months was too small to eliminate accidental features. This is especially true of the character figures for reasons already stated.

The greater uncertainty of the character figures is borne out by the fact that while the mean percentage value from the 3 months of largest sunspot frequency exceeded the corresponding mean from the 3 months of least frequency in every single year in the case of H ranges, the same phenomenon occurred in only 7 of the 11 years in the case of character figures.

The 4 days retardation, shown in Tables V. and VII., would lead to some association of sunspot frequency with magnetic phenomena in the following month, but even the H range figures in Table XVIII. suggest more connection than this would account for.

§ 32. In the case of the range, R, of mean diurnal inequality for the year in H at Kew, the formula found by applying the method of least squares to the observations of the 11 years, 1890–1900, may be written

$$R = R_0 (1 + 1{\cdot}07 \times 10^{-2} S), \quad \ldots \ldots \ldots \quad (1)$$

where R_0 denotes the range in an ideal year of no sunspots and S is WOLFER'S sunspot frequency.

A rise of 100 in S would increase R by 107 per cent. of R_0. Hitherto, in the present paper, we have been employing as unit not R_0 but what is practically the mean value of R for the period concerned. Taking, for instance, the whole 11 years, for which the mean value of S was 41·7, and representing by $\overline{R}$ the mean value of R for the period, we may replace (1) by

$$\begin{aligned} R &= \overline{R}(1+1{\cdot}07\times10^{-2}S)\div(1+1{\cdot}07\times0{\cdot}417) \\ &= \overline{R}(1+1{\cdot}07\times10^{-2}S)/1{\cdot}446 \quad \ldots\ldots\ldots\ldots \quad (2) \end{aligned}$$

In the case of the 11 years in Table IV. the difference between the extreme values of the Greenwich spot areas during the 31 days was 150 per cent. of the mean value. No serious error will arise in regarding Greenwich areas and WOLFER'S frequencies as standing to one another in a constant ratio, or in assuming the mean value of the frequency for the representative 31 days to be exactly 41·7. If, then, the variation in absolute ranges on individual days followed, except for a lag, the same law as that of inequality ranges in individual years, the anticipated variation of H ranges in Table V. would have been

$$\overline{R}(1{\cdot}07\times0{\cdot}626)/1{\cdot}446,$$

and the change expressed as a percentage of the mean value would thus have been 46·3.

The percentage change actually seen in the H ranges was

$$111{\cdot}6-93{\cdot}5 = 18{\cdot}1,$$

or only 0·39 of that just deduced from the formula.

Again, taking the data of Table XVIII., in columns *n*, we have a percentage change of 8·2 in the absolute range, corresponding to a difference of 25·9 per cent. in sunspot frequency.

If the change in the absolute range had, in this case, followed the law embodied in (2), its amplitude as a percentage of its mean value would have been

$$1{\cdot}07\times25{\cdot}9/1{\cdot}446 = 19{\cdot}2.$$

The ratio of the observed to the calculated value in this case is

$$8{\cdot}2/19{\cdot}2 = 0{\cdot}43.$$

A still larger value for this ratio is obtainable from the H range data in Table V. for the years 1892 to 1894. The range of sunspot areas in the representative 31 days was 135 per cent. of the mean value, and the mean value of WOLFER'S frequency for the 3 years was 78·6.

Thus the percentage change of H range calculated as in (2) would have been

$$(1{\cdot}07 \times 78{\cdot}6 \times 1{\cdot}35) \div (1 + 1{\cdot}07 \times 0{\cdot}786) = 62,$$

while the percentage change given in Table V. is 40. Thus the ratio of the observed to the calculated change is 0·65.

§ 33. Even mean annual values of the absolute H ranges do not vary with sunspot frequency at all as closely as do the diurnal inequality ranges. Still, if we compare any one of the 3 years of sunspot maximum, 1892, 1893, 1894 with any one of the 3 years of minimum, we find a greater difference between the absolute ranges than between the inequality ranges. Thus everything points to the conclusion that the magnetic wave, with crest 4 days after that of sunspots, represents only a part—in general, probably the smaller part—of the sunspot influence.

In addition, there seems to be an influence which maintains a high average range of diurnal variation in years of many sunspots, so that even when sunspot area for several days in succession falls to a comparatively low level, the daily range continues to exceed that normal to the same month of a year having the same mean sunspot area as the specified days.

Also there is a more distinctively disturbance element whose amplitude does not appear to be directly proportional to sunspot area, and which seems largely responsible for the 27–28-day period shown in Tables XI. and XIV.

It must be remembered that Tables V. and VII. cover only a sufficient number of days to show a sunspot influence which acts on the earth within 15 days of the sunspot phenomenon on the sun. A period longer than this, but shorter than 2 months, is not contradicted by Table XVIII.

Again, sunspots may not themselves be the actual sources of the solar influence, but only symptoms that something is happening, has already happened, or may only be about to happen, which exerts an influence on the earth.

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(RESEARCH EXECUTED IN THE DAVY FARADAY RESEARCH LABORATORY OF THE ROYAL INSTITUTION OF GREAT BRITAIN, LONDON, W.).

BY

WALTER WAHL, PH.D.,
ROSENBERG RESEARCH FELLOW OF THE UNIVERSITY OF HELSINGFORS.

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Communicated by Sir JAMES DEWAR, *F.R.S.*

(Received April 20,—Read May 23, 1912.)

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PART II.—OPTICAL DETERMINATION OF DIAGRAMS OF STATE.

HISTORICAL.

IN the course of his well-known investigations concerning the compressibility of gases and liquids, AMAGAT made some series of measurements taking observations through

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two small glass windows fitted to his high-pressure bomb ("méthode des regards"),* and he also twice made an attempt to use a similar arrangement for the determination of melting and crystallization at high pressures. His first paper on these subjects deals with the melting and with the formation of two different kinds of crystals of carbon tetrachloride.† The highest pressure employed was 1,160 atmospheres. The second paper, in which a somewhat different arrangement of the glass windows was used, deals with the crystallization of ice at temperatures below zero under the influence of high pressures.‡ In a summarizing paper AMAGAT§ states that he occasionally was able to reach pressures of about 1,600 atmospheres before the glass windows were broken, but observations were not actually made at higher pressures than 1,000 atmospheres. In this paper a sketch of the apparatus is also given. AMAGAT states that he met with severe difficulties during these investigations, and he has not pursued the subject further.

Later melting-points and transition-points of some "liquo-crystalline" substances have been measured in Jena glass tubes up to 300 atmospheres by HULLETT,‖ and other optical observations at pressures above that of the atmosphere have been made by ROTHMUND (maximum 500 atmospheres),¶ RÖNTGEN and ZEHNDER,** SIERSTEMA,†† LIVEING and DEWAR,‡‡ HUTTON and PETAVEL,§§ and DUFFIELD,‖‖ but in these investigations the pressures have, as a rule, not exceeded 100 atmospheres.

By a volumetric method melting-points were first determined at comparatively high pressures by BARUS in 1891.¶¶ BARUS, who undertook these measurements in connection with an extensive series of measurements of compressibilities,*** determined the melting-point of naphthalene up to pressures of 1,435 atmospheres. In 1898, MACK measured the melting-point of naphthalene at pressures between that of the atmosphere and 2,140 kg./cm.^{2}, by observing the volume change as indicated by the manometer when melting occurred.††† But our chief knowledge about equilibrium

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* E. H. AMAGAT, 'Journ. d. Chem. Phys.,' 1893, 6 ser., XXIX., p. 68, 96, 505.

† E. H. AMAGAT, 'Compt. Rend.,' CV. (1887), p. 165.

‡ E. H. AMAGAT, 'Compt. Rend.,' CXVII. (1893), p. 507.

§ 'Notice sur les Travaux Scientifiques de M. E. H. AMAGAT,' Paris, 1896.

‖ G. A. HULLETT, 'Zeitschr. f. Phys. Chem.,' 28, p. 622 (1899).

¶ V. ROTHMUND, 'Zeitschr. f. Phys. Chem.,' 20, p. 168 (1896).

** RÖNTGEN and ZEHNDER, 'WIEDEMANN'S Annal.,' 44 (1891), p. 280.

†† L. H. SIERSTEMA, 'Communications from the Phys. Lab., University of Leyden,' No. 35, No. 39, No. 49, and Suppl. 1.

‡‡ LIVEING and DEWAR, 'Phil. Mag.,' 26, p. 286 (1888); 'Roy. Soc. Proc.,' 46, p. 226 (1889).

§§ HUTTON and PETAVEL, 'Phil. Mag.,' p. 569 (1903).

‖‖ G. DUFFIELD, 'Phil. Trans.,' A, vol. 208, p. 111 (1908).

¶¶ C. BARUS, 'Amer. Journ. of Sc.,' 3 ser., XLII., p. 125 (1891); 'Bull. of the United States Geological Survey,' 96 (1892).

*** C. BARUS, 'Bull. of the United States Geological Survey,' Nos. 92 and 97, Washington, 1892.

††† E. MACK, 'Compt. Rend.,' 127, p. 361 (1898).

between solids and liquids and solids and solids is due to the work of TAMMANN carried out at Dorpat and later at Göttingen.*

TAMMANN has used two different volumetric methods: working partly at constant temperature and altering the pressure, and partly at constant pressure altering the temperature, but the former method was chiefly employed. Only in the case of Bismuth, Tin, and Lead, TAMMANN has used a thermometric method. The actual determination of pressure extends in TAMMANN'S work to between 3,000 and 4,000 kg./cm.^{2}, but in a few instances melting-point temperatures have been reached which correspond to extrapolated pressures of between 5,000 and 10,000 atmospheres.

Only quite recently BRIDGMAN has published a series of measurements on the melting-point of mercury at pressures from 1 to 12,000 kg./cm.^{2}.† The change of the state of the mercury was observed by three different methods, one electric and two volumetric. The pressures were measured by the change of the electrical resistance of a mercury thread and of manganin wire; the influence of pressure upon the resistance having first been determined by standardizing with absolute manometers of the Amagat type, constructed by BRIDGMAN, and rendering possible the exact measurement of pressures up to 6,800 and 12,000 kg./cm.^{2}.‡ At pressures above 12,000 kg./cm.^{2} the determination of the pressure in BRIDGMAN'S work is entirely based upon the change of the resistance of manganin wire, but BRIDGMAN has been able to measure accurately pressures as high as 20,000 kg./cm.^{2} by this method, and states that he occasionally has reached pressures as high as 40,000 kg./cm.^{2}.

Of a recent date are also the determination of the melting-points of Pb, Sn, Bi, and Cd by the thermometric method at pressures from 1 to 2,000 atmospheres, undertaken at the geophysical laboratory of the Carnegie Institution of Washington, D.C.,§ and COHEN'S investigation of the transition of $ZnSO_4+7H_2O$ at pressures up to 1,500 kg./cm.^{2} by means of electrical measurements.‖

One of the most interesting results of TAMMANN'S high-pressure investigations is the discovery of the occurrence of crystallized modifications which are stable only at high pressure, as, for instance, in the case of phenol, water, methylene iodide, and silver iodide. Of great interest also is the tracing of the boundary lines between the different crystalline modifications and between these and the liquid phase in the diagram of state, viz., the fixing of the triple points. These inquiries it has been

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* G. TAMMANN, 'Ann. d. Physik,' 68, pp. 553, 629 (1899). 'Kristallisieren u. Schmelzen,' Hamburg, 1903. 'Zeitschr. f. Phys. Chem.,' 69, p. 569 (1909); 72, p. 609 (1910); 75, pp. 75–733 (1910). 'Zeitschr. f. Anorg. Chem.,' 40, p. 54 (1904); 63, p. 285 (1909).

† P. W. BRIDGMAN, 'Proc. Amer. Acad. Arts and Sciences,' 47 (12), p. 377, December (1911).

‡ P. W. BRIDGMAN, 'Proc. Amer. Acad. Arts and Sciences,' 44 (8), p. 201; 44 (9), p. 221; 47 (11), p. 321.

§ J. JOHNSTON and L. H. ADAMS, 'Amer. Journ. of Science,' 4 ser., XXXI., p. 501.

‖ E. COHEN, 'Zeit. f. Phys. Chem.,' 75, p. 1 (1911).

possible to carry out by the volumetric methods of TAMMANN in those cases where the volume difference between the different phases is considerable. This is mostly the case with regard to the crystallization and melting of the solid form, and the volumetric method is therefore nearly always applicable to the determination of the melting-point curves. In the case of the transition of crystalline forms, one into another, many instances are known where the transition occurs with only slight change of volume, and in such cases a volumetric method, of course, is not applicable. The same remarks apply to the thermometric method of the determination of transition-points, though this method has not until now been at all employed at pressures differing from the atmospheric. In cases like that above referred to, the simplest method of studying the transition phenomena at ordinary pressure is the optical, and this method has further the advantage over the volumetric and the thermometric methods that only a quite small quantity of the substance is needed, which in many cases, of course, is of essential importance. Further, the change of the optical characters of a substance at the transition-point between two crystalline forms is generally much more striking than the volume change or the evolution of the latent heat, and this is probably the chief cause why optical observation has been used in most investigations at ordinary temperatures. The well-known polarization-microscope, with a device for heating, constructed by LEHMANN, has been the principal instrument employed.

The above considerations, together with the desirability of determinations of the optical properties of crystals and liquids, especially of those of liquids (refractive index) being undertaken at homogeneous pressures other than the atmospheric, led the present writer to undertake the working out of methods of optical determinations at high pressures and varying temperatures, that is, methods for the optical investigation both of the boundary lines in the diagram of state of a substance, and of the variation of the optical properties of the different phases within their existence fields.

PART I.—APPARATUS FOR OPTICAL DETERMINATIONS AT HIGH PRESSURE.

The apparatus consists of three chief units :—

(1) The plant for the production and measurement of high pressures ;
(2) The "pressure-bomb" to hold the substances under investigation ;
(3) The optical installation for observation and for optical measurements.

These may conveniently be described apart.

1. *The High-pressure Plant.*

The apparatus for producing the pressures consists of two screw-compressors—one for pressures up to 6,000 atmospheres, and one for pressures not exceeding 600 atmospheres—a small hand-compressing pump for filling the larger compressor with oil at pressures of about 800 atmospheres, a steel vessel, to which both compressors and the pressure-bomb holding the substance are connected by means of drawn-steel capillary tubes of 7 mm. outer diameter and 1 mm. bore, and a high-pressure valve, by which the smaller compressor, together with its manometers, can be shut off from the rest of the apparatus when working at pressures above 600 atmospheres. The whole of this apparatus is fixed to a heavy oak bench. The various parts are connected as shown by the diagram (fig. 1), thus forming a pressure-plant which may be used for any kind of high-pressure work. The large compressor for high pressures (A, fig. 1) is of the Cailletet type, but made entirely of steel, and is of much larger size than the ordinary Cailletet apparatus. It is very similar to those used by Tammann in his high-pressure experiments.* As in the case of the Cailletet apparatus, a plunger is forced into a cylindrical compressing chamber in the central steel block A by a powerful screwing gear. Oil is pumped into this compressing chamber by means of the compressing pump B, which is connected to the oil reservoir C. D is a valve by which the compressing chamber is shut off from the pump B before the compressor is worked. By the valve E a fine capillary channel, which connects the compression chamber with the high-pressure manometer F and with the pressure-transmitting pipe G, can be shut off from these, thus leaving only the manometer connected with the pressure-transmitting pipe and the pressure-bomb, in which the investigation is

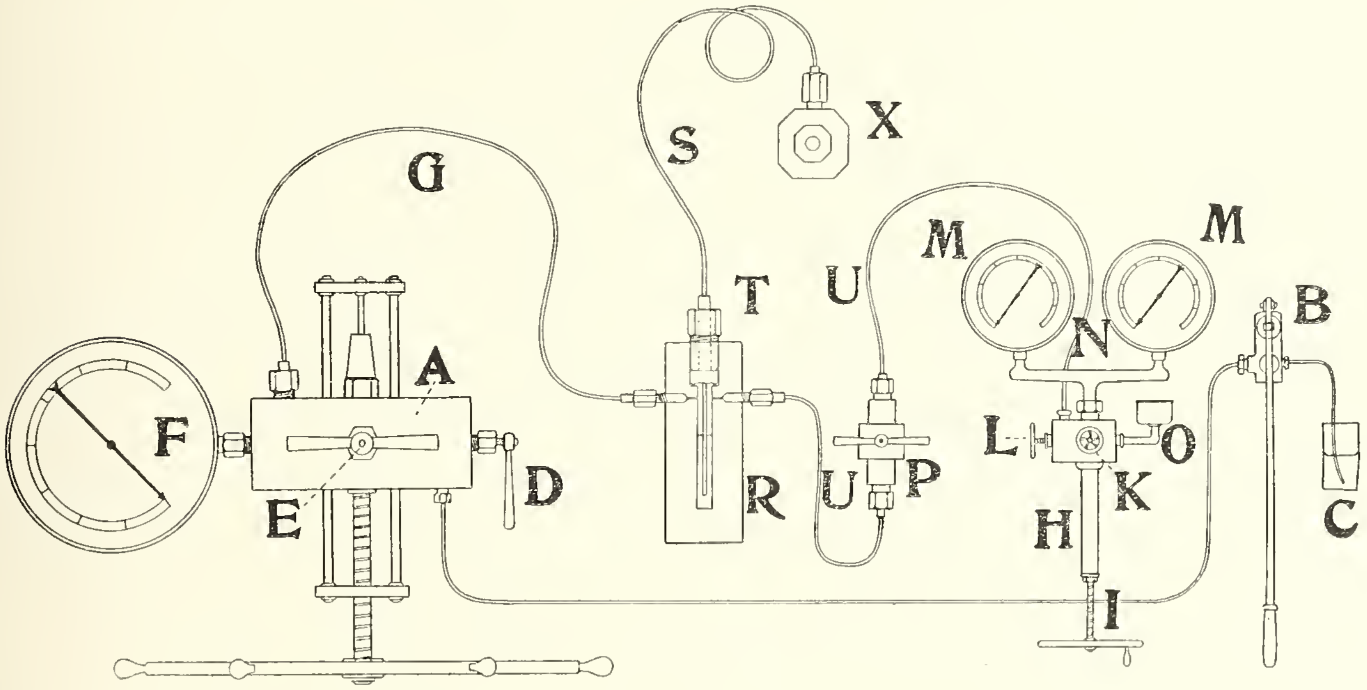

Fig. 1.

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* G. Tammann, 'Kristallisieren u. Schmelzen,' p. 195.

carried out. The manometer F is a "Stahlplatten-Hydraulik-Manometer," manufactured by Schäffer and Budenberg, of Magdeburg-Buckau, Germany, and is graduated to 4,500 kg./cm.^{2}, every division corresponding to 20 kg./cm.^{2}. The diameter of this manometer is 36 cm., and the scale is accordingly large, so that 2 kg./cm.^{2} may be easily read off on it. A second manometer of the same construction can be attached directly to the pressure-transmitting pipe, thus enabling a comparison of the manometers. This manometer is graduated to 5,000 kg./cm.^{2} and has been used as a standard.

The smaller compressor H is a screw compressor with a plunger of 15 mm. diameter, moved up and down in the compression chamber, in this case a thick walled bronze tube, directly by the screw I. K is a valve by which the oil reservoir O is shut off from the compressing chamber. L a valve which shuts off the compressing chamber from the pressure-conducting capillary tube and the manometers M, which then remain connected with the investigation bomb. The manometers M are of 26 cm. diameter, and graduated up to 600 kg./cm.^{2}, each division on the scale representing 1 kg./cm.^{2}. The two manometers are attached to a **T**-piece of bronze by which they communicate with each other and with the compressor. Each manometer is further provided with a safety-valve, protecting it against very sudden big changes in pressure by which they otherwise might be damaged. Also these manometers are of the "Stahlplatten-Hydraulic-Manometer" type, and manufactured by Schäffer and Budenberg. P is a valve capable of withstanding a pressure of more than 4,000 kg./cm.^{2}, by which the smaller compressor can be entirely shut off from the rest of the compressing machine.

The pressure-conducting pipes, G, from the large compressor, and U (U containing the valve P) from the small compressor, are connected to the upper part of the steel vessel R, through the top of which the long steel capillary tube S communicates with the lower part of the vessel, which thus forms a kind of strong steel bottle, on the same principle as wash-bottles. This steel flask or bomb contains mercury in its lower part, and as the pipe connected to the bomb containing the substance to be investigated dips into the mercury with its lower end, the mercury shuts off this part of the apparatus from the oil in the compressors and transmits the pressure without permitting the contents of the investigation bomb X to come into contact with the oil of the compressors. Oil can thus always be used in the compressors, any liquid being used in the pressure-bomb X. By the screw connection at T the investigation bomb is attached to, and detached from, the pressure plant, and this screw is the only one of the whole pressure plant which is opened between different series of experiments when a new substance is introduced into the investigation bomb X.* All the joints between different parts of the pressure apparatus are constructed on the principle of a hard, circular steel-edge, being forced by as crew

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* The compressing machine and manometers were manufactured by Messrs. Schäffer and Budenberg, of Magdeburg-Buckau, Germany.

into a softer steel surface, in the centre of which a capillary pressure-conducting channel enters. These steel edges have to be very carefully hardened, yet must be only slightly harder than the supporting surface. If they are too hard they easily break, and in any case a very much harder edge soon spoils the supporting steel surface. A joint which once has been got into good working order keeps perfectly tight for any length of time, and at any pressure it will stand without breaking. The oil used in compressors and pump was castor oil.

All four manometers have been standardized at the works of Schäffer and Budenberg in Magdeburg-Buckau by means of a hydraulic plant of a similar type to the Amagat absolute manometer. The manometers were standardized by the direct application of weights, the high-pressure ones up to 4,000 kg./cm.^{2} (the limit to which the testing plant can be used) and the smaller pair to 600 kg./cm.^{2}. The accuracy of the large manometers is about 5 kg./cm.^{2}, and that of the smaller ones about $\frac{1}{2}$ kg./cm.^{2}. The one large manometer is used as a standard whereby the three working manometers may be checked from time to time, to secure that their indications are constant. As all three working manometers communicate up to pressures of 600 kg./cm.^{2}, the two smaller ones give the exact value of the correction for the zero-point of the large one. If the indications of a single high-pressure manometer are not in some interval of pressure checked by another manometer grave errors may result with regard to the real position of the zero-point.

2. *The Pressure-Bomb in which the Optical Investigation is carried out and the Thermostat.*

The pressure-bomb fits into a U-shaped iron support, into which it can be firmly fixed by means of a screw. The U-piece is by a strong screw-bolt fixed to another inverted U-piece, which again is firmly screwed to an iron plate 3 feet long and 1 foot 2 inches wide. The connecting screw-bolt runs through the bottom of a water-jacket, and the joints are rendered tight by screw nuts and packings. There are also mica packings between the screw-bolt and the U-pieces in order to lessen the conduction of heat as much as possible. The water-jacket is of a square shape, flat, and only a few millimetres wider than the pressure-bomb. It holds about 2 litres. Opposite the two windows in the pressure-bomb are two holes in the sides of the water-jacket, and a short piece of brass tube with an outer, flat, ring-shaped edge can be screwed on to the window part of the pressure-bomb, pressing the side-plate of the water-jacket tightly against the pressure-bomb. These joints are rendered perfectly tight by inserting a sufficient number of rings of sheet lead 1 mm. thick on both sides of the water-jacket plate before the brass-tube caps are screwed on. In this way the pressure-bomb is kept fixed firmly inside the water-jacket, and a free view secured through the glass windows of the pressure-bomb. The details of construction of the pressure-bomb and the water-jacket are seen from fig. 2.

The water-jacket is heated by means of two small gas-burners, which are regulated by a mercury-regulator of ordinary type. In some series of measurements electrical heating by a platinum resistance coil has been used, and the regulator for the heating current was then electro-magnetic. The liquid in the bath was well stirred by a small turbine stirrer driven by an ordinary hot-air engine.

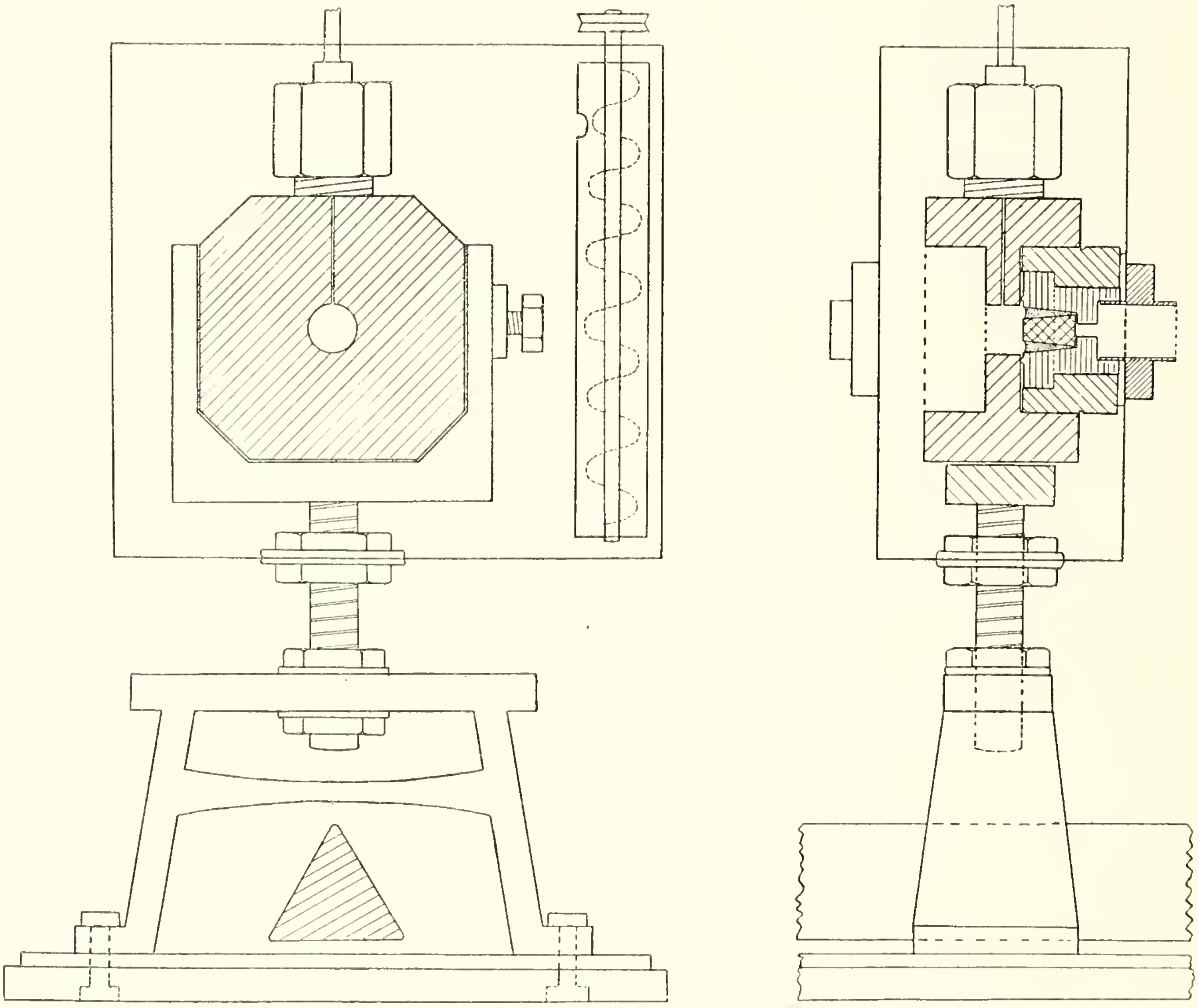

Fig. 2.

Temperatures were measured by thermometers, divided into tenths of a degree, which have been compared with similarly graduated thermometers standardized at the "Physikalisch-Technische Reichsanstalt" in Charlottenburg.

3. *The Optical Installation.*

(1) *The Optical Bench.*—The optical observations are made by means of an optical bench, each end of which is fitted with a screw-adjusting gear, the whole resting on

the iron plate to which the water-jacket and pressure-bomb are attached. With the aid of an autocollimation Gauss' eye-piece, the whole optical bench can, by means of the screw-adjusting gear, be brought exactly into such a position that its optical axis is at right angles to the surface of the window in the pressure-bomb, or any polished surface inside of this. The adjusting gear for the optical bench works practically in the same way as the crystal adjustment on a modern goniometer for measuring crystals, except that it, of course, can be adjusted at only a very small angle, and instead of the crystal or refractive index prism being adjusted on a goniometer, the object to be measured here remains in a fixed position, and the whole optical apparatus is adjusted with regard to this fixed position.

The optical part itself consists of an illuminating lens, polarizing Nicol-prism, condenser, objective, analysing Nicol-prism, and micrometer eye-piece. These optical parts are very much the same as those of the well-known Fuess Goniometer No. II. For crystal optical measurements the eye-piece can be replaced by a compensator eye-piece, and a stronger condenser-lens and objective-lens can be clamped on to the ends of the eye-piece and collimator-tubes, just as in the case of the Fuess Goniometer II., when used for optical axial-angle measurements. For such a purpose the eye-piece tube is also provided with a " Bertrand lens." The eye-piece system is focussed on infinite distance, but can be converted into a microscope of small enlarging power by means of an attachable lens. Thus, with this optical bench, the same measurements can be carried out as with the optical part of the Fuess Goniometer II. The description of the use of it for the determination of the refractive index and the dispersion of compressed liquids must be left for a paper dealing with this question.

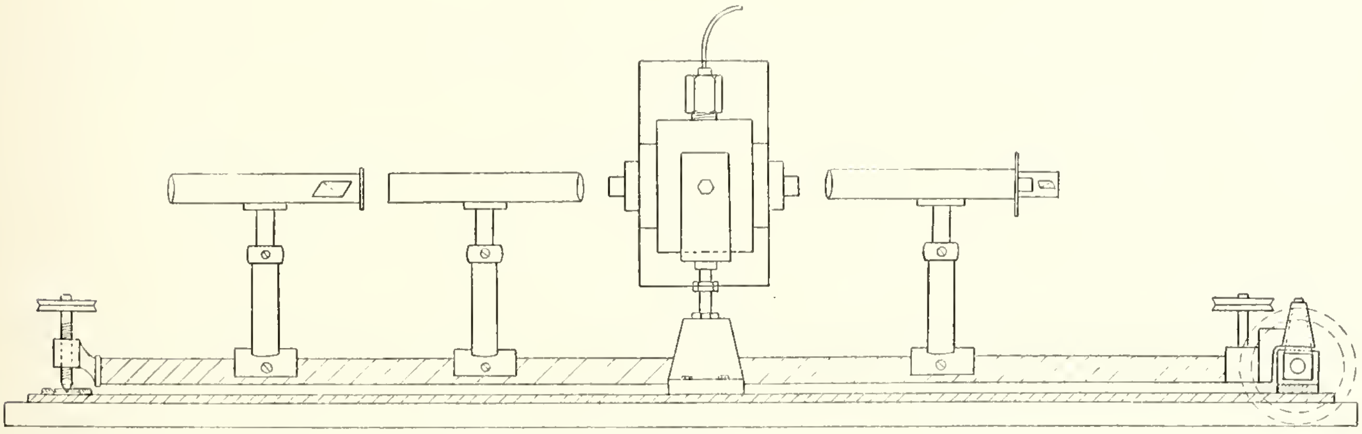

Fig. 3.

The optical bench and other optical parts were made by R. Fuess, of Steglitz, Berlin. The water-jacket with its fittings, and the gear for adjusting the optical bench, were made by the mechanician of the Davy Faraday Laboratory of the Royal Institution, Mr. Harry Payne, who also rendered valuable aid in getting the whole pressure plant with its numerous joints into good working condition.

(2) *The Glass Windows.*—AMAGAT states, in his first paper on the solidification of liquids by pressure, that he observed the liquid and the resulting crystals by means of a small glass window inserted into the wall of the pressure chamber in which the liquid was compressed. In form the window was a truncated cone, the smaller base being towards the observer. It was made of annealed glass, and was surrounded by a thin enveloping cone of ivory. With this arrangement of the windows AMAGAT was able to reach pressures of about 1,200 atmospheres. In the large series of measurements on the compressibility of liquids by the "méthode des regards," AMAGAT used cylindrical windows which were fixed simply by marine glue, this part of the apparatus always being kept cool, so that the marine glue did not get too soft. Experiments with windows fitted in this way were carried out up to 1,000 atmospheres. Later, also, AMAGAT used similar cylindrical windows, fitted with marine glue, for the measurement of the influence of pressure upon the freezing-point of water. In this paper AMAGAT states that he had met with very serious difficulties in getting the windows to withstand higher pressures than 1,000 atmospheres. Some of them stood 1,400 atmospheres, and in a single case he had even been able to carry the pressure up to 1,700 atmospheres before the glass was cracked, but generally about 1,200 atmospheres was the pressure-limit reached, and the work was then entirely given up by AMAGAT.

The first bomb intended for this research was constructed on the same principle as the bomb employed by AMAGAT in his earlier work. The method of gluing in the glass windows later used by AMAGAT would not permit work at higher temperatures in the case of the windows being close to each other, as is necessary in some cases of crystal-optical research, where the objective of the polarization instrument must be brought as close as possible to the crystal or section investigated. The "windows" were truncated cones 15 mm. thick, the diameter of the inner base being 10 mm. and that of the outer 7 mm. The enveloping conical mantle of ivory was about 1·5 mm. thick. The first cones tried were made out of an optical borosilicate-glass from Schott & Genossen, of Jena. In polarized light they very soon showed vivid polarization colours when pressure was increased, and at about 900 kg./cm.^{2} it became very difficult to see through them at all, but apparently they did not crack, and pressure was carried up to 2,000 kg./cm.^{2}—the limit for which the then used pressure apparatus had been tested—the apparatus being perfectly tight all the time. On relieving pressure, the compressed oil in the bomb, however, began to leak out at the windows, and when the apparatus was unscrewed it was found that the window cones now consisted of a very great number of thin plates, with surfaces as smooth as if polished. Some of these glass plates were very thin, others a millimetre or more thick, and it was possible to further cleave these by pressing a knife against the conic side of such a piece, the glass, after having been compressed in this way, thus behaving very much like mica. Tests were then made with different kinds of glass for cones and different material for the conical envelopes, soft ebonite and moderately hard vulcan-fibre being substituted for the comparatively hard ivory. Quartz-glass, a heavy soft "flint," and a hard "crown" behaved in very much the same way as the borosilicate, but usually a cracking was noticeable when the glass was split up into lamellæ, and this occurred in the case of flint glass, even at as low pressures as between 200 and 300 kg./cm.^{2}. During these tests some very remarkable optical phenomena were observed in the glasses in polarized light, but the description of these, as well as of the details of preliminary work, cannot be entered on here, it being sufficient to state that it was found that the "cleavage" developed in the glass windows was due to tension and not compression of the glass cones, these being more rigid than the enveloping cone which flows slightly, somewhat similarly to the way in which a rubber stopper flows and is stretched when it is forced into a bottle neck. The softer the material of the cone enveloping the glass the more marked this effect was, and the sooner cracks were developed, and always at right angles to the axis of the glass cone, that is, at right angles to the direction in which the hydraulic pressure in the interior of the bomb acts.

It was therefore thought that better results might be obtained by providing the glass windows with a steady support against which they would be pressed, so that no part of the glass could be stretched as described above. But as it at the same time was essential to have a conical joint between the glass and the steel wall of the bomb, in order to secure a tight fit even at high pressures, the following way of fitting the glass windows was finally adopted :—The glass cone was inserted the opposite way into the conical place in the steel bolt, the smaller basis of the cone thus being acted upon by the pressure transmitting fluid in the interior of the bomb, and the glass cone resting with its larger basis on a washer by which it is separated from its steel support. The steel and the washer supporting the glass cone are provided with a hole through the centre part, through which the observations are made, and the glass cone rests thus only with its outer part against the washer and steel. The remaining circular space between the conical glass and the conical bore in the steel is wedge-shaped, and thus the material in it is forced in towards the narrower part, and, if softer than the glass, makes the joint tight, and transmits at the same time an all-sided pressure to the glass cone. This conical wedge-shaped envelope has to be cut on the lathe exactly to the same angles as the conical surfaces of the glass and of the surrounding steel, the glass cone being finally ground in with very fine emery to fit exactly. This composite cone, consisting of the glass and its envelope of "fibre" or ebonite, is then ground into the conical space of the steel bomb, sufficient space being left for the washer supporting the base of the glass cone. The arrangement is shown in fig. 4, where *a* is the glass cone, *b* the conical wedge-shaped fibre envelope, *c* the washers, flat rings supporting the glass cone, *d* the steel-pressure bomb, *e* the steel bolt into which the glass window is fitted, and *f* a screw.

The chief object of these washers and conical packings may be described as being that of keeping the glass all the time surrounded by a half-plastic mass, which flows slightly, and thus transmits the pressure to the glass body in as even a manner as possible.

Originally the washers consisted of two flat rings about 0·5 mm. thick each, the one on which the glass rests directly being of ivory, the other one of fibre. The conical washer for temperatures up to about 70° C. has been of "galalith," a material used instead of ebonite for electric fittings, and for higher temperatures of fibre. With this arrangement of the windows a great many of the measurements up to about 1,600 kg./cm.^{2} have been carried out, and with some practical experience as to the way in which the glasses are fitted it is not difficult to get a pressure-bomb of this kind for optical investigations in working order. The glass used has chiefly been a borosilicate from Schott & Genossen, of Jena, which is used for the manufacture of "Durax-glass" high-pressure-and-temperature tubing. Suitable pieces of the glass were cut from glass rods, the pieces annealed very carefully, and the cones then ground from these pieces. When overstrained, a 20 mm. thick cone of this glass shows interference colours of the first order at about 200 atmospheres below the point at which it breaks. It is always necessary to watch the glass windows in polarized light when pressure is applied to them the first time after they have been fitted into the steel bomb, as the appearance of interference colours at once suggests that the fitting is not satisfactory, for glass cones which stand pressures of several thousand atmospheres break at a few hundred if precaution is not taken to watch their behaviour in polarized light, and to refit them if they show interference colours already at comparatively low pressures. Later it was found that the limit of 1,600 kg./cm.^{2}, mentioned above, was not really due to the resisting strength of the glass being reached at that pressure, but to the circumstance that the ivory washers began to flow readily at this pressure, and in consequence of the structure of the bone did not give way evenly, with the result that the support suddenly became less in some parts than in others, and the glass cracked. Later, washers made out of two layers of thin lead foil have been used, and also washers made out of rolled plates

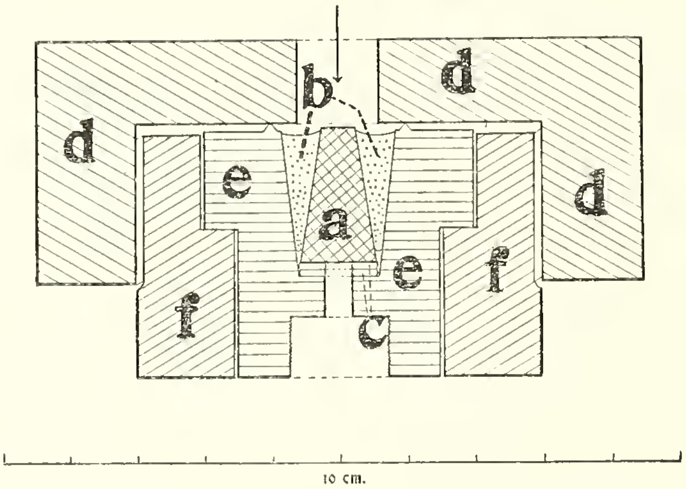

Fig. 4.

of silver chloride, these being protected from contact with the steel by lead paper. With both these arrangements pressures of up to 4,000 atmospheres have been reached without the glass being in any way injured. But in any case glass must be regarded as a very treacherous material when submitted to high pressure, and often a glass cone, which has withstood very high pressures, suddenly may crack at comparatively low pressures without having shown any signs of strain, and thus measurements are often suddenly interrupted. This circumstance adds, of course, to the difficulties experienced in this kind of research at high pressures, and to the time required to carry through such research.

The expenses for the construction of the above apparatus were defrayed by a grant made to the author from the "Herman Rosenberg Fund" of the University of Helsingfors.

The preliminary experiments with glass windows of varying construction were carried out during the winter of 1910 in the laboratory of physical chemistry at Göttingen. Prof. G. TAMMANN kindly lent me a set of his pressure apparatus for several months, and thus enabled me to make the tests which were necessary before the apparatus described above could be constructed. I am also greatly indebted to Prof. TAMMANN for many valuable suggestions, and for information on various points concerning the practice of high-pressure work.

The apparatus has been mounted and brought into working condition in the Davy Faraday Research Laboratory of the Royal Institution of Great Britain, and the actual research work which forms the subject of Part II. of this paper has been carried out entirely in the Davy Faraday Laboratory.

I have to acknowledge the liberality with which the Managers of the Royal Institution and the Director of the Laboratory, Prof. Sir JAMES DEWAR, have placed the technical resources of the Laboratory at my disposal. My thanks are also due to Sir JAMES DEWAR for the personal interest with which he has furthered the progress of the work.

PART II.—OPTICAL DETERMINATION OF DIAGRAMS OF STATE.

4. *General Methods.*

(1) *Method of Observing the Substance.*—In the case of the investigation of a body which remains liquid at all temperatures, and pressures at which the optical measurements are carried out, the substance may be allowed to fill up the entire interior space of the pressure bomb and the capillary tube through which the hydraulic pressure is transmitted. But, if the liquid has to be crystallized, the crystallization

may occur in any part of the apparatus between the manometer and the investigation bomb, and, especially if the entire contents of this is solidified, the part of the substance observed may remain under a very different pressure from that indicated by the manometers. Evident enough as such a cause of error may appear, it has been one of the principal practical difficulties to get over in all high-pressure work, and is one of the chief causes of errors in earlier work of this kind. TAMMANN refers in several instances to this circumstance as a cause of erroneous experimental results, and he has had to renew several of his earlier series of measurements. He has, in consequence, paid much attention to the problem of bringing the substance into the pressure bomb under such conditions that it is really submitted to homogeneous pressure during the entire investigation. In his most recent work TAMMANN has used a kind of bag or cylinder made out of parchment paper and coated with a varnish of collodium.* This cylindrical bag, when containing the substance and closed at both ends, is surrounded on all sides in the pressure bomb by some pressure-transmitting fluid, and as it is entirely soft the hydraulic pressure is evenly transmitted. The material for such a pressure-transmitting cover has of course to be chosen with regard to the nature both of the substance investigated and of the surrounding fluid, and in many instances it is not possible to find a material which is entirely insoluble, and which is not chemically acted upon by the substance to be investigated, especially when a large amount of substance is used, and the investigation is carried on at comparatively high pressures and temperatures.

In the case of an optical investigation it is, of course, essential to make observations upon a sufficiently thin layer of substance, so that it is possible to see the changes in the optical properties due to polymorphic transition. At first a small glass tube of about 2 mm. diameter was used as a vessel to hold the substance to be investigated. Both ends of the glass tube were bent over, approaching each other, and connected one to another by a small piece of rubber tube. The whole was filled with the substance, and the rubber tube part acted as pressure transmitter. Some melting-point determinations on dimethylether of oxalic acid were made in this way, but it was not easy to observe the optical characters of the crystallized body with this device, and subsequently the following arrangement has been used in most cases. The substance is melted between two circular glass plates, about $\frac{3}{4}$ mm. thick and of 10 mm. diameter, care being taken not to superheat the substance. When the substance has crystallized, a piece of black rubber tube, 5 mm. long and about 5 mm. wide, is slipped over the joint edges of the two glass plates, thus forming a surrounding cap, which at the same time gently presses the two glasses against each other, the whole forming a slightly elastic extremely narrow vessel. The rubber piece used is previously kept for some time in the molten substance to be investigated, and as the substance during the experiments comes into contact with the rubber only

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* G. TAMMANN, 'Zeitschr. f. Anorg. Chem.,' 63, p. 285 (1909), and 'Zeitschr. f. Phys. Chem.,' 75, p. 77 (1910).

at the extremely narrow fringe at the edge of the glasses, this device has proved itself to work very satisfactorily in most cases.

It has indeed been found that with the help of this little piece of apparatus the substances could be equally well observed at high pressures inside the pressure apparatus as under the ordinary polarization microscope between object-glass and cover-glass. Also, most crystal-optical determinations, such, for example, as those serving to identify the rock-forming minerals in thin sections of rocks, can be used during a research at high pressures with the above described apparatus.

(2) *Isothermal Melting and Crystallization.*—When an alteration of pressure at will is possible, the melting-point of a substance can, of course, be determined either at constant temperature by altering the pressure, or at constant pressure by altering the temperature. The determination at constant temperature, what one may conveniently call *isothermal crystallization* and *isothermal melting*, is by far the more convenient method of the two, and has throughout been employed in this research for the determination of melting-points. In the case of the determination of transition-points the method of work at constant pressure is of special use in some cases, and will be further referred to in cases where it has been applied. But, with regard to isothermal crystallization, there are some peculiarities which should be briefly discussed at this point. When a crystallized substance is melted in the ordinary way by being heated, it melts gradually at constant temperature, but at the same rate as the heat is supplied to it. It is not possible to heat instantly a melting mass of a substance through and through; the heat is taken up by the parts of the mass in contact with the heating device or vessel which is being heated, and spreads from those parts to the other parts of the mass. But in the case of isothermal melting matters are different in this respect, that any change of hydraulic pressure almost instantly takes place throughout the entire mass. As most crystals need a certain amount of time both to grow and to melt, the result is that, when working isothermally, we are able either slightly to compress the crystals in the "melt" of the substance to pressures above their melting-point pressure, or to lower the pressure beneath the pressure of the melting-point pressure. The extent to which this can be done depends almost entirely upon the velocity with which a crystal melts or crystallizes at its melting-point, and the rate at which this velocity is altered with increase or decrease of pressure, and these factors are very different for different substances. The two cases, pressures above and pressures below the actual melting-point pressures, correspond to a superheating of crystals in the presence of the liquid-phase or super-cooling of the liquid-phase in the presence of the crystal-phase at constant pressures. Only in the case of a totally melted substance is a super-cooling in most cases actually possible, and it has generally been thought that a superheating of a crystallized body to temperatures above its melting temperature could not be effected. According to some recent work, however, it seems probable that a superheating occurs in the case of some extremely slowly

melting substances.[*] A practical consequence of this difference between the ordinary "isobaric" melting at constant pressure and the "isothermic" melting, is that the melting-point can be instantly passed in either direction, and regions of a different degree of super-cooling and a correspondingly different degree of velocity of crystallization and of rate of spontaneous formation of crystal-nuclei can be experimentally reached and studied. In nearly all the cases investigated observations bearing upon the above have been made, and the more important will be quoted in connection with the description of the determination of the diagrams of state.

5. *The Diagram of State of Carbon Tetrabromide* CBr_4.

LEHMANN first observed that carbon tetrabromide, which crystallizes from the molten state in growth-structures belonging to the cubic system and appearing quite dark between crossed nicols, on further cooling down, changes into highly double-refracting crystals.[†] SCHWARZ found that this transition from one crystalline form to another takes place at 46°·1 C.[‡]

This transition-point, and the influence of admixtures of carbon tetrachloride on it, has since been very carefully studied by ROTHMUND by means of a thermometric method.[§] ROTHMUND gives the transition-point of pure carbon tetrabromide as 46°·91 C. The melting-point is 92° C. The double-refracting modification of carbon tetrabromide crystallizes also from solutions in acetone. The crystals are monoclinic, but have crystal angles which differ very little from those of the cubic octahedron; they have been measured by ZIRNGIEBL.[||]

In order to determine the diagram of state of carbon tetrabromide a small quantity of it was brought into the pressure-bomb between two round object-glasses in the manner described on p. 130. The carbon tetrabromide had been purified by recrystallization from petrol-ether, and finally by sublimation in a charcoal vacuum from room temperature to that of liquid air.

(1) *Melting-point Determinations.*—When the pressure is increased at temperatures above 92° C.—the melting-point at ordinary pressure—crystalline growth-structures suddenly appear and grow rapidly. At constant temperature this does not always take place at exactly the same pressure, and these pressures at which the rapid growth, in the form of growth-structures, begins are not identical with the pressure corresponding to the melting-point, but slightly higher. At the melting-point pressure the crystals grow only slowly, and the rate of growth is about equal in all directions, so that compact crystals result, and no growth-structures; but if the

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[*] A. L. DAY and E. T. ALLEN, 'Publications of the Carnegie Institution,' Washington, No. 31, p. 57 (1905); G. TAMMANN, 'Zeit. f. Phys. Chem.,' 68, p. 257 (1910).

[†] O. LEHMANN, 'Molekularphysik,' I., p. 178 (1888).

[‡] W. SCHWARZ, 'Preisschrift Göttingen,' 1892, p. 47.

[§] V. ROTHMUND, 'Zeitschr. f. Phys. Chem.,' 24, p. 705 (1897).

[||] Quoted by GROTH, 'Chem. Kristallographie,' I., p. 230.

pressure is rapidly raised, the crystals begin at a certain pressure to grow more rapidly in a certain direction than in others, and so the cubic structures of growth are produced. In this way it is possible to determine at each temperature two crystallization pressures: one at which the crystals can just be observed to grow—this is the pressure closest to the true crystallization pressure we are able to observe—and a second higher pressure at which very rapid growth in a certain crystallographic direction takes place.

This behaviour is not peculiar to carbon tetrabromide, but is common to all substances hitherto investigated, and is probably a phenomenon of quite general character. It depends upon the following circumstances:—

GERNEZ* and MOORE† have shown that the velocity of crystallization, when measured in thin-walled glass tubes, increases with decreasing temperature, that is, when the degree of super-cooling increases. Later, TAMMANN and his pupils have found‡ that this increase of the velocity of crystallization occurs only up to a certain temperature, when a maximum of velocity is reached, which in many cases remains constant for a certain interval of temperature, and then very rapidly diminishes and assumes quite small values. The general case may be diagrammatically represented by fig. 5: *a* represents the melting-point temperature, at which the velocity of crystallization is very small. With descending temperature the velocity at first increases slowly, but at temperatures *b* a much more rapid increase takes place, and continues until the maximum velocity *c* is reached. At temperatures *d* the velocity again very rapidly drops to small values, and diminishes then at low temperatures *e* quite slowly. The part *a* to *c* of this curve is that which is of interest in this particular case, because it gives the explanation of the crystallization phenomena observed when pressure is increased. The comparatively short interval of temperature, where the rapid increase of the velocity of crystallization takes place, evidently corresponds to the pressures at which such an amount of super-cooling is reached that rapid crystallization ensues and the growth-structures are produced. This view is

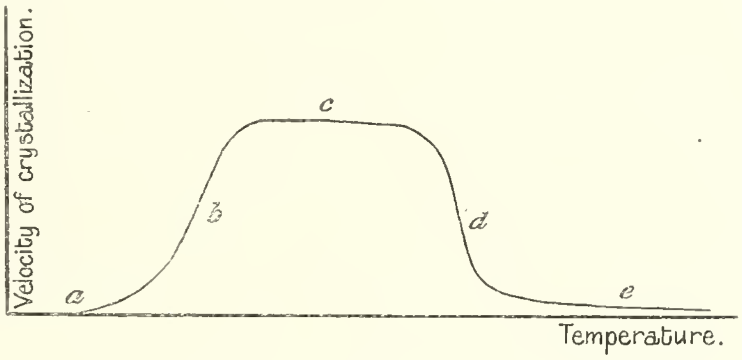

Fig. 5.

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* G. GERNEZ, 'Compt. Rend.,' 95, p. 1278 (1892).

† B. MOORE, 'Zeitschr. f. Phys. Chem.,' 12, p. 545 (1893).

‡ G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 27 (1897), p. 152; 29 (1899), p. 58.

supported by the observation by TAMMANN that at temperatures near *a* the growth in some cases occurs in the form of comparatively large crystals, which point in different directions inside the tube, and crystal faces are richly developed, but that at temperatures *b* growth occurs in a certain direction only, so that long crystal threads are produced in the tube.* In the case of the unstable modification III. of benzophenane melting at 26° C., TAMMANN found that the crystal grows inside the tube pushing forward a crystal corner, terminated by even crystal faces.*

As TAMMANN occasionally points out, every crystal face probably possesses its own velocity of crystallization at a given degree of super-cooling, and it is also probable that the velocity of the different crystal faces changes at a different rate with the degree of super-cooling. The result of this is that at a certain temperature, or pressure corresponding to this temperature, the velocity of crystallization in one crystal direction so much exceeds the velocity in other directions that, in consequence, only these crystal faces are developed and crystal-growth structures produced. It may suffice in this place to point out that these considerations give the clue to the general explanation of the production of growth-structures and of spherulites, and are of interest with regard to the origin of crystal-growths and spherulites in the igneous rocks; a fuller discussion of these problems, however, being outside the scope of the present communication. But the possibility of determining two distinct crystallization pressures, one at which the growths of the crystal only just takes place (at *a*, fig. 5), and one at which the formation of growth-structures begins (at *b*, fig. 5), is also of practical importance when the melting-point is determined at constant temperature, and the problem has therefore been discussed here already before the data of measurements are given. These two pressures will in the following tables be indicated as P_1 = the melting-point pressure, and as P_2 = the higher pressure at which growth-structures are developed.

As seen from the figures in Table I. the melting-point of CBr_4 is raised very rapidly by pressure, the pressure required to raise the melting-point 1° C. being only 16 kg./cm.^{2}. This ratio remains constant, within the limits of accuracy of the measurements, up to about 10° C. above the melting-point at 1 atmosphere. Unfortunately it is not possible to determine the melting-points at higher temperatures and pressures as a slight decomposition then begins, and as the decomposition products tend to lower the melting-point, higher melting-point pressures are recorded the longer the substance has been kept at high temperatures. This becomes still more marked at 120° C. and at 130° C., at which temperatures the melting-point pressures in different series of measurements differ very widely from each other. The melting-point pressure for preparations on which even only a single rapidly carried out observation at 120° C. was made, was, after cooling down, at 95°·4 C. about 200 kg./cm.^{2} higher than it originally had been. Under such circumstances it is, of course, not possible to determine if the raising of the melting-

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* G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 23, p. 68 (1899).

point by pressure continues at high pressures to be linear as it is at low pressures. This slight decomposition of CBr_4 at temperatures above that of the melting-point at ordinary pressures is not surprising, since it is known that CBr_4 decomposes on distillation, and that the carbon tetraiodide decomposes even when only just melting.

TABLE I.

Temperatures (corrected).	Pressures, P_1 (corrected).	Pressures, P_2 (corrected).
° C.		
94·84	45 kg./cm.^{2}.	65 kg./cm.^{2}.
97·84	98 ,,	—
100·29	134 ,,	160 kg./cm.^{2}.
104·92	274 ,,	295 ,,
104·87	280 ,,	295 ,,
(110·94	420 ,,	440 ,,)
(115·48	630 ,,	—)

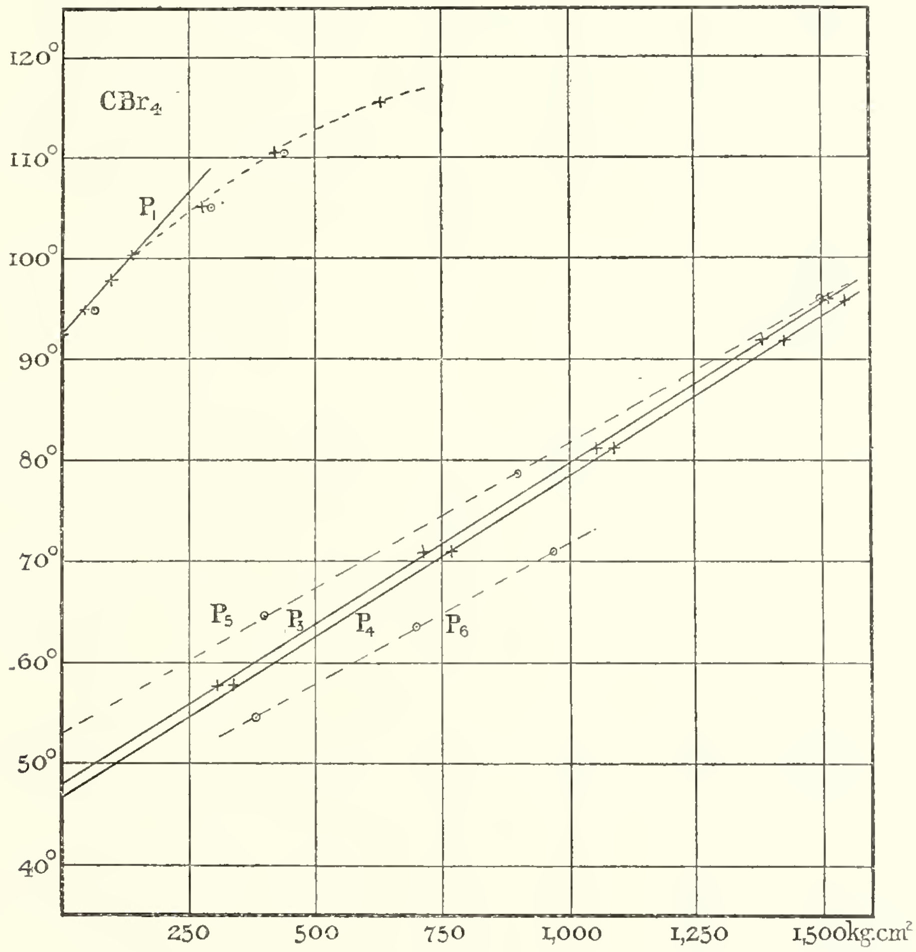

Fig. 6.

It is, therefore, not probable that the increased pressure plays any part in producing this decomposition, although this, of course, cannot be proved.

These melting-points are plotted in the diagram, fig. 6, and connected by the upper curve P_1 of that diagram. The curve P_2 is not shown in the diagram as it runs very close and parallel to P_1.

The difference between the pressures P_1 and P_2 is about 20 kg./cm.^{2}, and the amount of super-cooling necessary to reach the part C of the crystallization-velocity curve as shown in fig. 5, where the velocity of crystallization attains large values and growth-structures also appear, is thus only about one degree in the case of CBr_4—one degree on the melting-point curve corresponding to 20 kg./cm.^{2}. From the fact that the difference between the values P_1 and P_2 does not change at higher pressure, it may be concluded that pressure does not influence the degree of super-cooling which is necessary in order that growth-structures may be produced. The curves showing the velocity of crystallization in its dependence on the degree of super-cooling (diagram, fig. 5) will, therefore, be similar in shape at all pressures, although the absolute value of the velocity at corresponding degrees of super-cooling may vary with the pressure.

(2) *Transition-point Determinations.*—When the molten carbon tetrabromide is cooled between glass plates it first crystallizes in isotropic crystals, and on further cooling a crystallization of the anisotropic crystal modification suddenly starts. The anisotropic crystallization begins usually from one or from a few points at the border line of the isotropic crystal mass, and the anisotropic crystals grow at the expense of the isotropic just as if they were growing in the liquid phase. The growth is rapid, and long, blade-like crystals are formed which cover the space earlier occupied by several of the isotropic crystals, and no connection whatever seems to exist between the border lines of the isotropic crystals and the growing anisotropic crystals. On the other hand, when the transition of the anisotropic modification to the isotropic occurs, on raising the temperature of the preparation, the isotropic crystals are not seen to grow at all, but it looks rather as if the anisotropic crystals were simply melting. Dark isotropic spots of quite irregular shape appear both at the border lines and in the interior of the crystals, and continue to be formed and to grow larger until the whole has changed into an isotropic mass.

Pressure raises this transition-point rapidly, as seen from Table II., and the same general difference which exists between the transition from isotropic to anisotropic, and from anisotropic to isotropic at ordinary pressure, exists also when transition takes place at high pressures. But, in addition, it is found that the transition from isotropic (*i.e.*, regular) form takes place extremely slowly at the true transition-point pressure. When the transition-point curve is passed at constant temperature by lowering the pressure slowly, the anisotropic phase at first appears in the form of small, bright, coloured spots on the dark field. These are a kind of crystal globulæ, crystal germs, which then grow to bigger crystals. This, as is well known, is the general case when crystals begin to form in a liquid, and the related phenomena have been described at length by VOGELSANG, who especially investigated the growth of sulphur crystals, but it has not been known that the crystallization of one crystal phase out of one other crystalline phase may take place in exactly the same way. These anisotropic crystal germs appear at any point inside the isotropic crystal grains or at their border. They are very few at the melting-point pressure, and are scarcely seen to grow at all, but if the pressure is lowered they begin to be more numerous, and grow more and more rapidly. The lower pressure given in Table II. at any given temperature is the pressure at which the anisotropic crystal germs are seen only just to begin to grow with noticeable speed. The higher pressure given again is that at which the transition from anisotropic to isotropic form is seen to take place when pressure is increased. In this case it is not possible to see when transition really begins, and only a quite small increase of pressure is necessary in order to produce a very rapid transition into the isotropic modification. The change is thus more like melting, and the opposite change, from isotropic to anisotropic crystal form, takes place in a similar way to crystallization.

TABLE II.

Temperatures (corrected).	Pressures, P_3 (corrected).	Pressures, P_4 (corrected).
° C.		
57·54	310 kg./cm.^{2}	340 kg./cm.^{2}
70·89	715 ,,	770 ,,
81·20	1,055 ,,	1,090 ,,
91·96	1,385 ,,	1,430 ,,
95·72	1,515 ,,	1,550 ,,

The difference between the pressure values P_3 and P_4 range between 30 and 55 kg., the average being 40 kg./cm.^{2}, but this value is apparently not dependent upon the pressure at which the transition takes place.

Determinations were further made at constant pressure, both at rising temperature, Table III., and at falling temperature, Table IV., Series A and B.

TABLE III.

Observations at rising temperatures, about	Constant pressures, P_5.
° C.	
64·5	400 kg./cm.^{2}
78·6	900 ,,
96·0	1,500 ,,

TABLE IV.

Observations at falling temperatures, about	Constant pressures, P_6.
SERIES A.	
° C.	
71	970 kg./cm.^{2}
63·5	700 ,,
54·5	385 ,,
SERIES B.	
73·2	1,000 kg./cm.^{2}
67·8	760 ,,
61·3	510 ,,
55·0	299 ,,
51·9	200 ,,

The pressures P_3, P_4, P_5, and P_6, given in the Tables II., III., and IV., Series A, are plotted in the diagram, fig. 6, and form the lower group of curves in this. The curve P_3 intersects with the temperature axis of the diagram at 47°·8 C. and the curve P_4 at 46°·6 C.

The significance of these transition-point curves P_3, P_4, P_5, and P_6, may be explained in the following manner :—

P_3 represents the temperatures and pressures at which the growth of the anisotropic modification just attains a noticeable velocity when both modifications coexist. P_4 again the pressures and temperatures at which the isotropic modification is formed with noticeable speed under these same conditions. In the small strip between these two curves the two modifications of carbon tetrabromide will thus coexist without changing one into the other. The true equilibrium curve must lie between these two curves of "false equilibrium," probably nearer to the curve P_4 than to P_3, as the velocity of transition seems to increase more rapidly in directions at right angles to this curve than to the curve P_3.

If we work by a volumetric method we may, according to these curves, expect to find that the transformation takes place at a lower temperature when working at descending temperature than when working at rising temperature, and the horizontal distance (40 kg./cm.^{2}) between the curves would represent the pressure values obtainable by the method at constant temperature which has been employed by TAMMANN in his transition-point determinations.

The curves P_5 and P_6 again represent the temperatures and pressures at which each modification is at first spontaneously formed from the other. The much greater distance at which these run from the true equilibrium curve shows to what a much larger extent the equilibrium can be exceeded when no crystal germs of the modification, stable at that temperature and pressure, are present.

The curve P_5 runs nearer and nearer to P_3 as the temperature of the transition-point rises, which means that the unstable region grows gradually smaller at high temperatures, and probably would disappear at about 1,700 kg./cm.^{2}

As seen from both series of measurements (Table III.), which were made at a different rate of cooling, the transition-point is exceeded to a higher degree at high temperatures than at low. The unstable region in the case of the transition from the isotropic to the anisotropic modification would thus become larger with increasing temperature, which is just opposite to what takes place in the case of the inverse transition, as we have seen, and is not what one should expect. The extent to which the equilibrium curve may be crossed on cooling at constant pressure seems also to depend to a certain amount on the rate at which the cooling takes place, but this circumstance does not furnish an explanation for the general trend of the curve P_6, as this remains similar in direction in the different series of measurements. The conclusion to be drawn, in the present state of knowledge, would thus be that pressure influences this transition from the isotropic state to the anisotropic in such a way as to facilitate a retardation of the transition.

The distance between the curves P_3 and P_4 remains quite constant, and this shows that the conditions of transition of the one form of the substance to the other form are not influenced by pressure as far as regards the degree to which the equilibrium-curve is crossed, just as the conditions of crystallization are not changed by pressure, as far as regards the degree of super-cooling, as pointed out on p. 136. This may be considered a proof that the curve for the velocity of crystallization and the curve for the velocity of transition of polymorphic crystal forms of a substance are similar in shape, a similarity which might be expected. So far a curve of velocity of transformation has only once been actually measured, that is in the case of the transformation of a "monotropic," unstable modification to the stable one (Benzophenone III. to I.).[*]

This group of four curves, limiting the areas in the diagram of state where a false equilibrium exists between the two crystalline forms of carbon tetrabromide or where spontaneous formation does not occur, are quite analogous to those found by TAMMANN in his latest researches on phenol,[†] silver iodide,[‡] and ice.[§] In these cases the equilibrium curve is found to split up at low temperatures into four different curves, corresponding to the above. The distance between the curves is at low temperatures very large, and the transformation at last entirely ceases to take place when the temperature is sufficiently lowered. The transition in the case of carbon

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[*] G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 29, pp. 58, 67 (1899).

[†] G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 75, pp. 75 (1911).

[‡] G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 75, p. 733 (1911).

[§] G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 72, p. 602 (1910).

tetrabromide is, on the other hand, one which takes place more readily than in most cases of enantiotropic transformation which are known, and the possibility of studying the same phenomena of "false equilibrium" in a substance like this indicates the sensitiveness of the method.

As seen from the Tables I. and II., 16 kg./cm.^{2} suffice to raise the melting-point of CBr_4 1°, whereas the transition-point is only raised 0·5 degree by this pressure. The melting-point curve and the transformation-point curve will, therefore, not intersect at high pressure to form a triple-point. The consequence of this direction of the melting-point curve and the transition-point curve is *that the anisotropic monoclinic modification of carbon tetrabromide cannot be caused to melt*, even at any pressure. The theoretical triple-point deduced from these curves would lie at low temperature and high negative pressures (0° and -1500 kg./cm.^{2}). A case like this has not been experimentally met with earlier, but the possibility of the occurrence of such a case has been theoretically foreseen by BACKHUIS ROOZEBOOM in his treatise on the applications of the phase-rule.[*]

6. *The Diagram of State of αβ-bibrompropionic Acid*, $CH_2Br.CHBr.COOH$.

Among "monotrope"-polymorphic substances bibrompropionic acid is probably unique in this respect, that it melts twice when slowly heated. The unstable modification of lower melting-point is nearly always obtained when the fused substance is allowed to cool, and on heating again it melts at 51° C., but at a few degrees higher the stable modification crystallizes out of the "melt" and then on further heating melts at 64° C. This behaviour was described in detail by TOLLENS,[†] who first prepared this substance, and it has later been studied by LEHMANN.[‡] The crystals of both these modifications have been measured by ZEPHAROWICH,[§] who found that both crystallize in the monoclinic system.

This behaviour of αβ-bibrompropionic acid, together with the comparatively great stability of the "unstable" modification, made it probable that it, in this case, would be possible to determine the melting-point curve of two different modifications of a polymorphic substance, which would be of interest, as hitherto only melting-point curves of stable modifications have been measured.[||] Before giving the results of

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[*] H. W. BACKHUIS ROOZEBOOM, 'Die Heterogenen Gleichgewichte I.,' p. 185, fig. 41 (Braunschweig, 1901).

[†] TOLLENS, 'LIEBIG'S Ann.,' 167, pp. 222, 337.

[‡] O. LEHMANN, 'Molekularphysik,' I., p. 690.

[§] ZEPHAROWICH, 'Jahresber.,' 1878, p. 693.

[||] TAMMANN'S statements about melting-point curves of alleged unstable modifications of *p*-xylol, carbon tetrachloride, acetic acid, diethylamin, trimethylcarbinol, and ethylendibromide ('WIED. Ann.,' 66, p. 473, and 68, pp. 553, 629) have been withdrawn by him in his later publication of the measurements in "Kristallisieren u. Schmelzen."

these determinations the crystallization at ordinary temperature must be briefly described.

When the acid is fused between two glass plates and allowed to cool super-cooling invariably takes place. When crystallization sets in a few round crystal germs of the modification melting at 51° C. are formed, and these then grow at moderate speed in all directions, forming hexagons remarkably regular in shape. These are, however, not homogeneous crystals, but are built up of crystal fibres radiating from a central crystal germ. If a small particle of the stable modification is brought into contact with these crystals, a transition begins to occur and the stable modification grows at the expense of the unstable, very much in the same way as this grows in the "melt." The growth of the stable modification melting at 64° C. is fan-like, the crystal threads being very similar to those of the modification melting at 51° C. Both modifications show approximately the same interference colours, and this adds to the similarity of their appearance when crystallized between two glass plates. At ordinary temperatures the velocity of crystallization of the unstable modification is greater than the velocity of transformation to the stable form.

Considerable difficulty was met with in trying to get a sufficiently pure preparation for the melting-point determinations. The substance is very soluble in most solvents, and the degree of purity is not much improved by repeated crystallization. It was at length found that a pure product may be obtained by treating the acid with a large quantity of petrolether at ordinary temperature, and evaporating part of the petrolether by an air current. Crystals of the unstable modification about 1 mm. in diameter are formed, but these clear, transparent crystals change, while still in the evaporating solution, into the stable form whereby they become porcelain-like, white and non-transparent.

Unfortunately a great many measurements on unstable melting-points were made on a specimen that was not quite pure, and these had then to be repeated on a pure one. But as some interesting observations were made during these measurements with the less pure material they are given here in Table VII., beside the measurements carried out with the pure substance, Table VI.

(1) *Determination of the Melting-point Curve of the Stable Modification.*—Under pressure the molten acid behaves very much in the same way as at ordinary pressure in this respect, that it almost invariably crystallizes to the unstable modification. It is therefore not possible to work at constant pressure, and a curve connecting the points where this modification is spontaneously formed has therefore not been determined. In order to determine the melting-point curve of the stable modification it is necessary to melt the acid between glass plates, and when it has crystallized to the unstable form, to inoculate with a crystal of the stable form, whereby the transition takes place, and then to bring the preparation into the pressure apparatus. Care must be taken during the whole series of measurements not to melt the stable form totally, as we then nearly always pass over to the unstable curve, when the

"melt" is crystallized either by decreasing temperature or by increasing pressure. The crystals both grow very slowly and melt very slowly. The growth of the crystals is not much hastened even by increasing the pressure by as much as 200 atmospheres, but a great many new crystal germs then appear and grow in all directions to remarkably evenly-developed small crystals. In spite of the slowness with which these crystals grow, the force developed in crystallizing is so great that they, even at pressures above 1,000 atmospheres, tend to push the glass plates apart in spite of the strong outer pressure acting on these. As a result the glass plates are bent, and if the crystals are allowed to grow too large the glass plates are broken by the pressure. For these reasons the curve connecting the points where formation of crystal growth-structures eventually would occur has not yet been determined.

In consequence of the slowness with which melting takes place at the equilibrium curve crystal—liquid, it is possible to slightly superheat the crystals by decreasing the pressure at constant temperature as described on p. 131. We are able to determine a pressure at which the melting of the crystals begins to take place with sufficient rapidity to be observed, and on further gradually decreasing the pressure the crystals are seen to melt slightly faster, but when a certain pressure, below the pressure at which melting is first seen to take place, is reached the melting suddenly becomes very rapid. This pressure is, at about 5° C. above the melting-point at ordinary temperatures, 40 atmospheres lower than the pressure at which melting is seen to take place quite slowly, and at temperatures about 15° C. above the melting-point it is 30 atmospheres lower. The extent to which the crystals may be superheated therefore diminishes towards higher temperatures on the melting-point curve, apparently because the rapidity of melting increases with the temperature of the melting-point. The pressure at which melting can be just observed is not so easy to determine accurately as the pressure at which crystallization can be just observed, and only the latter therefore has been determined. The points of the actual equilibrium curve are to be found between these two pressures, which,

TABLE V.

Temperatures, *t* (corrected).	Pressures, P_1 (corrected).	Pressures, P_2 (corrected).
° C.		
(64	1 kg./cm.^{2})	—
66·04	160 ,,	—
68·86	260 ,,	220 kg./cm.^{2}
73·24	470 ,,	440 ,,
79·21	790 ,,	760 ,,
84·73	1060 ,,	—

however, lie only a couple of atmospheres apart. The pressures at which the velocity of crystallization attains noticeable values are given in Table V. as P_1, and the pressures at which rapid melting takes place are given there as P_2.

(2) *Determinations of the Melting-point of the Unstable Modification.*—The melting and crystallization of the unstable modification at different pressures occurs in very much the same manner as in the case of the stable modification. The only difference is that the velocity of crystallization is greater. Working isothermically, it has been possible to determine the pressures at which growth-structures are suddenly formed. These pressures lie about 350 kg./cm.^{2} above the melting-point pressures, which corresponds to approximately 6°·5 C. All that has been said with regard to the superheating of the stable modification applies also to this case, but the slowness with which the melting takes place is here still more marked. The point where a rapid melting suddenly begins is not reached before at about 150 kg./cm.^{2} lower pressure than the melting-point pressure. This corresponds to a superheating of about 2°·5 C.

In consequence of the extreme slowness with which the melting and the crystallization takes place in the vicinity of the equilibrium-curve crystal—liquid we would, when working isothermically and increasing or decreasing pressure at a moderate speed, only be able to observe a somewhat sudden volume change at the pressures at which rapid melting and rapid crystalline-growth takes place. We would thus obtain pressure values as much as 500 kg./cm.^{2} apart, corresponding to 9° C., and if we assume—as is generally done—that the true equilibrium pressure lies halfway between the obtained limiting pressures, we would be about 100 kg./cm.^{2}, corresponding to 1°·8 C. in error. This is, of course, an extreme case, but it serves well to indicate the uncertainty of the volumetric methods, both with regard to the determination of melting-point curves and the determination of transition-point curves between different crystalline modifications in such cases where transition takes place very slowly.

TABLE VI.

Temperatures (corrected).	Pressures, P_3 (corrected).
° C.	
(51	1 kg./cm.^{2})
52·60	215 ,,
55·52	300 ,,
60·56	535 ,,
65·39	775 ,,
70·64	1,045 ,,
75·40	1,325 ,,

The pressures at which crystallization begins to take place at noticeable speed, determined on a very carefully purified sample, are given as P_3 in Table VI., and plotted in the diagram, fig. 7, forming the curve P_3. The values above 500 kg./cm.^{2} lie all on a straight line, which also passes through the melting-point at 1 kg./cm.^{2}, 51° C. At only a few degrees above the melting-point it is very difficult to judge exactly at what pressure the crystals really grow on account of the extreme slowness with which this takes place, and the pressure values obtained are much too large at temperatures just above 51° C.; but the difference between the obtained values and the values on the curve grows less with rising temperature and disappears at about 58° C. That these high values, up to values 200 kg./cm.^{2} too high, are obtained at temperatures near the melting-point at 1 atmosphere depends upon the circumstance that the absolute value of the velocity of crystallization is so very small that the crystallization becomes noticeable first at pressures much higher and further apart from the true melting-point curve than at higher temperatures. With rising temperature the absolute value of the velocity of crystallization gradually increases, and the values obtained for the pressure at which the growth of the crystals becomes noticeable asymptotically approach the equilibrium curves until they, from about 500 kg./cm.^{2}, are found to lie practically on a straight line.

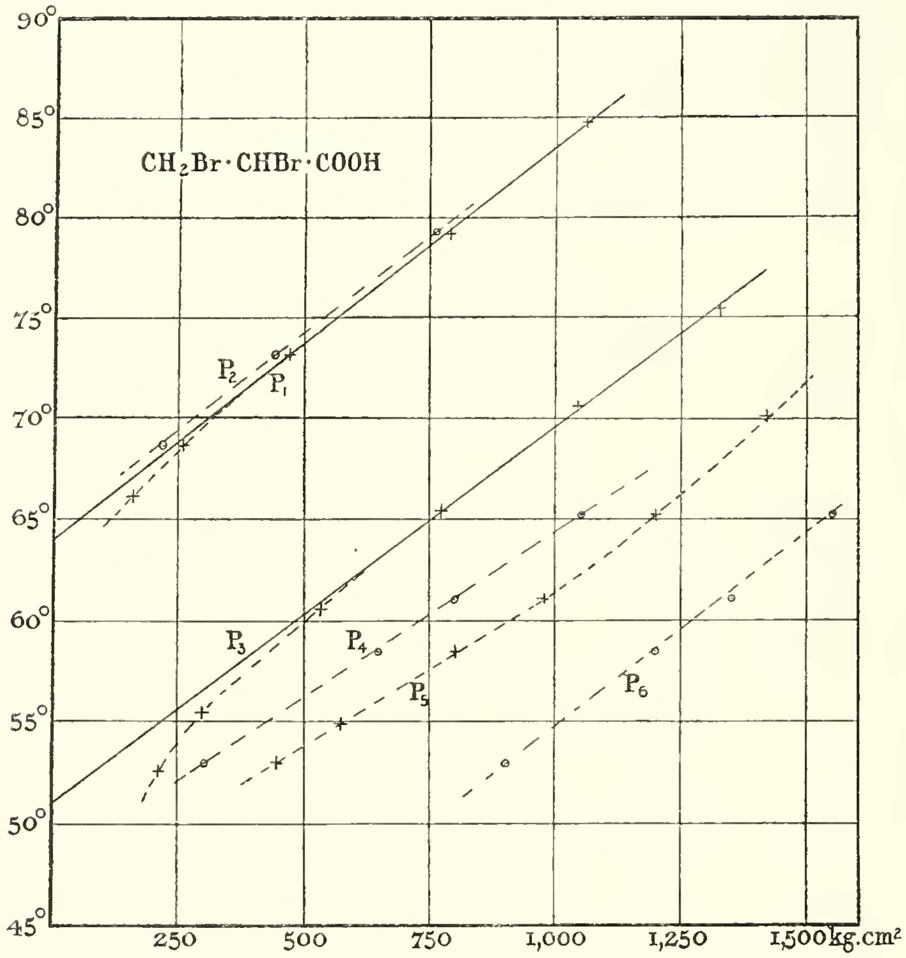

Fig. 7.

The pressure values at which crystallization begins to take place in the case of a not sufficiently purified sample of the acid are given as P_5 in Table VII. In this case the pressures at which rapid growth and the formation of growth-structures takes place were also determined, and are given as P_6 in the same table. Several points on the curve, where suddenly rapid melting sets in, were also determined, and are given as pressures, P_4. An interesting feature of this melting-point curve, P_5, is that it at higher pressure bends slightly towards the temperature axis, which the curve of the pure substance does not do. This behaviour of the curve will be discussed at a later stage with regard to its bearing upon the problem of the influence of impurities upon the form of the melting-point curve.

TABLE VII.

Temperatures (corrected).	Pressures, P_4.	Pressures, P_5 (corrected).	Pressures, P_6.
° C.			
(51	—	1 kg./cm.^{2}	—)
53	(about 300 kg./cm.^{2})	450 ,,	900 kg./cm.^{2}
55	—	575 ,,	1,000 ,,
58·6	650 kg./cm.^{2}	800 ,,	1,200 ,,
61·1	800 ,,	980 ,,	1,350 ,,
65·24	1,050 ,,	1,200 ,,	1,550 ,,
70·14	—	1,420 ,,	—

As seen from the diagram, fig. 7, and from the Tables V. and VI., the melting-point of the stable modification is raised one degree by a pressure of 51·28 kg./cm.^{2}, and the melting-point of the unstable modification one degree by a pressure of 53·48 kg./cm.^{2}. The melting-point curves will thus run further apart as the pressure is increased, and *the, at ordinary pressure, unstable modification will at all pressures melt at a lower temperature than the modification melting at* 64° *C. and remain unstable.*

7. *Discussion of Results.*

The fact that the melting-point curves of $\alpha\beta$-bibrompropionic acid do not intersect at high pressures, taken together with the somewhat similar relation between the melting-point curve and the transition-point curve of carbon tetrabromide, as given in the diagram, fig. 6, are of interest with regard to the theoretical explanations given as the cause of the occurrence of two different classes of polymorphic substances, the "enantiotropic" and the "monotropic." These terms were first used by LEHMANN, who called those polymorphic substances which pass reversibly into each other at a given transition-point "enantiotropic," and those which have one stable and one or several unstable modifications "monotropic." Later an explanation for this different behaviour of the two classes was given almost simultaneously by OSTWALD* and by

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* W. OSTWALD, 'Zeitschr. f. Phys. Chem.,' 22, p. 312 (1897).

Schaum,* who both considered the difference due to a different relative position of the transition-point with regard to the melting-point. In the case of enantiotropy the transition-point is situated below the melting-point, and the modification which is stable at temperatures below the transition-point cannot be melted; but if we suppose the transition-point of a modification to lie above its melting-point such a transition-point could not be observed, and we would have a case of monotropy. As pressure changes the melting-point and also the transition-point, it has been generally expected that it might be possible to change an "enantiotropic" body into a "monotropic" by pressure, and *vice versâ*. The pressures at which this ought to be possible were, in the case of sulphur, calculated by Roozeboom.† Tammann then found that sulphur really behaves in this way,‡ and determined the triple-point temperature and pressure, above which the monoclinic sulphur changes from an enantiotropic condition to a monotropic, as 153°·5 C. and 1,470 kg./cm.^{2}. This experimental result in the case of sulphur has generally been thought to be a verification of the theoretic explanation given by Ostwald and Schaum,§ and it has been expected that the change of an unstable, monotropic modification to a stable modification also would take place at high pressures.

Roozeboom, in his systematical treatise of the application of the phase-rule, has pointed out that the explanation given by Ostwald and Schaum is a possible one, but not necessarily the true one.‖ The experimental data given in this paper show that carbontetrabromide at all pressures remains an "enantiotropic" body, of which the modification, stable below the transition-point, cannot be caused to melt, and that $\alpha\beta$-bibrompropionic acid remains at all pressures a "monotropic" body, the unstable modification remaining unstable at all pressures. It remains, therefore, an open question whether the explanation given by Ostwald and Schaum for the non-existence of a definite transition-point, in the case of monotropic bodies, is the true one or not. And the deduction from this theory, that a monotropic body might be changed into an enantiotropic by pressure, which, if it were true, would at the same time prove the correctness of the theory, is opposed by the behaviour of the melting-point curves of $\alpha\beta$-bibrompropionic acid.

The determination of the melting-point curves of the two modifications of $\alpha\beta$-bibrompropionic acid is also of interest in another respect. Generally it must be expected

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* R. Schaum, 'Habilitationschrift,' Marburg, 1897, p. 27.

† Backhuis Roozeboom, 'Rec. Tr. Chim. Pays-Bas,' 6, p. 314 (1887), and 'Zeitschr. f. Phys. Chem.,' 2, p. 475 (1888).

‡ G. Tammann, 'Wied. Ann.,' 68, p. 675 (1899); 'Ann. d. Phys.,' 3, p. 178 (1900); and "Kristallisieren u. Schmelzen," pp. 269–275.

§ Some other cases where Tammann claims to have found a triple-point at higher pressures (dimethyl-ether of oxalic acid, ortho-kresol) will be dealt with in a further communication, and in the case of acetic acid the curves given by Tammann do not intersect at the triple-point in the way required by theory. These substances, therefore, cannot be quoted as evidence in this case.

‖ Backhuis Roozeboom, 'Die Heterogenen Gleichgewichte,' I., p. 160.

that a relation of some kind exists between the physical constants of polymorphic modifications if these are formed from the same molecules of the liquid phase, and, as will be shown, the measurements given above also indicate the existence of such a relationship. Conclusions may, to a certain extent, be drawn, even as to the nature of this relationship, but as this case is only a single one—the only one which until now has been investigated—the relationship observed might, of course, depend upon a singular coincidence, although this is not probable, and the discussion to follow is therefore given with all reserve.

The two melting-point curves are perfectly straight lines within the limits as set by the accuracy of the measurements. The upper one has been followed over a pressure range of 1,060 kg./cm.^{2}, the lower one over one of 1,330 kg./cm.^{2}. If we continued these melting-point curves towards negative pressures in the diagram we should find that they would intersect at a pressure value of about $-17,000$ kg./cm.^{2}, and at a temperature between $-270°$ C. and $-280°$ C., that is, *at the absolute zero.* The conclusion to be drawn therefrom is that *the difference between the absolute melting-points of the two modifications at any pressure is similar to the difference of the absolute melting-points at ordinary pressure*, the melting-point values thus converging towards unit value at the absolute zero.

If we further inquire into the cause of this relation, we find that the direction of the melting-point curve is determined by the product of the absolute melting-point into the quotient given by the volume change at the melting-point divided by the latent heat of crystallization in the Clapeyron-formula for the change of the melting-point by pressure. If the ratio between the absolute melting-points of two crystalline forms remains constant at all temperatures and the melting-point values converge toward unit value at the absolute zero, as in this case, it is therefore necessary that the ratio between these quotients in the Clapeyron-formula should also remain constant at all temperatures, and that the absolute values of the quotients should themselves also converge towards unit value at the absolute zero. Nothing at present is known about the absolute values of the factors entering into this quotient in the Clapeyron-formula, and of the absolute change of these factors with changing temperature, but the fact that a volume factor, as well as a heat factor, in the case of both modifications is affected by pressure in a similar way is of considerable interest.

The changes of the latent heats of crystallization must depend on the changes of the specific heats of the liquid and of the crystals, and to these changes the changes of the latent heat of transition between the two modifications probably also corresponds. The volume changes again must depend upon the compressibility of the liquid and of the crystals. The intersection of the melting-point curves at the absolute zero thus points to the probability that the values of all these properties for both modifications converge toward unit value at the absolute zero.

It may suffice here to point out briefly that in the case of the energy factors this is what is required by the heat theorem of NERNST, and that the other factors again are those which, according to the formula of LINDEMANN, determine the "molecular frequency" of the atoms. It seems therefore probable that the relation between the "molecular frequency" of the two crystalline forms determines the entire relationship between the physical constants of one form as compared with those of the other.

As a general result of the intersection of the melting-point curves at the absolute zero, we thus find that the physical properties of the two modifications—which apparently behave like two distinct crystalline substances—would, when the absolute temperature is lowered, change gradually, and in a similar way, and become identical at the triple-point, the absolute zero, which thus also would represent a "critical-point" between these two modifications of the $\alpha\beta$-bibrompropionic acid.

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A NEW TREATMENT OF OPTICAL ABERRATIONS.

BY

R. A. SAMPSON, F.R.S.

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V. *A New Treatment of Optical Aberrations.*

By R. A. Sampson, *F.R.S.*

Received March 15,—Read May 23, 1912.

The method developed by Gauss in his 'Dioptrische Untersuchungen' is probably the most powerful, as well as the readiest, method in geometrical optics. It has in effect hitherto been restricted to systems in which the relations of original and emergent rays are strictly linear, or, in optical language, those in which the aberrations can be neglected. It is true that Seidel bases his celebrated discussion of aberrations upon Gauss's method, but he soon modifies it and replaces its system of co-ordinates and characteristic steps by others. The following pages show how the method may be extended and retained throughout the discussion of the aberrations of any co-axial system. They will be found to throw light upon the general relationships of the well-known Petzval condition and Abbe Sine condition, to furnish a ready method of describing, analysing and measuring the faults of an optical image, and to be particularly adapted to numerical calculations, to the order to which these are necessary for telescopic objectives.

It will be convenient to state here the essentials of the method in the form in which they will be used later. Let $Oxyz$, $O'x'y'z'$ be rectangular axes in the original and emergent media, of which the refractive indices are μ, μ' respectively. Ox, $O'x'$ are the axes of the optical system. Take the equations of any ray before and after its passage through the system in the respective forms

$$\begin{aligned} y &= \beta x+b, & z &= \gamma x+c, \\ \text{and} \qquad y' &= \beta' x'+b', & z' &= \gamma' x'+c', \end{aligned} \qquad \qquad (1)$$

then, provided there is a strict linear correspondence as well as symmetry about the axis, we may put

$$\begin{aligned} b' &= gb+h\beta, & c' &= gc+h\gamma, \\ \beta' &= kb+l\beta, & \gamma' &= kc+l\gamma, \end{aligned} \qquad \qquad (2)$$

Published separately, July 27, 1912.

where g, h, k, l are constants involving the curvatures of the refracting surfaces, the distances between them and the refractive indices; also

$$gl - hk = \mu/\mu'.$$

Following SEIDEL, we shall call such systems normal systems.

In particular, for a single refracting surface,

$$2x = \mathrm{B}(y^2+z^2)+\ldots,$$

without change of origin, the scheme

$$\begin{Bmatrix} g, & h \\ k, & l \end{Bmatrix},$$

as I shall call it, becomes

$$\begin{Bmatrix} 1, & * \\ -\left(1-\frac{\mu}{\mu'}\right)\mathrm{B}, & \frac{\mu}{\mu'} \end{Bmatrix}$$

where * is put in place of zero. Or again, a simple shift of origin by a distance d may be represented by the scheme

$$\begin{Bmatrix} 1, & d \\ *, & 1 \end{Bmatrix}.$$

If two instruments be represented by the schemes

$$\begin{Bmatrix} g_1, & h_1 \\ k_1, & l_1 \end{Bmatrix}, \qquad \begin{Bmatrix} g_2, & h_2 \\ k_2, & l_2 \end{Bmatrix},$$

light passing through (1) first and then through (2), and the emergent origin for the first being made the same as the original origin of the second, their combined effect is given by the scheme

$$\begin{Bmatrix} g_1g_2+k_1h_2, & h_1g_2+l_1h_2 \\ g_1k_2+k_1l_2, & h_1k_2+l_1l_2 \end{Bmatrix}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which may be written down by multiplying the rows of the later scheme into the columns of the former, as if they were determinants. It will be shown hereafter that this rule is remarkably well adapted for numerical calculation—a fact that does not seem to have been remarked before. The scheme corresponding to any system, as, for example, any thick lenses, arranged at intervals along an axis, may be built up from its elements by this rule, by writing down the schemes in order belonging to the successive refracting surfaces and shifts of origin, and compounding these; if we have to compound in this manner a sequence of schemes

$$\{g_1, \ldots\}, \quad \{g_2, \ldots\}, \quad \{g_3, \ldots\}, \quad \ldots, \quad \{g_n, \ldots\},$$

then, provided we do not change the order in which the schemes present themselves, the composition may be effected in such groups as may be convenient, and may be performed either from left to right or from right to left.*

The product of the determinants of the component scheme $(g_1l_1-h_1k_1)$, $(g_2l_2-h_2k_2)$, ... gives the value of the determinant $\mathrm{GL}-\mathrm{HK}$ of the compounded scheme.

The analytical scheme corresponding to any instrument of which the cardinal points are known may be written down at sight, and conversely, by the relations

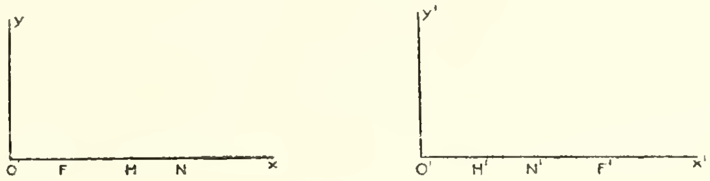

Fig. 1.

$$\mathrm{OF} = l/k, \quad \mathrm{HF} = n/k, \quad \mathrm{NF} = 1/k; \qquad \mathrm{O'F'} = -g/k, \quad \mathrm{H'F'} = -1/k, \quad \mathrm{N'F'} = -n/k,$$

where

$$n = gl-hk \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and H, H′, N, N′, F, F′ denote, as usual, the unit points, nodal points, and principal foci respectively.

If it is desired to work geometrically, we may set the original and emergent axes across one another in a figure at any angle, H and H′ being superposed (or else

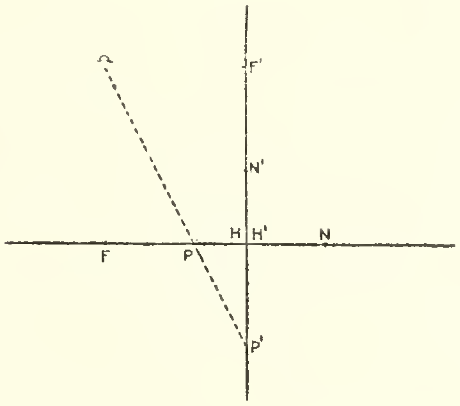

Fig. 2.

N, N′), and finding a point Ω with co-ordinates HF, H′F′; then any straight line ΩPP′ through Ω determines points PP′, which are conjugate foci.

The following method of compounding any two given systems may also be mentioned :—

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* A general discussion of the linear system by the author will be found in 'Proc. London Math. Soc.,' vol. 29, p. 33.

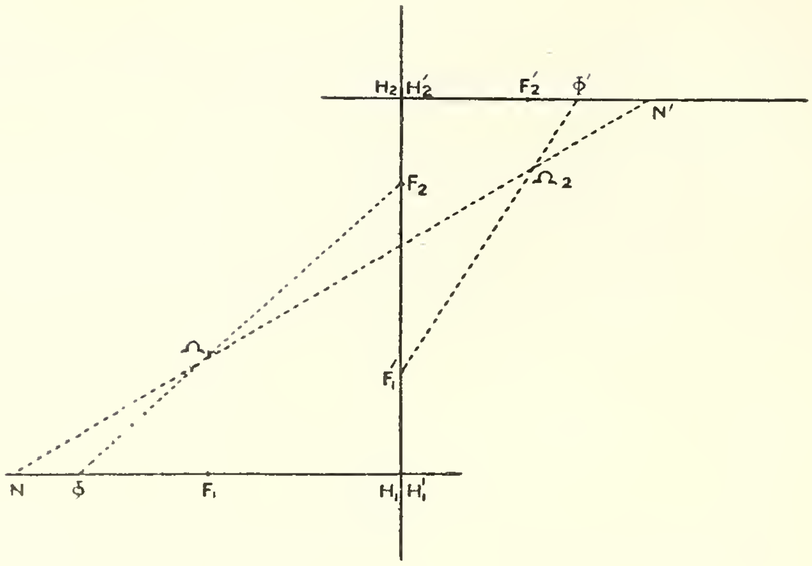

Fig. 3.

Set the axes as shown in the figure, the distance between the points $H_1H'_1$ and $H_2H'_2$ being annulled. Then the lines $F_2\Omega_1$, $F'_1\Omega_2$ give Φ, Φ', the principal foci, and the line $\Omega_1\Omega_2$ gives points N, N′ which are conjugate to one another and are the nodal points of the compound system.

We see that it is always possible to determine a geometrical system that shall correspond to any given values of g, h, k, l. Thus, for example, $n = 0$ implies that F′ is conjugate to *every* point of the original system, or, what is the same thing, that every emergent ray goes through F′.

If the emergent origin is at the principal focus, $g = 0$.

If the original origin is at the principal focus, $l = 0$.

If the original and emergent origins are conjugate points, $h = 0$.

We shall now consider the case of refraction of a general ray at a symmetrical surface centred upon the x-axis and shall show that a scheme $\{g+\delta g, \ldots\}$ may be derived for it, which shall include the aberrations; these, represented by the additional terms δg, ..., will, of course, vary from point to point with the squares and products of the co-ordinates and angles of incidence upon the surface, whereas for the pure linear scheme g, ... are the same for every ray of the beam.

Taking rectangular axes $Oxyz$, let the equation of the surface separating the region of index μ from that of index μ' be

$$2x = B(y^2+z^2)+\tfrac{1}{4}C(y^2+z^2)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

Let a ray

$$y = \beta x+b, \qquad z = \gamma x+c,$$

in the original medium be transformed by refraction at the surface into

$$y' = \beta' x'+b', \qquad z' = \gamma' x'+c',$$

where the axes are, in fact, the same but are accented to indicate the difference of medium.

The positive direction of the x-axis is that in which the light is travelling.

In the diagram P_0 is the point where the original and emergent rays meet at the surface, PP_0 is the original ray, $P'P_0$ the emergent ray, and $(0, b, c)$ are the coordinates of P, $(0, b', c')$ those of P′, and we shall take (a_0, b_0, c_0) as those of P_0.

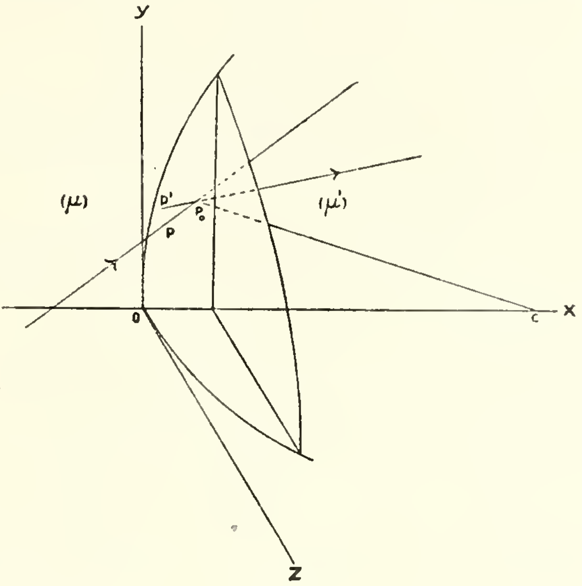

Fig. 4.

If (l, m, n) (l', m', n') are the direction cosines of an original and emergent ray, (p, q, r) those of the normal to the surface at the point of incidence, we have the known equations

$$(\mu l-\mu' l')/p = (\mu m-\mu' m')/q = (\mu n-\mu' n')/r = \mu \cos\theta-\mu'\cos\theta',$$

where θ, θ' are the angles made by the two rays and the normal.

Now

$$\begin{aligned} l &= m/\beta &&= n/\gamma &&= 1-\tfrac{1}{2}\beta^2-\tfrac{1}{2}\gamma^2 \\ l' &= m'/\beta' &&= n'/\gamma' &&= 1-\tfrac{1}{2}\beta'^2-\tfrac{1}{2}\gamma'^2 \\ -p &= q/\mathrm{B}b_0+\tfrac{1}{2}\mathrm{C}b_0(b_0^2+c_0^2) &&= r/\mathrm{B}c_0+\tfrac{1}{2}\mathrm{C}c_0(b_0^2+c_0^2) &&= -1+\tfrac{1}{2}\mathrm{B}^2b_0^2+\tfrac{1}{2}\mathrm{B}^2c_0^2 = -1+\tfrac{1}{2}q^2+\tfrac{1}{2}r^2 \end{aligned}$$

if we neglect higher powers of the small quantities.

Further

$$\cos\theta = 1-\tfrac{1}{2}\theta^2, \qquad \cos\theta' = 1-\tfrac{1}{2}\theta'^2,$$

where

$$\theta^2 = (\beta-q)^2+(\gamma-r)^2, \qquad \theta'^2 = (\beta'-q)^2+(\gamma'-r)^2,$$

and we have approximately

$$\mu(\beta-q) = \mu'(\beta'-q), \qquad \mu(\gamma-r) = \mu'(\gamma'-r).$$

Substituting above for m, m', we have

$$\mu\beta(1-\tfrac{1}{2}\beta^2-\tfrac{1}{2}\gamma^2)-\mu'\beta'(1-\tfrac{1}{2}\beta'^2-\tfrac{1}{2}\gamma'^2) = (\mu-\mu')q-\tfrac{1}{2}q(\mu\theta^2-\mu'\theta'^2).$$

But since

$$\theta/\mu' = \theta'/\mu,$$

therefore

$$\mu\theta^2 - \mu'\theta'^2 = -(\mu-\mu')\,\theta\theta',$$

and

$$\theta\theta' = (\beta-q)(\beta'-q)+(\gamma-r)(\gamma'-r).$$

Hence the right-hand member of this equation reads

$$\begin{aligned}
&(\mu-\mu')\,q\left[1+\tfrac{1}{2}(\beta\beta'+\gamma\gamma')+\tfrac{1}{2}(q^2+r^2)-\tfrac{1}{2}\beta q-\tfrac{1}{2}\beta' q-\tfrac{1}{2}\gamma r-\tfrac{1}{2}\gamma' r\right] \\
&\quad = q\left[(\mu-\mu')+\tfrac{1}{2}(\mu-\mu')(q^2+r^2)\right. \\
&\qquad\qquad \left.+\tfrac{1}{2}(\mu-\mu')(\beta\beta'+\gamma\gamma')-\tfrac{1}{2}(\beta+\beta')(\mu\beta-\mu'\beta')-\tfrac{1}{2}(\gamma+\gamma')(\mu\gamma-\mu'\gamma')\right] \\
&\quad = q\left[(\mu-\mu')+\tfrac{1}{2}(\mu-\mu')(q^2+r^2)-\tfrac{1}{2}\mu(\beta^2+\gamma^2)+\tfrac{1}{2}\mu'(\beta'^2+\gamma'^2)\right],
\end{aligned}$$

or, since

$$q = -\mathrm{B}b_0\,(1-\tfrac{1}{2}q^2-\tfrac{1}{2}r^2)-\tfrac{1}{2}\mathrm{C}b_0\,(b_0{}^2+c_0{}^2)$$

and

$$b_0 = b+a_0\beta = b+\tfrac{1}{2}\beta\,(q^2+r^2)/\mathrm{B},$$

therefore

$$q\,(1+\tfrac{1}{2}q^2+\tfrac{1}{2}r^2) = -b\left[\mathrm{B}+\tfrac{1}{2}\mathrm{C}\,(b^2+c^2)\right]-\tfrac{1}{2}\beta\,(q^2+r^2),$$

and the equation becomes

$$\begin{aligned}
&\beta\left[\mu-\tfrac{1}{2}\mu(\beta^2+\gamma^2)+\tfrac{1}{2}(\mu-\mu')(q^2+r^2)\right]-\beta'\left[\mu'-\tfrac{1}{2}\mu'(\beta'^2+\gamma'^2)\right] \\
&\qquad = -b\left[(\mu-\mu')\,\mathrm{B}+\tfrac{1}{2}(\mu-\mu')\,\mathrm{C}\,(b^2+c^2)+\tfrac{1}{2}\mu\mathrm{B}\,(\beta^2+\gamma^2)+\tfrac{1}{2}\mu'\mathrm{B}\,(\beta'^2+\gamma'^2)\right],
\end{aligned}$$

or dividing by the coefficients of β' and writing

$$\mu/\mu' = n,$$

$$\begin{aligned}
\beta' = b\left[-(1-n)\,\mathrm{B}-\tfrac{1}{2}(1-n)\,\mathrm{C}\,(b^2+c^2)+\tfrac{1}{2}n\mathrm{B}\,(\beta'^2+\gamma'^2-\beta^2-\gamma^2)\right]& \\
+\beta\left[n+\tfrac{1}{2}n\,(\beta'^2+\gamma'^2-\beta^2-\gamma^2)-\tfrac{1}{2}(1-n)(q^2+r^2)\right]&.
\end{aligned}$$

Also

$$b_0 = b+a_0\beta = b'+a_0\beta'.$$

Therefore

$$b' = b+a_0\,(\beta-\beta')\,;$$

but approximately

$$\beta' = -(1-n)\,\mathrm{B}b+n\beta\,;$$

therefore

$$b' = b\left[1+\tfrac{1}{2}(1-n)(q^2+r^2)\right]+\beta\left[\tfrac{1}{2}(1-n)(q^2+r^2)/\mathrm{B}\right];$$

or if we write

$$\begin{aligned}
\omega &= \tfrac{1}{2}(1-n)(q^2+r^2) = \tfrac{1}{2}(1-n)\,\mathrm{B}^2(b^2+c^2), \\
\psi &= \tfrac{1}{2}n\,(\beta'^2+\gamma'^2-\beta^2-\gamma^2),
\end{aligned} \qquad (6)$$

we may put

$$\begin{aligned}
b' &= b\,[1+\omega]+\beta\,[\omega/\mathrm{B}], \\
\beta' &= b\left[-(1-n)\,\mathrm{B}+\mathrm{B}\psi-\frac{\mathrm{C}}{\mathrm{B}^2}\,\omega\right]+\beta\,[n+\psi-\omega].
\end{aligned} \qquad (7)$$

In the same way it follows

$$\begin{aligned} c' &= c\,[1+\omega]+\gamma\,[\omega/\mathrm{B}], \\ \gamma' &= c\left[-(1-n)\,\mathrm{B}+\mathrm{B}\psi-\frac{\mathrm{C}}{\mathrm{B}^2}\,\omega\right]+\gamma\,[n+\psi-\omega]\,; \end{aligned} \qquad (8)$$

for the case of the paraboloid

$$\mathrm{C}/\mathrm{B}^2 = 0,$$

sphere

$$\mathrm{C}/\mathrm{B}^2 = \mathrm{B}.$$

We shall generally write

$$\mathrm{C}/\mathrm{B}^2 = \epsilon\mathrm{B}.$$

We remark that the coefficients that transform the (b, β) system into (b', β') are the same as those which transform (c, γ) into (c', γ'), and for any surface each is expressed in terms of the two functions ψ, ω defined by equation (6), in addition to the refractive index and curvature.

These equations therefore permit us to treat rays which cross the axis with the same readiness as those which intersect it, a thing which is very troublesome in the trigonometrical discussion of the question. They also apply equally easily to the sphere, the paraboloid, and any intermediate form.

Before proceeding with the discussion of these formulæ I shall verify that they cover the known expression for longitudinal aberration on the axis after refraction at a single spherical surface, as it is given in the text books.

Suppose the ray meets the axis at $x = v$, $x' = v'$, so that

$$b+\beta v = 0, \qquad b'+\beta' v' = 0\,;$$

then the equation connecting v, v' for the case of the sphere is

$$-vv'\,[-(1-n)\,\mathrm{B}+\mathrm{B}\,(\psi-\omega)]+v'\,[n+\psi-\omega]-v\,[1+\omega]+\omega/\mathrm{B} = 0,$$

or, dividing by vv' and rearranging the terms,

$$\frac{1}{v'}-\frac{n}{v}-(1-n)\,\mathrm{B} = \left(\mathrm{B}-\frac{1}{v}\right)\left(-\psi+\omega-\frac{\omega}{\mathrm{B}v'}\right);$$

but

$$\psi = \tfrac{1}{2}n\,(\beta'^2-\beta^2) = \tfrac{1}{2}nb^2\left(\frac{1}{v'^2}-\frac{1}{v^2}\right) = \tfrac{1}{2}nb^2\left(\frac{1}{v'}-\frac{1}{v}\right)\left(\frac{1}{v'}+\frac{1}{v}\right)$$

and

$$\frac{\mathrm{B}-\dfrac{1}{v'}}{n} = \frac{\mathrm{B}-\dfrac{1}{v}}{1} = \frac{\dfrac{1}{v'}-\dfrac{1}{v}}{1-n}\,;$$

also

$$\frac{\omega}{\mathrm{B}} = \tfrac{1}{2}\,(1-n)\,\mathrm{B}b^2 = \tfrac{1}{2}b^2\left(\frac{1}{v'}-\frac{n}{v}\right).$$

Hence the right-hand member above is equal to

$$\left(\mathrm{B}-\frac{1}{v}\right)\left[-\tfrac{1}{2}b^2(1-n)\left(\mathrm{B}-\frac{1}{v'}\right)\left(\frac{1}{v'}+\frac{1}{v}\right)+\tfrac{1}{2}b^2\left(\mathrm{B}-\frac{1}{v'}\right)\left(\frac{1}{v'}-\frac{n}{v}\right)\right]$$

$$=\tfrac{1}{2}b^2\left(\mathrm{B}-\frac{1}{v}\right)\left(\mathrm{B}-\frac{1}{v'}\right)\left[-(1-n)\left(\frac{1}{v'}-\frac{1}{v}\right)+\left(\frac{1}{v'}-\frac{n}{v}\right)\right]$$

$$=\tfrac{1}{2}b^2\left(\mathrm{B}-\frac{1}{v}\right)\left(\mathrm{B}-\frac{1}{v'}\right)\left(\frac{n}{v'}-\frac{1}{v}\right).$$

This is one of the usual expressions; compare HERMAN's 'Optics,' p. 189, (iii.). After a slight transformation it leads to the Zinken-Sommer expression for the separation of the focal lines in any co-axial system, and thence, as WHITTAKER has shown ('Theory of Optical Instruments,' p. 26), to the expressions of SEIDEL's theory.

We may verify also that these expressions lead to the known results in the case of the parabolic mirror.

Consider the focus for rays parallel to the axis, *i.e.*, when $\beta = \gamma = 0$.

$$0 = 1+\omega+v'[-(1-n)\mathrm{B}+\mathrm{B}\psi].$$

But

$$n = -1, \qquad \omega = \tfrac{1}{2}(1-n)(q^2+r^2) = \mathrm{B}^2(b^2+c^2),$$

$$\psi = \tfrac{1}{2}n(\beta'^2+\gamma'^2) = \tfrac{1}{2}n(1-n)^2\mathrm{B}^2(b^2+c^2) = -2\mathrm{B}^2(b^2+c^2),$$

so that

$$v' = [1+\mathrm{B}^2(b^2+c^2)]/[2\mathrm{B}+2\mathrm{B}^3(b^2+c^2)] = 1/2\mathrm{B},$$

so that the longitudinal aberration vanishes at the principal focus. More generally, the ray $y' = \beta'x+b'$, $z' = \gamma'x+c'$, corresponding to a general incident ray for which, say, $\gamma = 0$, meets the plane $x' = d'$ in points whose co-ordinates are

$$y' = b[-(1-n)\mathrm{B}d'+1+\mathrm{B}d'\psi+\omega]+\beta[d'(n+\psi-\omega)+\omega/\mathrm{B}],$$
$$z' = c[-(1-n)\mathrm{B}d'+1+\mathrm{B}d'\psi+\omega].$$

For the paraboloidal reflector

$$\omega = \mathrm{B}^2(b^2+c^2),$$
$$\psi = \tfrac{1}{2}n(\beta'^2+\gamma'^2-\beta^2) = -2\mathrm{B}^2(b^2+c^2)-2\mathrm{B}b\beta,$$

since $\beta' = -\beta-2\mathrm{B}b$, $\gamma' = 2\mathrm{B}c$; therefore taking the focal plane $d' = 1/2\mathrm{B}$, we have

$$\left.\begin{aligned} y' &= -\beta/2\mathrm{B}-\mathrm{B}b^2\beta-\beta[\tfrac{1}{2}\mathrm{B}(b^2+c^2)+b\beta], \\ z' &= -\mathrm{B}bc\beta \qquad ; \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

these are known expressions, leading to the theory of the coma of a parabolic reflector; *cf.* PLUMMER, 'Mon. Not. R. A. S.,' LXII., p. 365, (9), (10).

If we compare the scheme

$$\begin{Bmatrix} 1+\omega, & \omega/\mathrm{B} \\ -(1-n)\,\mathrm{B}+\mathrm{B}\psi-\epsilon\mathrm{B}\omega, & n+\psi-\omega \end{Bmatrix} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7), (8)$$

with the equations (4), we see the aberrational scheme is the equivalent of a linear scheme, for a single surface, for which the plane of origin passes through the point $x = \omega/(1-n)\,\mathrm{B}$, that is, through the actual point of incidence $x = \frac{1}{2}\mathrm{B}\,(b_0{}^2+c_0{}^2)\ldots$; if we take the curvature as $\mathrm{B}\,(1+\frac{1}{2}\epsilon q^2+\frac{1}{2}\epsilon r^2)$, and the refractive indices $\mu\,(1-\frac{1}{2}\beta^2-\frac{1}{2}\gamma^2)$, $\mu'\,(1-\frac{1}{2}\beta'^2-\frac{1}{2}\gamma'^2)$ respectively.

As to the latter it may be noticed that the exact equation for refraction of a ray impinging at the origin, and in the plane Oxy, is

$$\mu \sin(\tan^{-1}\beta) = \mu' \sin(\tan^{-1}\beta')$$

or, to our order,

$$\mu\,(1-\tfrac{1}{2}\beta^2)\,.\,\beta = \mu'\,(1-\tfrac{1}{2}\beta'^2)\,.\,\beta'.$$

Hence the aberration ψ may be described as due purely to the obliquity of the ray to the axis, and the aberration ω to the lateral separation from the axis, and we see that the somewhat remarkable fact that two functions ω, ψ suffice to express the aberrations of every ray may be stated in the form that there is no term which is produced jointly by obliquity and lateral separation.

If in any instrument we have a number of surfaces each introducing aberrational terms, and if the schemes preceding and following the surface (r) be compounded so as to read, say, $\{g, \ldots\}$, $\{g', \ldots\}$, then the whole may be represented by

$$\begin{Bmatrix} g, & h \\ k, & l \end{Bmatrix} \begin{Bmatrix} 1+\omega_r, & \omega_r/\mathrm{B}_r \\ -(1-n_r)\,\mathrm{B}_r+\mathrm{B}_r\psi_r-\epsilon_r\mathrm{B}_r\omega_r, & n_r+\psi_r-\omega_r \end{Bmatrix} \begin{Bmatrix} g', & h' \\ k', & l' \end{Bmatrix} \quad . \quad . \quad (10)$$

and the portions added to the general scheme in consequence of the aberrations of the r^{th} surface will be

$$\begin{Bmatrix} \delta\mathrm{G}_r, & \delta\mathrm{H}_r \\ \delta\mathrm{K}_r, & \delta\mathrm{L}_r \end{Bmatrix} = \omega_r \begin{Bmatrix} g, & h \\ k, & l \end{Bmatrix} \begin{Bmatrix} 1 & 1/\mathrm{B}_r \\ -\epsilon_r\mathrm{B}_r, & -1 \end{Bmatrix} \begin{Bmatrix} g', & h' \\ k', & l' \end{Bmatrix} + \psi_r \begin{Bmatrix} g, & h \\ k, & l \end{Bmatrix} \begin{Bmatrix} * & * \\ \mathrm{B}_r, & 1 \end{Bmatrix} \begin{Bmatrix} g', & h' \\ k', & l' \end{Bmatrix} (11)$$

and in this the schemes $\{g, \ldots\}$, $\{g', \ldots\}$ may be taken at their "normal" values without regard to aberrations introduced by surfaces other than the surface (r). If then we write, adding the effects of all the surfaces,

$$\delta\mathrm{G} = \Sigma_r \delta\mathrm{G}_r, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and if we now denote by $\{g, \ldots\}$ the scheme got by compounding all the normal schemes of the instruments in succession, whether these are refractions, or mere shifts of origin from one surface to the next, we have for the relation between any original ray

$$y = \beta x + b, \qquad z = \gamma x + c,$$

and the corresponding emergent ray

$$y' = \beta' x' + b', \qquad z' = \gamma' x' + c',$$

$$\begin{aligned} (b, \beta)\begin{Bmatrix} G+\delta G, & H+\delta H \\ K+\delta K, & L+\delta L \end{Bmatrix} &= (b'+\delta b', \beta'+\delta\beta'), \\ (c, \gamma)\begin{Bmatrix} G+\delta G, & H+\delta H \\ K+\delta K, & L+\delta L \end{Bmatrix} &= (c'+\delta c', \gamma'+\delta\gamma'), \end{aligned} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where b', β', c', γ' are the values that would result if δG, ... were all zero; and turning back to the expressions (6) we see that ω_r, ψ_r are expressed in terms of the incidence—(b, β, c, γ)—upon the plane Oyz by the equations

$$\omega_r = \tfrac{1}{2}(1-n_r)\, B_r^2 (b_r^2 + c_r^2),$$

where

$$b_r = g_r b + h_r \beta, \qquad c_r = g_r c + h_r \gamma\,;$$

$$\psi_r = \tfrac{1}{2} n_r (\beta'^2_r + \gamma'^2_r - \beta_r^2 - \gamma_r^2), \qquad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where

$$\beta_r = k_r b + l_r \beta, \qquad \gamma_r = k_r c + l_r \gamma,$$

$$\beta'_r = k_{r+1} b + l_{r+1} \beta, \qquad \gamma'_r = k_{r+1} c + l_{r+1} \gamma.$$

We notice that the determinants—$(gl - hk)$—of the scheme multiplied by each ψ_r will always be zero, and that of the scheme multiplied by ω_r also, for the case of the sphere. This supplies a useful check.

The numerical management of these formulæ for actual systems is dealt with later. I shall now consider their analytical and geometrical properties.

If

$$(b, \beta)\begin{Bmatrix} G+\delta G, & H+\delta H \\ K+\delta K, & L+\delta L \end{Bmatrix} = (b', \beta'),$$

and δG, ... are quadratic functions of b, c, β, γ, with the symmetries implied in the forms above, we may put

$$\begin{aligned} \delta G &= \tfrac{1}{2}\{\delta_1 G\,(b^2+c^2) + 2\delta_2 G\,(b\beta + c\gamma) + \delta_3 G\,(\beta^2+\gamma^2)\}, \\ \delta H &= \tfrac{1}{2}\{\delta_1 H\,(b^2+c^2) + 2\delta_2 H\,(b\beta + c\gamma) + \delta_3 H\,(\beta^2+\gamma^2)\}, \\ \delta K &= \tfrac{1}{2}\{\delta_1 K\,(b^2+c^2) + 2\delta_2 K\,(b\beta + c\gamma) + \delta_3 K\,(\beta^2+\gamma^2)\}, \\ \delta L &= \tfrac{1}{2}\{\delta_1 L\,(b^2+c^2) + 2\delta_2 L\,(b\beta + c\gamma) + \delta_3 L\,(\beta^2+\gamma^2)\}. \end{aligned} \qquad . \quad . \quad . \quad . \quad (15)$$

In these expressions the values of δ_1G, ... are not unrestricted. Thus, for example, the rays which originate in the point (b, c) must upon emergence be normal to a surface. Consider the conditions that

$$y' = \beta' x' + b', \qquad z' = \gamma' x' + c',$$

where b', β', c', γ' are functions of two variables β, γ, as above, should be normal to a surface.

If (x', y', z') is a point upon the surface, then we have for all directions upon the surface

$$dx' + \beta' dy' + \gamma' dz' = 0,$$

or, since x', y', z' are functions of β, γ only,

$$\frac{\partial x'}{\partial \beta} + \beta' \frac{\partial y'}{\partial \beta} + \gamma' \frac{\partial z'}{\partial \beta} = 0, \qquad \frac{\partial x'}{\partial \gamma} + \beta' \frac{\partial y'}{\partial \gamma} + \gamma' \frac{\partial z'}{\partial \gamma} = 0.$$

Also

$$y' = \beta' x' + b', \qquad z' = \gamma' x' + c'.$$

Therefore

$$\frac{\partial x'}{\partial \beta}(1+\beta'^2+\gamma'^2) + \beta'\left(x' \frac{\partial \beta'}{\partial \beta} + \frac{\partial b'}{\partial \beta}\right) + \gamma'\left(x' \frac{\partial \gamma'}{\partial \beta} + \frac{\partial c'}{\partial \beta}\right) = 0,$$

$$\frac{\partial x'}{\partial \gamma}(1+\beta'^2+\gamma'^2) + \beta'\left(x' \frac{\partial \beta'}{\partial \gamma} + \frac{\partial b'}{\partial \gamma}\right) + \gamma'\left(x' \frac{\partial \gamma'}{\partial \gamma} + \frac{\partial c'}{\partial \gamma}\right) = 0;$$

or, say,

$$\frac{\partial}{\partial \beta}\{x'(1+\beta'^2+\gamma'^2)^{1/2}\} + \left(\beta' \frac{\partial b'}{\partial \beta} + \gamma' \frac{\partial c'}{\partial \beta}\right)(1+\beta'^2+\gamma'^2)^{-1/2} = 0,$$

$$\frac{\partial}{\partial \gamma}\{x'(1+\beta'^2+\gamma'^2)^{1/2}\} + \left(\beta' \frac{\partial b'}{\partial \gamma} + \gamma' \frac{\partial c'}{\partial \gamma}\right)(1+\beta'^2+\gamma'^2)^{-1/2} = 0,$$

so that the necessary and sufficient condition is

$$\frac{\partial\{b', \beta'/(1+\beta'^2+\gamma'^2)^{1/2}\}}{\partial(\beta, \gamma)} + \frac{\partial\{c', \gamma'/(1+\beta'^2+\gamma'^2)^{1/2}\}}{\partial(\beta, \gamma)} = 0.$$

Retaining only the terms of lowest order we have

$$\frac{\partial b'}{\partial \beta} = \mathrm{H} \qquad \frac{\partial b'}{\partial \gamma} = \delta_2\mathrm{G} \,.\, bc + \delta_3\mathrm{G} \,.\, b\gamma + \delta_2\mathrm{H} \,.\, c\beta + \delta_3\mathrm{H} \,.\, \beta\gamma,$$

$$\frac{\partial \beta'}{\partial \beta} = \mathrm{L} \qquad \frac{\partial \beta'}{\partial \gamma} = \delta_2\mathrm{K} \,.\, bc + \delta_3\mathrm{K} \,.\, b\gamma + \delta_2\mathrm{L} \,.\, c\beta + \delta_3\mathrm{L} \,.\, \beta\gamma,$$

$$\frac{\partial c'}{\partial \beta} = \delta_2\mathrm{G} \,.\, bc + \delta_3\mathrm{G} \,.\, c\beta + \delta_2\mathrm{H} \,.\, b\gamma + \delta_3\mathrm{H} \,.\, \beta\gamma \qquad \frac{\partial c'}{\partial \gamma} = \mathrm{H},$$

$$\frac{\partial \gamma'}{\partial \beta} = \delta_2\mathrm{K} \,.\, bc + \delta_3\mathrm{K} \,.\, c\beta + \delta_2\mathrm{L} \,.\, b\gamma + \delta_3\mathrm{L} \,.\, \beta\gamma \qquad \frac{\partial \gamma'}{\partial \gamma} = \mathrm{L},$$

whence the condition

$$\begin{vmatrix} \mathrm{H} & \delta_3\mathrm{G}-\delta_2\mathrm{H} \\ \mathrm{L} & \delta_3\mathrm{K}-\delta_2\mathrm{L} \end{vmatrix} (b\gamma-c\beta) = 0,$$

or

$$\frac{\delta_3\mathrm{G}-\delta_2\mathrm{H}}{\mathrm{H}} = \frac{\delta_3\mathrm{K}-\delta_2\mathrm{L}}{\mathrm{L}} = \mathfrak{P}, \text{ say.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Also, this result must remain valid if we pass the emergent beam through any further optical system. This is a step that must frequently be taken, and it will be convenient to write down generally the formulæ to which it gives rise.

If we have

$$\begin{Bmatrix} g+\delta g, & h+\delta h \\ k+\delta k, & l+\delta l \end{Bmatrix} \begin{Bmatrix} g'+\delta g', & h'+\delta h' \\ k'+\delta k', & l'+\delta l' \end{Bmatrix} = \begin{Bmatrix} \mathrm{G}+\delta\mathrm{G}, & \mathrm{H}+\delta\mathrm{H} \\ \mathrm{K}+\delta\mathrm{K}, & \mathrm{L}+\delta\mathrm{L} \end{Bmatrix},$$

and if

$$\begin{aligned} \delta g &= \tfrac{1}{2}\{\delta_1 g\,(b^2+c^2)+2\delta_2 g\,(b\beta+c\gamma)+\delta_3 g\,(\beta^2+\gamma^2)\}, \ \ldots, \\ \delta g' &= \tfrac{1}{2}\{\delta_1 g'\,(b'^2+c'^2)+\ \ldots \qquad\qquad\qquad\qquad\qquad\qquad \}, \\ &= \tfrac{1}{2}\{\delta_1 g\,[(gb+h\beta)^2+(gc+h\gamma)^2]+\ \ldots \qquad\qquad\quad \}, \ \ldots, \end{aligned}$$

and, further,

$$\delta\mathrm{G} = \tfrac{1}{2}\{\delta_1\mathrm{G}\,(b^2+c^2)+2\delta_2\mathrm{G}\,(b\beta+c\gamma)+\delta_3\mathrm{G}\,(\beta^2+\gamma^2)\}, \ \ldots,$$

then the following formulæ result:—

$$\begin{aligned} \delta_1\mathrm{G} &= g'\delta_1 g+h'\delta_1 k+g\,\{g^2\delta_1 g'+2gk\delta_2 g'+k^2\delta_3 g'\}+k\,\{g^2\delta_1 h'+2gk\delta_2 h'+k^2\delta_3 h'\}, \\ \delta_1\mathrm{H} &= g'\delta_1 h+h'\delta_1 l+h\,\{\qquad \textit{ibid.} \qquad\}+l\,\{\qquad \textit{ibid.} \qquad\}, \\ \delta_1\mathrm{K} &= k'\delta_1 g+l'\,\delta_1 k+g\,\{g^2\delta_1 k'+2gk\delta_2 k'+k^2\delta_3 k'\}+k\,\{g^2\delta_1\,l'+2gk\delta_2 l'+k^2\delta_3 l'\}, \\ \delta_1\mathrm{L} &= k'\delta_1 h+l'\,\delta_1 l+h\,\{\qquad \textit{ibid.} \qquad\}+l\,\{\qquad \textit{ibid.} \qquad\}, \end{aligned}$$

$$\begin{aligned} \delta_2\mathrm{G} &= g'\delta_2 g+h'\delta_2 k+g\,\{gh\delta_1 g'+(gl+hk)\,\delta_2 g'+kl\delta_3 g'\}+k\,\{gh\delta_1 h'+(gl+hk)\,\delta_2 h'+kl\delta_3 h'\}, \\ \delta_2\mathrm{H} &= g'\delta_2 h+h'\delta_2 l+h\,\{\qquad \textit{ibid.} \qquad\}+l\,\{\qquad \textit{ibid.} \qquad\}, \\ \delta_2\mathrm{K} &= k'\delta_2 g+l'\,\delta_2 k+g\,\{gh\delta_1 k'+(gl+hk)\,\delta_2 k'+kl\delta_3 k'\}+k\,\{gh\delta_1 l'+(gl+hk)\,\delta_2 l'+kl\delta_3 l'\}, \\ \delta_2\mathrm{L} &= k'\delta_2 h+l'\,\delta_2 l+h\,\{\qquad \textit{ibid.} \qquad\}+l\,\{\qquad \textit{ibid.} \qquad\}, \end{aligned}$$

$$\begin{aligned} \delta_3\mathrm{G} &= g'\delta_3 g+h'\delta_3 k+g\,\{h^2\delta_1 g'+2hl\delta_2 g'+l^2\delta_3 g'\}+k\,\{h^2\delta_1 h'+2hl\delta_2 h'+l^2\delta_3 h'\}, \\ \delta_3\mathrm{H} &= g'\delta_3 h+h'\delta_3 l+h\,\{\qquad \textit{ibid.} \qquad\}+l\,\{\qquad \textit{ibid.} \qquad\}, \\ \delta_3\mathrm{K} &= k'\delta_3 g+l'\,\delta_3 k+g\,\{h^2\delta_1 k'+2hl\delta_2 k'+l^2\delta_3 k'\}+k\,\{h^2\delta_1 l'+2hl\delta_2 l'+l^2\delta_3 l'\}, \\ \delta_3\mathrm{L} &= k'\delta_3 h+l'\,\delta_3 l+h\,\{\qquad \textit{ibid.} \qquad\}+l\,\{\qquad \textit{ibid.} \qquad\}. \end{aligned}$$

These formulæ with

$$\begin{aligned} \mathrm{G} &= gg'+kh', & \mathrm{H} &= hg'+lh', \\ \mathrm{K} &= gk'+kl', & \mathrm{L} &= hk'+ll', \end{aligned}$$

are of fundamental importance and cover all cases; they will be quoted as

. . . . (17)

Apply them to the equation (16); we have

$$\delta_3 \mathrm{G} - \delta_2 \mathrm{H} = g'(\delta_3 g - \delta_2 h) + h'(\delta_3 k - \delta_2 l) + hn(\delta_2 g' - \delta_1 h') + ln(\delta_3 g' - \delta_2 h'),$$

$$\delta_3 \mathrm{K} - \delta_2 \mathrm{L} = k'(\delta_3 g - \delta_2 h) + l'(\delta_3 k - \delta_2 l) + hn(\delta_2 k' - \delta_1 l') + ln(\delta_3 k' - \delta_2 l'),$$

where

$$n = gl - hk.$$

If we write in this

$$\frac{\delta_3 g - \delta_2 h}{h} = \frac{\delta_3 k - \delta_2 l}{l} = \mathfrak{p}, \qquad \frac{\delta_3 g' - \delta_2 h'}{h'} = \frac{\delta_3 k' - \delta_2 l'}{l'} = \mathfrak{p}',$$

we have

$$\delta_3 \mathrm{G} - \delta_2 \mathrm{H} = \mathfrak{p}(hg' + lh') + n\{h(\delta_2 g' - \delta_1 h') + \mathfrak{p}' lh'\},$$

$$= (\mathfrak{p} + n\mathfrak{p}')\mathrm{H} + nh\{(\delta_2 g' - \delta_1 h') - \mathfrak{p}' g'\},$$

$$\delta_3 \mathrm{K} - \delta_2 \mathrm{L} = (\mathfrak{p} + n\mathfrak{p}')\mathrm{L} + nh\{(\delta_2 k' - \delta_1 h') - \mathfrak{p}' k'\}.$$

In the same manner we find

$$\delta_2 \mathrm{G} - \delta_1 \mathrm{H} = (\mathfrak{p} + n\mathfrak{p}')\mathrm{G} + nk\{(\delta_3 g' - \delta_2 h') - \mathfrak{p}' h'\},$$

$$\delta_2 \mathrm{K} - \delta_1 \mathrm{L} = (\mathfrak{p} + n\mathfrak{p}')\mathrm{K} + nk\{(\delta_3 k' - \delta_2 l') - \mathfrak{p}' l'\}.$$

Compare these with (16) and remember that the two systems $(gh \ldots)$, $(g'h' \ldots)$ are arbitrary and independent of one another. Then we see that if for these systems

$$\frac{\delta_2 g - \delta_1 h}{g} = \frac{\delta_3 g - \delta_2 h}{h} = \frac{\delta_2 k - \delta_1 l}{k} = \frac{\delta_3 k - \delta_2 l}{l} = \mathfrak{p},$$

$$\frac{\delta_2 g' - \delta_1 h'}{g'} = \ \ldots \ = \ \ldots \ = \ \ldots \ = \mathfrak{p}',$$

then

$$\frac{\delta_2 \mathrm{G} - \delta_1 \mathrm{H}}{\mathrm{G}} = \frac{\delta_3 \mathrm{G} - \delta_2 \mathrm{H}}{\mathrm{H}} = \frac{\delta_2 \mathrm{K} - \delta_1 \mathrm{L}}{\mathrm{K}} = \frac{\delta_3 \mathrm{K} - \delta_2 \mathrm{L}}{\mathrm{L}} = \mathfrak{P} \quad . \quad . \quad . \quad . \qquad (18)$$

where

$$\mathfrak{P} = \mathfrak{p} + n\mathfrak{p}'.$$

Now if we examine the case of the single surface, for which

$$\delta_1 g = (1-n)\mathrm{B}^2, \quad \delta_2 g = 0, \quad \delta_3 g = 0, \qquad \delta_1 h = (1-n)\mathrm{B}, \quad \delta_2 h = 0, \quad \delta_3 h = 0,$$

$$\delta_1 k = (1-n)(-\epsilon + n - n^2)\mathrm{B}^3, \quad \delta_2 k = -n^2(1-n)\mathrm{B}^2, \quad \delta_3 k = -n(1-n^2)\mathrm{B},$$

$$\delta_1 l = (1-n)(-1 + n - n^2)\mathrm{B}^2, \quad \delta_2 l = -n^2(1-n)\mathrm{B}, \quad \delta_3 l = -n(1-n^2),$$

and

$$g = 1, \quad h = 0, \quad k = -(1-n)\mathrm{B}, \quad l = n,$$

the conditions are fulfilled and we have

$$\mathfrak{p} = -(1-n)\mathrm{B} = \mu\left(\frac{1}{\mu'} - \frac{1}{\mu}\right)\mathrm{B};$$

for two surfaces B_0, B_2 with refractive indices, μ_{-1}, μ_1, μ_3, as in SEIDEL's convenient notation

$$\mathfrak{p}+n\mathfrak{p}' = \mu_{-1}\left[\left(\frac{1}{\mu_1}-\frac{1}{\mu_{-1}}\right)B_0+\left(\frac{1}{\mu_3}-\frac{1}{\mu_1}\right)B_2\right];$$

and for any sequence of surfaces whatever

$$\mathfrak{P} = \mu_{-1}\Sigma\left(\frac{1}{\mu_{2r+1}}-\frac{1}{\mu_{2r-1}}\right)B_{2r}. \qquad (19)$$

This will be recognized as the expression which figures in the well-known "Petzval condition for flatness of field." It was given by PETZVAL without proof in 1843, and it is a comment upon the difficulty which the geometrical method finds in removing a condition that may have been tacitly introduced that its proper position has so far remained obscure. Its general geometrical implications will be considered later.

Besides the condition that the rays of any thin bundle should always be normal to a surface there is another general property to which they are subject in all systems. For normal systems in which we have stigmatic correspondence this is usually called the Helmholtz magnification theorem connecting the linear and angular magnifications. For aberrational systems it would at first appear as if both linear and angular magnifications lost their meaning, but I have succeeded in generalizing the theorem in the paper already referred to.[*] In the first place focal lines in the original system are shown to correspond one to one and not pair to pair with focal lines in the emergent system; and rays which issue from any point in a focal line in a plane perpendicular to that line lie in a plane in the emergent system perpendicular to the conjugate focal line which they meet in a point. Such planes are called planes of correspondence. The behaviour of any ray may be traced through the behaviour of its projections upon the planes of correspondence. The separation of two parallel focal lines compared with the separation of their two conjugates preserves the idea of linear magnification and the angles in the planes of correspondence that of angular magnification. Then if a is the separation of two focal lines which lie parallel to one another in a plane perpendicular to an original ray at any point and a' that of their two conjugates, and if α is the angle between two rays issuing from one of these lines in a plane of correspondence perpendicular to both and α' the angle between the same rays on emergence, it is proved that

$$\mu a\alpha = \mu' a'\alpha'.$$

This is completely general. Now return to the case of surfaces centred upon an axis. It is clear that for any point off the axis, say the point $(0, b, 0)$, one of the planes of correspondence, is the meridianal plane passing through the axis and the point itself.

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[*] 'Proc. L. M. S.,' vol. 29, p. 70.

Now consider the substitution

$$b' = (\mathrm{G}+\delta\mathrm{G})\,b+(\mathrm{H}+\delta\mathrm{H})\,\beta,$$
$$\beta' = (\mathrm{K}+\delta\mathrm{K})\,b+(\mathrm{L}+\delta\mathrm{L})\,\beta.$$

Then if we shift the origin in the emergent system to d' the first will read

$$b' = \{(\mathrm{G}+\delta\mathrm{G})+d'(\mathrm{K}+\delta\mathrm{K})\}\,b+\{(\mathrm{H}+\delta\mathrm{H})+d'(\mathrm{L}+\delta\mathrm{L})\}\,\beta.$$

Choose d' so as to make the coefficient of β zero; then

$$b' = \{(\mathrm{G}+\delta\mathrm{G})-(\mathrm{K}+\delta\mathrm{K})(\mathrm{H}+\delta\mathrm{H})/(\mathrm{L}+\delta\mathrm{L})\}\,b,$$

and the coefficient

$$\mathrm{G}+\delta\mathrm{G}-(\mathrm{K}+\delta\mathrm{K})(\mathrm{H}+\delta\mathrm{H})/(\mathrm{L}+\delta\mathrm{L})$$

is the linear magnification for narrow pencils emerging in the general direction (β) from the point $(0, b, 0)$ in the meridianal plane. Again from

$$\beta'_1-\beta'_2 = (\mathrm{L}+\delta\mathrm{L})(\beta_1-\beta_2),$$

the angular magnification for the same is $\mathrm{L}+\delta\mathrm{L}$.

Hence $(\mathrm{G}+\delta\mathrm{G})(\mathrm{L}+\delta\mathrm{L})-(\mathrm{H}+\delta\mathrm{H})(\mathrm{K}+\delta\mathrm{K})$ is equal to the ratio of the effective refractive indices. But we have seen on p. 157 that the change of ray effected by an aberrational system is equivalent to the use of refractive indices $\mu(1-\frac{1}{2}\beta^2)$, $\mu'(1-\frac{1}{2}\beta'^2)$, ... throughout. So that the expression above is equal to

$$\frac{\mu}{\mu'}(1-\tfrac{1}{2}\beta^2+\tfrac{1}{2}\beta'^2),$$

where β' may be taken as the final value of β after any number of transformations; or equal to

$$\mathrm{N}\,\{1+\tfrac{1}{2}(\mathrm{K}b+\mathrm{L}\beta)^2-\tfrac{1}{2}\beta^2\}.$$

Identifying term by term with the expression above we have the relations

$$\begin{aligned}\delta_1\mathrm{N} &= \mathrm{G}\delta_1\mathrm{L}+\mathrm{L}\delta_1\mathrm{G}-\mathrm{H}\delta_1\mathrm{K}-\mathrm{K}\delta_1\mathrm{H} = \mathrm{K}^2\mathrm{N},\\ \delta_2\mathrm{N} &= \mathrm{G}\delta_2\mathrm{L}+\mathrm{L}\delta_2\mathrm{G}-\mathrm{H}\delta_2\mathrm{K}-\mathrm{K}\delta_2\mathrm{H} = \mathrm{KLN}, \qquad . \;\; . \;\; . \;\; . \;\; . \quad (20)\\ \delta_3\mathrm{N} &= \mathrm{G}\delta_3\mathrm{L}+\mathrm{L}\delta_3\mathrm{G}-\mathrm{H}\delta_3\mathrm{K}-\mathrm{K}\delta_3\mathrm{L} = (\mathrm{L}^2-1)\,\mathrm{N}.\end{aligned}$$

The relations (20) may also be proved from a sequence formula out of the equation (17); thus

$$\begin{aligned}\frac{\delta_1\mathrm{N}}{\mathrm{N}} &= \frac{\delta_1 n}{n}+\left\{g^2\frac{\delta_1 n'}{n'}+2gk\frac{\delta_2 n'}{n'}+k^2\frac{\delta_3 n'}{n'}\right\},\\ \frac{\delta_2\mathrm{N}}{\mathrm{N}} &= \frac{\delta_2 n}{n}+\left\{gh\frac{\delta_1 n'}{n'}+(gl+hk)\frac{\delta_2 n'}{n'}+kl\frac{\delta_3 n'}{n'}\right\}, \qquad . \;\; . \;\; . \;\; . \;\; . \quad (21)\\ \frac{\delta_3\mathrm{N}}{\mathrm{N}} &= \frac{\delta_3 n}{n}+\left\{h^2\frac{\delta_1 n'}{n'}+2hl\frac{\delta_2 n'}{n'}+l^2\frac{\delta_3 n'}{n'}\right\};\end{aligned}$$

in fact, it was by such a method that I found them; but their real significance is contained in the proof given above.

We have thus found among the twelve aberrational coefficients six relations which may be expressed in terms only of the focal length and other cardinal elements of the normal system, or seven, if we include the Petzval expression as of that class.

Let us consider next what geometrical description can be given of the occurrence or absence of the twelve coefficients. It must be remembered that for different choice of origins the coefficients do not preserve an identity. Thus if we shift O, the original origin to the point $(-d, o, o)$, the new set—$\delta_1 G, \ldots$—is given in terms of the old set—$\delta_1 g', \ldots$—by writing in the equations of p. 160.

$$\delta_1 g = \delta_1 h = \ldots = 0$$

and

$$g = 1, \qquad h = d, \qquad k = 0, \qquad l = 1;$$

and if, on the other hand, we shift the emergent origin to d', we have $\delta_1 G, \ldots$ connected with $\delta_1 g, \ldots$, which now figures as the old set, as if in the same equations we wrote

$$\delta_1 g' = \delta_1 h' = \ldots = 0,$$

$$g' = 1, \qquad h' = d', \qquad k' = 0, \qquad l' = 1,$$

and in the event of both these changes being made a system $(g+\delta g, \ldots)$ is transformed into $(G+\delta G, \ldots)$, where

$$\begin{aligned} G &= g+d'k, & H &= h+dg+d'l+dd'k, \\ K &= k, & L &= l+dk; \end{aligned}$$

$$\begin{aligned}
\delta_1 G &= \delta_1 g + d'\delta_1 k, \\
\delta_1 H &= \delta_1 h + d\delta_1 g + d'(\delta_1 l + d\delta_1 k), \\
\delta_1 K &= \delta_1 k, \\
\delta_1 L &= \delta_1 l + d\delta_1 k, \\[1ex]
\delta_2 G &= \delta_2 g + d\delta_1 g + d'\delta_2 K, \\
\delta_2 H &= \delta_2 h + d(\delta_1 h + \delta_2 g) + d^2\delta_1 g + d'\delta_2 L, \\
\delta_2 K &= \delta_2 k + d\delta_1 k, \\
\delta_2 L &= \delta_2 l + d(\delta_1 l + \delta_2 k) + d^2\delta_1 k, \\[1ex]
\delta_3 G &= \delta_3 g + 2d\delta_2 g + d^2\delta_1 g + d'\delta_3 K, \\
\delta_3 H &= \delta_3 h + d(2\delta_2 h + \delta_3 g) + d^2(\delta_1 h + 2\delta_2 g) + d^3\delta_1 g + d'\delta_3 L, \\
\delta_3 K &= \delta_3 k + 2d\delta_2 k + d^2\delta_1 k, \\
\delta_3 L &= \delta_3 l + d(2\delta_2 l + \delta_3 k) + d^2(\delta_1 l + 2\delta_2 k) + d^3\delta_1 k.
\end{aligned} \quad . \quad . \quad . \quad (22)$$

But let us defer discussion of these and examine two particular cases of special importance, namely, let us assign meanings to $\delta_1 G, \ldots$: (1) where the emergent origin is the principal focus, so that $G = 0$, and therefore $\delta_2 G = \delta_1 H$, and (2) where the original and emergent origins are conjugate, so that $H = 0$, and therefore $\delta_3 G = \delta_2 H$. In the former the original origin may be anywhere, but may conveniently be supposed to lie at the tangent plane to the first refracting surface. The original rays are in constant direction, so that we may take

$$\beta = const., \qquad \gamma = 0, \quad \text{and, say,} \quad b = d\cos\phi, \qquad c = d\sin\phi.$$

Then if we receive the emergent ray on the plane parallel to $O'y'z'$ which passes through a point slightly removed from O', say at

$$x' = \delta f',$$

and it cuts this plane at $y' = b' + \delta b'$, $z' = c' + \delta c'$, we have

$$\begin{aligned} b' + \delta b' &= [* + K\delta f']\, b + [H + L\delta f']\, \beta \\ &\quad + \tfrac{1}{2} d\cos\phi\, [d^2\delta_1 G + 2d\beta\cos\phi\,\delta_2 G + \beta^2\delta_3 G] + \tfrac{1}{2}\beta\, [d^2\delta_1 H + 2d\beta\cos\phi\,\delta_2 H + \beta^2\delta_3 H], \\ c' + \delta c' &= [* + K\delta f']\, c \\ &\quad + \tfrac{1}{2} d\sin\phi\, [d^2\delta_1 G + 2d\beta\cos\phi\,\delta_2 G + \beta^2\delta_3 G]. \qquad (23) \end{aligned}$$

Let us take

$$b' = (H + L\delta f')\,\beta, \qquad c' = 0,$$

so that

$$\begin{aligned} \delta b' &= \tfrac{1}{2}\beta\, [d^2(\delta_1 H + \delta_2 G) + \beta^2\delta_3 H] \\ &\quad + \cos\phi\, d\, [K\delta f' + \tfrac{1}{2} d^2\delta_1 G + \tfrac{1}{2}\beta^2(\delta_3 G + 2\delta_2 H)] \\ &\quad + \cos 2\phi\, d^2\, [\tfrac{1}{2}\beta\delta_2 G], \\ \delta c' &= \sin\phi\, d\, [K\delta f' + \tfrac{1}{2} d^2\delta_1 G + \tfrac{1}{2}\beta^2\delta_3 G] \\ &\quad + \sin 2\phi\, d^2\, [\tfrac{1}{2}\beta\delta_2 G]. \qquad (24) \end{aligned}$$

These express the amounts by which the aberrations disturb the ray from its normal focus. Consider the lines in turn and examine their significance when the original ray traces out a circle $d = const.$

The terms

$$\tfrac{1}{2}\beta\, [d^2(\delta_1 H + \delta_2 G) + \beta^2\delta_3 H] \quad \text{or} \quad \tfrac{1}{2}\beta\, [2d^2\delta_2 G + \beta^2\delta_3 H]$$

give a fixed point. It may be considered as adding to the focal length

$$H + L\delta f'$$

the terms

$$d^2\delta_2 G + \tfrac{1}{2}\beta^2\delta_3 H,$$

of which the former may be called the *comatic increase of focal length* and the latter the *distortional increase of focal length*, since these are evidently their characters.

The two terms

$$\cos\phi d\,[\mathrm{K}\delta f'+\tfrac{1}{2}d^2\delta_1\mathrm{G}+\tfrac{1}{2}\beta^2(\delta_3\mathrm{G}+2\delta_2\mathrm{H})],\qquad \sin\phi d\,[\mathrm{K}\delta f'+\tfrac{1}{2}d^2\delta_1\mathrm{G}+\tfrac{1}{2}\beta^2\delta_3\mathrm{G}]$$

represent an ellipse which may be varied by choosing $\delta f'$ at different values. If we take

$$\mathrm{K}\delta f'+\tfrac{1}{2}d^2\delta_1\mathrm{G}+\tfrac{1}{2}\beta^2(\delta_3\mathrm{G}+2\delta_2\mathrm{H}) = 0$$

the ellipse becomes the primary focal line; if we take

$$\mathrm{K}\delta f'+\tfrac{1}{2}d^2\delta_1\mathrm{G}+\tfrac{1}{2}\beta^2\delta_3\mathrm{G} = 0$$

it becomes the secondary focal line, in advance of the primary line by the amount $\beta^2\delta_2\mathrm{H}/\mathrm{K}$. Generally I shall call it the *focal ellipse* and, as a rule, shall take

$$\mathrm{K}\delta f'+\tfrac{1}{2}d^2\delta_1\mathrm{G}+\tfrac{1}{2}\beta^2(\delta_3\mathrm{G}+\delta_2\mathrm{H}) = 0,$$

which gives the *focal circle*

$$d\cos\phi\,[\tfrac{1}{2}\beta^2\delta_2\mathrm{H}],\qquad -d\sin\phi\,[\tfrac{1}{2}\beta^2\delta_2\mathrm{H}]$$

situated midway between the focal lines. This circle is described backwards as the original circle $d = const.$ is described forwards.

Finally the terms

$$d^2\cos 2\phi\,[\tfrac{1}{2}\beta\delta_2\mathrm{G}],\qquad d^2\sin 2\phi\,[\tfrac{1}{2}\beta\delta_2\mathrm{G}]$$

give another circle which I shall call the *comatic circle*; its radius $= \frac{1}{2}\beta\times$ *comatic increase of focal length*, so that they vanish together. As the original circle $d = const.$ is described once, forward, it is described twice, forward, each point upon it corresponding to two diametrically opposite points of the original circle.

Consider the focal circle and the comatic circle simultaneously; we may take

$$l\cos\phi+m\cos 2\phi,\qquad -l\sin\phi+m\sin 2\phi,$$

where

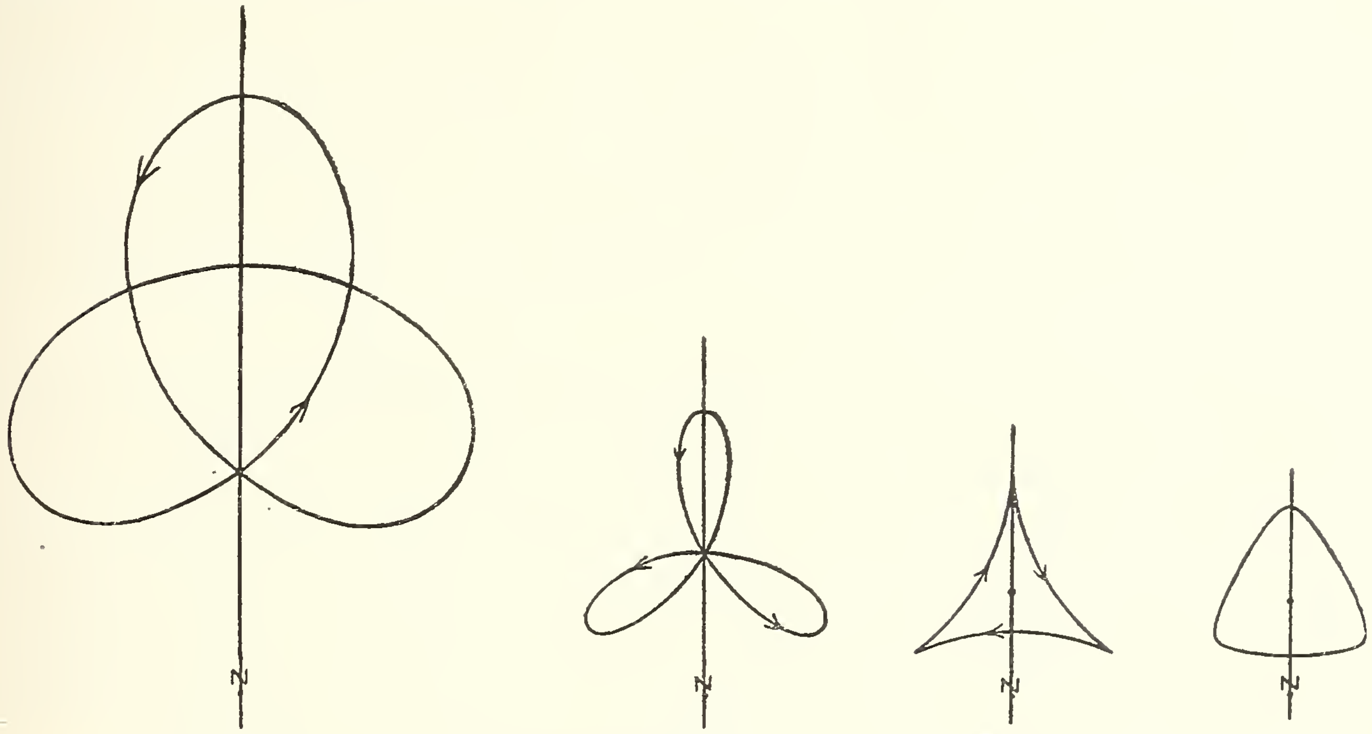
$$l = \tfrac{1}{2}d\beta^2\delta_2\mathrm{H},\qquad m = \tfrac{1}{2}d^2\beta\delta_2\mathrm{G};$$

this is a trochoidal curve, which becomes a three cusped hypocycloid for $l = 2m$ and goes through the types illustrated below for different values of β/d. For a given value of β all these types are present for different values of d, and are described about different centres owing to the comatic increase of focal length. These facts are well known in particular instances, and even experimentally, but as far as I can find they have not hitherto been expressly demonstrated generally.

The plane at which these phenomena are found is taken at $x' = \delta f'$, where

$$\delta f'/f' = -\mathrm{K}\delta f' = \tfrac{1}{2}d^2\delta_1\mathrm{G}+\tfrac{1}{2}\beta^2(\delta_3\mathrm{G}+\delta_2\mathrm{H}).$$

The part depending upon d^2 represents the spherical aberration; the part depending upon β^2, if it were present alone, would indicate that the images, if we can so call them, were found upon a sphere of curvature $-\mathrm{K}(\delta_3\mathrm{G}+\delta_2\mathrm{H})$; the corresponding expressions for the primary focal line in place of the focal circle would be $-\mathrm{K}(\delta_3\mathrm{G}+2\delta_2\mathrm{H})$ and for the secondary focal line $-\mathrm{K}\delta_3\mathrm{G}$. These expressions are positive when the sphere is convex to the incident rays.



l = 1, m = 2 l = 1, m = 1 l = 1, m = ½ l = 1, m = ¼

Fig. 5.

The angular values of the radii of the focal circle and the comatic circle are respectively

$$\overset{(1)}{206265'' \times \tfrac{1}{2}\delta_2\mathrm{H} \,.\, d\beta^2/f'} \quad \text{and} \quad \overset{(2)}{206265'' \times \tfrac{1}{2}\delta_2\mathrm{G} \,.\, d^2\beta/f'}.$$

Thus with increasing aperture (d) the focal radius increases with the first power and the comatic radius with the square, while with increasing breadth of field (β) the focal radius increases with the square and the comatic radius with the first power. To fix ideas we may consider the case of the parabolic reflector; here, as shown on p. 156,

$$\delta_1\mathrm{G} = 0, \quad \delta_2\mathrm{G} = +1/2f', \quad \delta_3\mathrm{G} = 0, \quad \delta_1\mathrm{H} = +1/2f', \quad \delta_2\mathrm{H} = -1, \quad \delta_3\mathrm{H} = 0.$$

Hence spherical aberration and distortion are absent. $\delta_3\mathrm{G} = 0$ implies that the secondary focal line lies in the normal focal plane, while the focal circle lies upon a surface of curvature $1/2f'$; and for the effects of astigmatism and coma we have the following table for different apertures and fields* :—

---

* *Cf.* POOR, 'Astrophysical Journal,' VII. (1898), p. 121.

	$d = f/30$.				$d = f/20$.				$d = f/10$.			
β.	15′.	30′.	45′.	60′.	15′.	30′.	45′.	60′.	15′.	30′.	45′.	60′.
Focal radius .	0″·06	0″·26	0″·59	1″·05	0″·10	0″·40	0″·89	1″·57	0″·19	0″·79	1″·77	3″·14
Comatic radius	0″·25	0″·50	0″·75	1″·00	0″·56	1″·13	1″·69	2″·25	2″·25	4″·50	6″·75	9″·00
Comatic magnification .	1·0005	1·0005	1·0005	1·0005	1·0012	1·0012	1·0012	1·0012	1·0050	1·0050	1·0050	1·0050
Comatic displacement .	0″·50	1″·00	1″·50	2″·00	1″·13	2″·25	3″·38	4″·50	4″·50	9″·00	13″·50	18″·00

The last two lines measure the same thing, the fourth representing $\frac{1}{2}(\delta_1\mathrm{H}+\delta_2\mathrm{G})\,d^2\beta$ in angle, and the third $1+\frac{1}{2}(\delta_1\mathrm{H}+\delta_2\mathrm{G})\,d^2\beta/\beta f'$, and owing to the relation $\delta_2\mathrm{G} = \delta_1\mathrm{H}$ the second line contains quantities one-half that of the fourth. Since these aberrations stand uncompensated, it is clear that the statement often made that the reflector has a very limited field is fully borne out, especially when, as is often the case, the ratio of semi-aperture to focal length is so great as 1/10. In this case, at only 30′ from the centre of the field, the light which comes from the outermost zone of the mirror would be spread around a little ring which was nearly a circle of 10″ diameter, having its centre 9″ from the correct normal position for the image.

Turn now to the other case which was proposed for discussion on p. 165, namely, where the original O, O′ are conjugate foci, so that $\mathrm{H} = 0$ and $\delta_3\mathrm{G} = \delta_2\mathrm{H}$. We have to study the delineation of any point in Oyz upon the plane $O'y'z'$ or planes close to it. We may take the point $b = const.$, $c = 0$, and then make β, γ vary, so that, *e.g.*, for $\beta^2+\gamma^2 = const.$ the ray through the point $(b, 0)$ describes a cone with axis parallel to Ox. Let us put

$$\beta = \theta\cos\psi, \qquad \gamma = \theta\sin\psi,$$

and we have, at the plane $x' = \delta f'$,

$$\begin{aligned} b'+\delta b' &= [\mathrm{G}+\mathrm{K}\delta f']\,b+[\;*\;+\mathrm{L}\delta f']\,\beta \\ &\quad +\tfrac{1}{2}b\,[b^2\delta_1\mathrm{G}+2b\theta\cos\psi\,\delta_2\mathrm{G}+\theta^2\delta_3\mathrm{G}]+\tfrac{1}{2}\theta\cos\psi\,[b^2\delta_1\mathrm{H}+2b\theta\cos\psi\,\delta_2\mathrm{H}+\theta^2\delta_3\mathrm{H}], \\ c'+\delta c' &= \qquad [\;*\;+\mathrm{L}\delta f']\,\gamma \\ &\quad + \qquad * \qquad +\tfrac{1}{2}\theta\sin\psi\,[b^2\delta_1\mathrm{H}+2b\theta\cos\psi\,\delta_2\mathrm{H}+\theta^2\delta_3\mathrm{H}]. \end{aligned} \tag{25}$$

Compare these with the expressions (23) of p. 165, and we see that they run upon exactly the same model, but with a change of *rôle* in which we replace

$$\begin{array}{llllllllll} & \delta_1\mathrm{G}, & \delta_2\mathrm{G}, & \delta_3\mathrm{G}, & \delta_1\mathrm{H}, & \delta_2\mathrm{H}, & \delta_3\mathrm{H}, & d, & \phi, & \beta, \\ \text{by} & & & & & & & & & \\ & \delta_3\mathrm{H}, & \delta_2\mathrm{H}, & \delta_1\mathrm{H}, & \delta_3\mathrm{G}, & \delta_2\mathrm{G}, & \delta_1\mathrm{G}, & \theta, & \psi, & b. \end{array}$$

Hence it is unnecessary to work out the expressions for focal lines and the rest afresh since they can all be inferred without other change from what has already been given.

SEIDEL'S five conditions are usually taken as the standard form for the conditions of existence of a correct normal image. We may follow these and express them in terms of the aberrational coefficients, proceeding *pari passu* with the two cases :—

	O′ principal focus.		O, O′ conjugate foci.
(1) Absence of spherical aberration .	$\delta_1 G = 0$	or	$\delta_3 H = 0$
(2) Absence of coma	$\delta_2 G = \delta_1 H = 0$	,,	$\delta_2 H = \delta_3 G = 0$
(3) Absence of astigmatism	$\delta_2 H = 0$	,,	$\delta_2 G = 0$
(4) Absence of distortion	$\delta_3 H = 0$	,,	$\delta_1 G = 0$
(5) A flat field, when (2) and (3) are satisfied	$\delta_3 G = 0$	,,	$\delta_1 H = 0$. (26)

It is of interest to consider the position occupied by the well-known conditions usually quoted as "PETZVAL'S condition for flatness of field," and "ABBE'S sine-condition."

PETZVAL'S condition, or $\mathfrak{P} = 0$, we see from (18) to imply

$$\delta_2 G - \delta_1 H = 0, \quad \delta_3 G - \delta_2 H = 0, \quad \delta_2 K - \delta_1 L = 0, \quad \delta_3 K - \delta_2 L = 0,$$

or, what is the same thing, simply

$$\delta_2 G = \delta_1 H \qquad \text{and} \qquad \delta_3 G = \delta_2 H$$

at all distances along $O'x'$.

If we confine attention to the two cases above, we see that in the first, where the emergent origin is the principal focus, $G = 0$, and therefore $\delta_2 G = \delta_1 H$ without the intervention of $\mathfrak{P} = 0$, and similarly in the second, when the emergent and original origins are conjugate normal foci, $H = 0$, and therefore $\delta_3 G = \delta_2 H$; the interpretation of these is the same, namely, that the comatic displacement is twice the comatic radius—"comatic displacement" being used to denote the expression $\frac{1}{2} d^2 \beta (\delta_1 H + \delta_2 G)$ as on p. 168—a well-known fact, usually put in the form that in the absence of astigmatism the successive comatic circles have two common tangents inclined to one another at 60 degrees. The other term remains as the true content of PETZVAL'S condition. Its interpretation may be put in different forms; as, apart from spherical aberration, at the normal focal plane of any image, the longitudinal axis of the focal ellipse is three times its transverse axis, which is an interpretation of the expressions of p. 166, for $\delta f' = 0$,

$$\delta b' = \ldots \cos \phi d \left[\tfrac{1}{2} d^2 \delta_1 G + \tfrac{1}{2} \beta^2 (\delta_3 G + 2\delta_2 H)\right], \qquad \delta c' = \ldots \sin \phi d \left[\tfrac{1}{2} d^2 \delta_1 G + \tfrac{1}{2} \beta^2 \delta_3 G\right],$$

of the first case, or the corresponding expression of the second case; or again, the distance of the focal circle beyond the normal focal plane is $2f'/d \times$ the radius of the focal circle. This shows the connection with flatness of field, but to restrict the reference to curvature of the field is a misconception of the significance of PETZVAL'S condition. If PETZVAL'S condition holds, the result stated above is true for all normal image planes.

ABBE'S sine-condition for absence of coma states that if the magnification produced by rays passing between two conjugate foci through all zones is the same, the relation must hold

$$\sin\theta'/\sin\theta = const.,$$

where θ, θ' are the original and emergent inclinations of the ray to the axis. In our notation this would run

$$(\beta'-\tfrac{1}{2}\beta'^3)/(\beta-\tfrac{1}{2}\beta^3) = const.;$$

or, if

$$\beta' = (\mathrm{L}+\delta\mathrm{L})\,\beta$$

it gives

$$\delta\mathrm{L}/\mathrm{L} = \tfrac{1}{2}(\mathrm{L}^2-1)\,\beta^2;$$

now we have seen on p. 163 that the linear magnification is

$$(\mathrm{N}+\delta\mathrm{N})/(\mathrm{L}+\delta\mathrm{L})$$

and the condition this should be constant is

$$\delta\mathrm{L}/\mathrm{L} = \delta\mathrm{N}/\mathrm{N},$$

and this, in accordance with p. 163, gives the conditions

$$\delta_1\mathrm{L}/\mathrm{L} = \mathrm{K}^2, \quad \delta_2\mathrm{L}/\mathrm{L} = \mathrm{KL}, \quad \delta_3\mathrm{L}/\mathrm{L} = \mathrm{L}^2-1.$$

To make these agree with the sine-condition we must take $b = 0$, so as to remove $\delta_1\mathrm{L}$, $\delta_2\mathrm{L}$ from the reckoning. We see then that such an assumption underlies the application of the sine-condition.

I shall next show how these formulæ may be applied to the numerical calculation of lenses. For this they are particularly appropriate if the calculations are made with any ordinary type of multiplying machine and not with logarithms. To the best of my judgment they appear to require a fraction only of the work involved in the equivalent complete trigonometrical calculation and, as will be shown, they are certainly not less accurate for telescopic object glasses. They show with remarkable clearness the contribution of each surface to each fault of the image. They also supply throughout their course a number of natural checks upon the computation which are searching and usually complete.

I shall take as my example the celebrated object glass of the Fraunhofer heliometer at Königsberg. This is a small lens of aperture 6·2 inches and focal length 101 inches which was constructed by FRAUNHOFER. BESSEL, in describing the heliometer and its corrections, with his customary masterly thoroughness, calculated this lens trigonometrically.* Later it was used as an illustration by SEIDEL,† who named his second condition the Fraunhofer condition, under the misapprehension that coma was effectively corrected in it.

In 1889, Dr. A. STEINHEIL gave a particularly thorough and instructive calculation of its field, and assigned first, the modifications of its curves necessary to remove a remaining trace of spherical aberration, and next, to correct the coma.‡ Finally, FINSTERWALDER recalculated SEIDEL'S sums for it, using the first corrected curves of STEINHEIL.§ In the following pages I shall first of all show how the calculations will run with my formulæ, and shall return to compare them with STEINHEIL'S results.

The data given by BESSEL are in "lines," of which 144 = 1 Bavarian foot. To render the arithmetical work more compact I have increased the unit to 1000 lines, which brings the measures of the radii of the surfaces and the focal length of the whole to the neighbourhood of a unit.

The radii and curvatures of the surfaces, with the spaces between them, are the following:—

$$\begin{array}{lll}
\rho_0 = +\ \cdot838164, & B_0 = +1\cdot193084, & d_1 = \cdot006, \\
\rho_2 = -\ \cdot333768, & B_2 = -2\cdot996093, & d_3 = \cdot000, \\
\rho_4 = -\ \cdot340536, & B_4 = -2\cdot936547, & d_5 = \cdot004. \\
\rho_6 = -1\cdot172508, & B_6 = -\ \cdot852873, &
\end{array}$$

The semi-aperture is 0·0351.

The refractive indices he takes as

$$\begin{array}{ll}
n = \mu_{-1}/\mu_1 = \cdot653966, & 1/n = 1\cdot529130, \\
m = \mu_3/\mu_5 = \cdot610083, & 1/m = 1\cdot639121.
\end{array}$$

We first form the normal scheme for the whole combination by writing down and combining the schemes that represent each surface and each space between two surfaces. To perform the step of combination

$$\left\{\begin{matrix} g, & h \\ k, & l \end{matrix}\right\} \left\{\begin{matrix} \gamma, & \eta \\ \kappa, & \lambda \end{matrix}\right\} = \left\{\begin{matrix} \gamma g+\eta k, & \gamma h+\eta l \\ \kappa g+\lambda k, & \kappa h+\lambda l \end{matrix}\right\}$$

—as to which it must be remembered that light passes through $\{g \ldots\}$ to reach $\{\gamma \ldots\}$—we set up the number γ as multiplier upon the multiplying machine, multiply it into g and h, and place the products as above, then set up η and multiply into k and l, placing the products as shown; this gives the top line of the combination completely; then set up κ, multiply into g and h, set up λ and multiply it into k and l.

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* 'Untersuchungen,' Bd. I., p. 101.

† 'Astronomische Nachrichten,' No. 1029, p. 325.

‡ K. Bayer. Akad. d. Wiss., 'Sitzungberichte d. math.-phys. Classe,' Bd. XIX., Heft III., 1889.

§ K. Bayer. Akad. d. Wiss., 'Abhandlungen,' Bd. XVII., Abth. III.

This completes the step. The proper way to check a sequence of such combinations is to proceed first from left to right and then from right to left; the final results will confirm one another and check the whole calculation, and the individual schemes arrived at will give in succession the steps across the surface (0), across the surface (0) and the space (1), across 0, 1 and the surface 2, and so on; and in the reverse order across the surface 6, across 5 and 6, across 4, 5, and 6, and so on. All these will be required after. I shall indicate them with the signs $\overrightarrow{0}$, $\overrightarrow{01}$, ..., $\overrightarrow{6}$, $\overrightarrow{56}$, ...

For the individual surfaces the values of $k = -(1-n)\,\mathrm{B}$ are

$$k_0 = -(1-n)\,\mathrm{B}_0 = -\ \cdot412848, \qquad k_2 = -(1-1/n)\,\mathrm{B}_2 = -1\cdot585323,$$
$$k_4 = -(1-m)\,\mathrm{B}_4 = +1\cdot145010, \qquad k_6 = -(1-1/m)\,\mathrm{B}_6 = -\ \cdot545089.$$

In the following arrangement the separate schemes are written in the middle column, that corresponding to $\overrightarrow{3}$ being omitted as nugatory; the calculations forwards are written on the left and those backwards on the right. The latter begin at the bottom and proceed upwards. Every figure used is recorded.

$$\overrightarrow{0}\quad \left\{\begin{array}{rr} 1\cdot000000 & * \\ -\cdot412848 & \cdot653966 \end{array}\right\} \qquad \left\{\begin{array}{rr} 1\cdot000712 & \\ -\quad 4019 & \\ \cline{1-1} \cdot996693 & +\cdot006366 \\ -\cdot253990 & \\ -\cdot629829 & \\ \cline{1-1} -\cdot883819 & +\cdot997672 \end{array}\right\}\overrightarrow{06}$$

$$\overrightarrow{01}\left\{\begin{array}{rr} 1\cdot000000 & \\ -\quad 2477 & \\ \cline{1-1} \cdot997523 & +\cdot003924 \\ -\cdot412848 & +\cdot653966 \end{array}\right\} \qquad \overrightarrow{1}\quad \left\{\begin{array}{rr} 1\cdot000000 & \cdot006000 \\ * & 1\cdot000000 \end{array}\right\} \qquad \left\{\begin{array}{rr} & +\cdot006004 \\ & +\quad 3731 \\ \cline{2-2} +1\cdot000712 & +\cdot009735 \\ & -\cdot001524 \\ & +1\cdot527096 \\ \cline{2-2} -\cdot253990 & +1\cdot525572 \end{array}\right\}\overrightarrow{16}$$

$$\overrightarrow{02}\left\{\begin{array}{rr} \cdot997523 & +\cdot003924 \\ -1\cdot581396 & -\cdot006221 \\ -\cdot631298 & +\cdot999999 \\ \hline -2\cdot212694 & +\cdot993778 \end{array}\right\} \qquad \overrightarrow{2}\quad \left\{\begin{array}{rr} 1\cdot000000 & * \\ -1\cdot585323 & +1\cdot529130 \end{array}\right\} \qquad \left\{\begin{array}{rr} 1\cdot004580 & \\ -\quad 3868 & \\ \cline{1-1} 1\cdot000712 & +\cdot003731 \\ +1\cdot329225 & \\ -1\cdot583215 & \\ \cline{1-1} -\cdot253990 & +1\cdot527096 \end{array}\right\}\overrightarrow{26}$$

$$\overrightarrow{04}\left\{\begin{array}{rr} \cdot997523 & +\cdot003924 \\ +1\cdot142174 & +\cdot004493 \\ -1\cdot349927 & +\cdot606287 \\ \hline -\cdot207753 & +\cdot610780 \end{array}\right\} \qquad \overrightarrow{4}\quad \left\{\begin{array}{rr} 1\cdot000000 & * \\ +1\cdot145010 & +\cdot610083 \end{array}\right\} \qquad \left\{\begin{array}{rr} 1\cdot000000 & \\ +\quad 4580 & \\ \cline{1-1} 1\cdot004580 & +\cdot002440 \\ -\cdot545089 & \\ +1\cdot874314 & \\ \cline{1-1} +1\cdot329225 & +\cdot998670 \end{array}\right\}\overrightarrow{46}$$

$$\overrightarrow{05}\left\{\begin{array}{rr} \cdot 997523 & +\ \cdot 003924 \\ -\quad 831 & +\quad 2443 \\ \hline \cdot 996692 & +\ \cdot 006367 \\ -\ \cdot 207753 & +\ \cdot 610780 \end{array}\right\} \qquad \begin{array}{c}\overrightarrow{5}\\ \left\{\begin{array}{cc} 1\cdot 000000 & \cdot 004000 \\ * & 1\cdot 000000 \end{array}\right\}\end{array} \qquad \left\{\begin{array}{rr} 1\cdot 000000 & +\ \cdot 004000 \\ & +1\cdot 639121 \\ & -\quad 2180 \\ \cline{2-2} -\ \cdot 545089 & +1\cdot 636941 \end{array}\right\}\overrightarrow{56}$$

$$\overrightarrow{06}\left\{\begin{array}{rr} \cdot 996692 & +\ \cdot 006367 \\ -\ \cdot 543286 & -\ \cdot 003471 \\ -\ \cdot 340532 & +1\cdot 001142 \\ \hline -\ \cdot 883818 & +\ \cdot 997671 \end{array}\right\} \qquad \begin{array}{c}\overrightarrow{6}\\ \left\{\begin{array}{cc} 1\cdot 000000 & * \\ -\ \cdot 545089 & 1\cdot 639121 \end{array}\right\}\end{array}$$

It may be well to repeat what these schemes imply. Take the scheme $\overrightarrow{16}$. If b, β refer to any ray where it meets the tangent plane to the surface (0) after crossing that surface but before crossing the space 1, and b', β' refer to the same ray where it meets the tangent plane to the surface (6) after crossing that surface, then the scheme $\overrightarrow{16}$ states that

$$b' = +1\cdot 000712b + \cdot 009735\beta,$$
$$\beta' = -\ \cdot 253990b + 1\cdot 525572\beta,$$

and *mutatis mutandis* the same holds for c, γ, c', γ'.

We conclude, from the expressions on p. 151, that for the whole combination the cardinal features of the normal combination are given by

$$\text{HF} = -1\cdot 131455 = -\text{H'F'}, \quad 0\text{F} = -1\cdot 128820, \quad 6\text{F}' = +1\cdot 127712.$$

We next work out the schemes multiplied into each of the aberrational functions ω, as given in (11), p. 157. The schemes $\{g, h, \ldots\}$, $\{g', h', \ldots\}$ which respectively precede and follow the surface to which ω refers are read at once from the computation of the normal system just completed. As the surfaces are supposed to be spherical, we have $\epsilon = 1$. The general arrangement is as above, and the check consists in forming the combination first forwards and then backwards. Again every figure is shown, but now the decimal places may be reduced to five.

ω_0 :—

$$\left\{\begin{array}{rr} 1\cdot 00000 & +\ \cdot 83816 \\ -1\cdot 19308 & -1\cdot 00000 \end{array}\right\} \qquad \left\{\begin{array}{rr} 1\cdot 00071 & +\ \cdot 83876 \\ -\ \cdot 01161 & -\ \cdot 00973 \\ \hline +\ \cdot 98910 & +\ \cdot 82903 \\ -\ \cdot 28398 & -\quad 21288 \\ -1\cdot 82012 & -1\cdot 52556 \\ \hline -2\cdot 07410 & -1\cdot 73844 \end{array}\right\}$$

$$\left\{\begin{array}{rr} 1\cdot 00071 & +\ \cdot 83876 \\ -\ \cdot 01161 & -\ \cdot 00973 \\ \hline \cdot 98910 & +\ \cdot 82903 \\ -\ \cdot 25398 & -\ \cdot 21288 \\ -1\cdot 82012 & -1\cdot 52556 \\ \hline -2\cdot 07410 & -1\cdot 73844 \end{array}\right\} \qquad \left\{\begin{array}{rr} 1\cdot 00071 & +\ \cdot 00974 \\ -\ \cdot 25398 & +1\cdot 52556 \end{array}\right\}$$

ω_2 :—

$$\left\{\begin{array}{rr} \cdot 99752 & + \cdot 00392 \\ - \cdot 41285 & + \cdot 65397 \end{array}\right\}$$

$$\left\{\begin{array}{rr} 1\cdot 00938 & + \cdot 00397 \\ + \cdot 13944 & - \cdot 22087 \\ \hline 1\cdot 14882 & - \cdot 21690 \\ + 4\cdot 31058 & + \cdot 01694 \\ + \cdot 59546 & - \cdot 94323 \\ \hline + 4\cdot 90604 & - \cdot 92629 \end{array}\right\}$$

$$\left\{\begin{array}{rr} \cdot 99752 & + \cdot 00392 \\ + \cdot 13780 & - \cdot 21828 \\ \hline 1\cdot 13532 & - \cdot 21436 \\ + 2\cdot 98866 & + \cdot 01174 \\ + \cdot 41285 & - \cdot 65397 \\ \hline + 3\cdot 40151 & - \cdot 64223 \end{array}\right\}$$

$$\left\{\begin{array}{rr} 1\cdot 00000 & - \cdot 33377 \\ + 2\cdot 99609 & - 1\cdot 00000 \end{array}\right\}$$

$$\left\{\begin{array}{rr} 1\cdot 00458 & - \cdot 33530 \\ + 731 & - 244 \\ \hline 1\cdot 01189 & - \cdot 33774 \\ + 1\cdot 32923 & - \cdot 44365 \\ + 2\cdot 99208 & - \cdot 99866 \\ \hline + 4\cdot 32131 & - 1\cdot 44231 \end{array}\right\}$$

$$\left\{\begin{array}{rr} + 1\cdot 14052 & - \cdot 21534 \\ + \cdot 00830 & - \cdot 00157 \\ \hline 1\cdot 14882 & - \cdot 21691 \\ + 1\cdot 50909 & - \cdot 28493 \\ + 3\cdot 39694 & - \cdot 64137 \\ \hline + 4\cdot 90603 & - \cdot 92630 \end{array}\right\}$$

$$\left\{\begin{array}{rr} 1\cdot 00458 & + \cdot 00244 \\ + 1\cdot 32923 & + \cdot 99867 \end{array}\right\}$$

ω_4 :—

$$\left\{\begin{array}{rr} \cdot 99752 & + \cdot 00392 \\ - 2\cdot 21269 & + \cdot 99379 \end{array}\right\}$$

$$\left\{\begin{array}{rr} 1\cdot 00924 & + \cdot 00397 \\ + \cdot 76236 & - \cdot 34240 \\ \hline 1\cdot 77160 & - \cdot 33843 \\ + 4\cdot 25130 & + \cdot 01671 \\ + 3\cdot 21132 & - 1\cdot 44231 \\ \hline + 7\cdot 46262 & - 1\cdot 42560 \end{array}\right\}$$

$$\left\{\begin{array}{rr} + \cdot 99752 & + \cdot 00392 \\ + \cdot 75351 & - \cdot 33843 \\ \hline 1\cdot 75103 & - \cdot 33451 \\ + 2\cdot 92927 & + \cdot 01151 \\ + 2\cdot 21269 & - \cdot 99379 \\ \hline + 5\cdot 14196 & - \cdot 98228 \end{array}\right\}$$

$$\left\{\begin{array}{rr} 1\cdot 00000 & - \cdot 34054 \\ + 2\cdot 93655 & - 1\cdot 00000 \end{array}\right\}$$

$$\left\{\begin{array}{rr} 1\cdot 00000 & - \cdot 34054 \\ + \cdot 01175 & - \cdot 00400 \\ \hline 1\cdot 01175 & - \cdot 34454 \\ - \cdot 54509 & + \cdot 18562 \\ + 4\cdot 80696 & - 1\cdot 63694 \\ \hline + 4\cdot 26187 & - 1\cdot 45132 \end{array}\right\}$$

$$\left\{\begin{array}{rr} + 1\cdot 75103 & - \cdot 33451 \\ \cdot 02057 & - \cdot 00393 \\ \hline + 1\cdot 77160 & - \cdot 33844 \\ - \cdot 95447 & + \cdot 18234 \\ + 8\cdot 41708 & - 1\cdot 60793 \\ \hline + 7\cdot 46261 & - 1\cdot 42559 \end{array}\right\}$$

$$\left\{\begin{array}{rr} 1\cdot 00000 & + \cdot 00400 \\ - \cdot 54509 & + 1\cdot 63694 \end{array}\right\}$$

ω_6 :—

$$\left\{\begin{array}{rr} \cdot 99669 & +\cdot 00636 \\ -\cdot 20775 & +\cdot 61078 \end{array}\right\} \qquad \left\{\begin{array}{rr} +\mathit{\cdot 99669} & +\mathit{\cdot 00636} \\ +\mathit{\cdot 24359} & -\mathit{\cdot 71615} \\ \hline +1\cdot 24028 & -\cdot 70979 \\ +\mathit{\cdot 85005} & +\mathit{\cdot 00542} \\ +\mathit{\cdot 20775} & -\mathit{\cdot 61078} \\ \hline +1\cdot 05780 & -\cdot 60536 \end{array}\right\}$$

$$\left\{\begin{array}{rr} +\mathit{\cdot 99669} & +\mathit{\cdot 00636} \\ +\mathit{\cdot 24359} & -\mathit{\cdot 71615} \\ \hline 1\cdot 24028 & -\cdot 70979 \\ +\mathit{\cdot 85005} & +\mathit{\cdot 00542} \\ +\mathit{\cdot 20775} & -\mathit{\cdot 61078} \\ \hline +1\cdot 05780 & -\cdot 60536 \end{array}\right\} \qquad \left\{\begin{array}{rr} 1\cdot 00000 & -1\cdot 17251 \\ +\cdot 85287 & -1\cdot 00000 \end{array}\right\}$$

In the case of the first and last, the combination consisting of only two terms, the check calculation is a mere duplicate, and is, therefore, less searching than the others. The signs, in particular, should be examined to guard against a double error.

We next form the corresponding schemes for the function ψ, again in accordance with the formulæ (11). Owing to the occurrence of two zeroes in the scheme at the surface the calculation is somewhat simpler.

ψ_0 :—

$$\left\{\begin{array}{rr} * & * \\ +1\cdot 19308 & +1\cdot 00000 \end{array}\right\} \qquad \left\{\begin{array}{rr} +\cdot 01161 & +\cdot 00973 \\ +1\cdot 82012 & +1\cdot 52556 \end{array}\right\}$$

$$\left\{\begin{array}{rr} +\cdot 01161 & +\cdot 00973 \\ +1\cdot 82012 & +1\cdot 52556 \end{array}\right\} \qquad \left\{\begin{array}{rr} 1\cdot 00071 & +\cdot 00973 \\ -\cdot 25398 & +1\cdot 52556 \end{array}\right\}$$

ψ_2 :—

$$\left\{\begin{array}{rr} \cdot 99752 & +\cdot 00392 \\ -\cdot 41285 & +\cdot 65397 \end{array}\right\} \qquad \left\{\begin{array}{rr} -\mathit{\cdot 00729} & -\mathit{\cdot 00003} \\ -\mathit{\cdot 00101} & +\mathit{\cdot 00160} \\ \hline -\cdot 00830 & +\cdot 00157 \\ -\mathit{2\cdot 98466} & -\mathit{\cdot 01173} \\ -\mathit{\cdot 41230} & +\mathit{\cdot 65309} \\ \hline -3\cdot 39696 & +\cdot 64136 \end{array}\right\}$$

$$\left\{\begin{array}{rr} * & * \\ -\mathit{2\cdot 98866} & -\mathit{\cdot 01174} \\ -\mathit{\cdot 41285} & +\mathit{\cdot 65397} \\ \hline -3\cdot 40151 & +\cdot 64223 \end{array}\right\} \qquad \left\{\begin{array}{rr} * & * \\ -2\cdot 99609 & +1\cdot 00000 \end{array}\right\} \qquad \left\{\begin{array}{rr} -\cdot 00731 & +\cdot 00244 \\ -2\cdot 99208 & +\cdot 99866 \end{array}\right\}$$

$$\left\{\begin{array}{rr} -\cdot 00830 & +\cdot 00157 \\ -3\cdot 39694 & +\cdot 64137 \end{array}\right\} \qquad \left\{\begin{array}{rr} +1\cdot 00458 & +\cdot 00244 \\ +1\cdot 32922 & +\cdot 99866 \end{array}\right\}$$

ψ_4 :—

$$\left\{\begin{array}{rr} \cdot 99752 & + \cdot 00392 \\ -2\cdot 21269 & + \cdot 99379 \end{array}\right\} \qquad \left\{\begin{array}{rr} - \cdot 01172 & - \cdot 00005 \\ - \cdot 00885 & + \cdot 00398 \\ \hline - \cdot 02057 & + \cdot 00393 \\ -4\cdot 79504 & - \cdot 01884 \\ -3\cdot 62204 & +1\cdot 62677 \\ \hline -8\cdot 41708 & +1\cdot 60793 \end{array}\right\}$$

$$\left\{\begin{array}{rr} * & * \\ +5\cdot 14196 & - \cdot 98228 \end{array}\right\} \qquad \left\{\begin{array}{rr} * & * \\ -2\cdot 93655 & +1\cdot 00000 \end{array}\right\} \qquad \left\{\begin{array}{rr} - \cdot 01175 & + \cdot 00400 \\ -4\cdot 80696 & +1\cdot 63694 \end{array}\right\}$$

$$\left\{\begin{array}{rr} - \cdot 02057 & + \cdot 00393 \\ -8\cdot 41708 & +1\cdot 60793 \end{array}\right\} \qquad \left\{\begin{array}{rr} 1\cdot 00000 & + \cdot 00400 \\ - \cdot 54509 & +1\cdot 63694 \end{array}\right\}$$

ψ_6 :—

$$\left\{\begin{array}{rr} \cdot 99669 & + \cdot 00636 \\ - \cdot 20775 & + \cdot 61078 \end{array}\right\} \qquad \left\{\begin{array}{rr} * & * \\ - \cdot 85005 & - \cdot 00542 \\ - \cdot 20775 & + \cdot 61078 \\ \hline -1\cdot 05780 & + \cdot 60536 \end{array}\right\}$$

$$\left\{\begin{array}{rr} * & * \\ - \cdot 85005 & - \cdot 00542 \\ - \cdot 20775 & + \cdot 61078 \\ \hline -1\cdot 05780 & + \cdot 60536 \end{array}\right\} \qquad \left\{\begin{array}{rr} * & * \\ - \cdot 85287 & +1\cdot 00000 \end{array}\right\}$$

The schemes in the middle columns which precede and follow those belonging to the surface are the same for ω and ψ. They should be written down independently and read against one another to guard against errors of transcription.

Now, for any surface (r), in accordance with (14),

$$\omega_r = \tfrac{1}{2}(1-n_r)\,\mathrm{B}_r^2(b_r^2+c_r^2), \qquad \psi_r = \tfrac{1}{2}n_r(\beta'^2_r+\gamma'^2_r-\beta_r^2-\gamma_r^2)$$

where b_r, c_r, β_r, γ_r, β'_r, γ'_r are read from the normal schemes on pp. 172, 173 in terms of b_0, c_0, β_0, γ_0, the specification of the original ray. We now calculate these, noting that since b_r, β_r, β'_r run exclusively together, as do also c_r, γ_r, γ'_r, we need speak explicitly of the former only.

We require to form from the original data $\frac{1}{2}(1-n_r)\,\mathrm{B}_r^2$, that is $-k_r \times \frac{1}{2}\mathrm{B}_r$. There is no check upon these values and they should be examined with care like other fundamental numbers. Their values are shown in the table below.

We have then as regards ω :—

r.	b_r.		b_r^2.			$\frac{1}{2}(1-n_r)\mathrm{B}_r^2$.	ω_r.			
	Co-efficient b_0.	Co-efficient β_0.	Co-efficient b_0^2.	Co-efficient $b_0\beta_0$.	Co-efficient β_0^2.		Co-efficient b_0^2.	Co-efficient $b_0\beta_0$.	Co-efficient β_0^2.	Sum of co-efficients.
0	$+1\cdot 00000$	*	$1\cdot 00000$	*	*	$+\ \cdot 24630$	$+\ \cdot 24630$	*	*	$+\ \cdot 24630$
2	$+\ \cdot 99752$	$+\cdot 00392$	$+\ \cdot 99505$	$+\cdot 00782$	$+\cdot 00002$	$-2\cdot 37488$	$-2\cdot 36312$	$-\cdot 01857$	$-\cdot 00005$	$-2\cdot 38174$
4	*ibid.*	*ibid.*	*ibid.*	*ibid.*	*ibid.*	$+1\cdot 68120$	$+1\cdot 67288$	$+\cdot 01315$	$+\cdot 00003$	$+1\cdot 68606$
6	$+\ \cdot 99669$	$+\cdot 00636$	$+\ \cdot 99339$	$+\cdot 01268$	$+\cdot 00004$	$-\ \cdot 23245$	$-\ \cdot 23091$	$-\cdot 00295$	$-\cdot 00001$	$-\ \cdot 23387$

The best way of forming the square, *e.g.*, of b_2, is to set up ·99752 on the machine, multiply it into itself and into twice 392, then set up 392 and multiply it into itself and twice ·99752, when the agreement of the middle terms is a check upon the operations. The last column, "sum of coefficients in ω_r," will be used below as a check for future work. If necessary, it may be checked by the equation, *e.g.*, for ω_2,

$$-2{\cdot}38174 = -2{\cdot}37488 \times ({\cdot}99752 + {\cdot}00392)^2.$$

Next, for formation of ψ_r arrange as below :—

r.	$\beta_r = \beta'_{r-2}$.		$\beta_r^2 = \beta'^2_{r-2}$.			$\beta'^2_r - \beta_r^2$.				$\frac{1}{2}n_r$.
	Coefficient b_0.	Coefficient β_0.	Coefficient b_0^2.	Coefficient $b_0\beta_0$.	Coefficient β_0^2.	Coefficient b_0^2.	Coefficient $b_0\beta_0$.	Coefficient β_0^2.	Sum of coefficients.	
0	*	+1·00000	*	*	1·00000	·17045	− ·53998	− ·57232	− ·94185	·32698
2	− ·41285	+ ·65397	+ ·17045	− ·53998	+ ·42768	4·72555	−3·85792	+ ·55994	+1·42757	·76457
4	−2·21269	+ ·99379	+4·89600	−4·39790	+ ·98762	−4·85284	+4·14412	− ·61457	−1·32329	·30504
6	− ·20775	+ ·61078	+ ·04316	− ·25378	+ ·37305	+ ·73798	−1·50974	+ ·62230	− ·14946	·81956
8	− ·88382	+ ·99767	+ ·78114	−1·76352	+ ·99535	+ ·78114	−1·76352	− ·00465	− ·98703	—

The last row under $\beta'^2_r - \beta_r^2$ is the sum of the numbers above it and is introduced as a check upon the subtractions; it is equal to $\beta'^2_6 - \beta_0^2$. The addition of mixed positive and negative numbers is best done with a machine. We now have

r.	ψ_r.			
	Coefficient b_0^2.	Coefficient $b_0\beta_0$.	Coefficient β_0^2.	Sum of coefficients.
0	+ ·05573	− ·17656	− ·18714	− ·30797
2	+3·61299	−2·94963	+ ·42811	+1·09147
4	−1·48032	+1·26413	− ·18747	− ·40366
6	+ ·60482	−1·23732	+ ·51001	− ·12249

The multiplication by $\frac{1}{2}n_r$ should be checked by the help of the column "sum of coefficients." It will be remembered that there is no check against setting up an erroneous multiplier for $\frac{1}{2}n_r$.

We are now ready to form δG, &c. Referring to (12) on p. 157 and the calculations above we have, for example,

$$\delta G = +{\cdot}98910\omega_0 + 1{\cdot}14882\omega_2 + 1{\cdot}77160\omega_4 + 1{\cdot}24028\omega_6 + {\cdot}01161\psi_0 - {\cdot}00830\psi_2 - 02057\psi_4 + *,$$

the coefficient of ψ_2, for example, being the figure that stands in the place of G in the scheme formed on p. 175 for ψ_2; and similarly for δH, δK, δL. It is unnecessary to write them at length because they are shown in a more convenient place in the following table :—

	Co-efficient δG.	δG.			Co-efficient δH.	δH.			Co-efficient δK.	δK.			Co-efficient δL.	δL.			Sum of Co-efficient.
		Co-efficient b_0^2.	Co-efficient $b_0\beta_0$.	Co-efficient β_0^2.		Co-efficient b_0^2.	Co-efficient $b_0\beta_0$.	Co-efficient β_0^2.		Co-efficient b_0^2.	Co-efficient $b_0\beta_0$.	Co-efficient β_0^2.		Co-efficient b_0^2.	Co-efficient $b_0\beta_0$.	Co-efficient β_0^2.	
ω_0 . . .	+ ·98910	+ ·24362	*	*	+ ·82903	+ ·20419	*	*	−2·07410	− ·51085	*	*	−1·73844	− ·42818	*	*	− ·49122
ω_2 . . .	+1·14882	−2·71480	− ·02133	− ·00006	− ·21691	+ ·51258	+ ·00403	+ ·00001	+4·90603	−11·59354	− ·09110	− ·00025	− ·92630	+2·18896	+ ·01720	+ ·00005	−11·69825
ω_4 . . .	+1·77160	+2·96367	+ ·02330	+ ·00005	− ·33841	− ·56615	− ·00445	− ·00001	+7·46261	+12·48403	+ ·09813	+ ·00022	−1·42559	−2·38484	− ·01875	− ·00004	+12·59517
ω_6 . . .	+1·24028	− ·28639	− ·00366	− ·00001	− ·70979	+ ·16390	+ ·00209	+ ·00001	+1·05780	− ·24426	− ·00312	− ·00001	− ·60536	+ ·13978	+ ·00179	− ·00001	− ·22938
		+ ·20610	− ·00169	− ·00002		+ ·31452	+ ·00167	+ ·00001		+ ·13538	+ ·00391	− ·00004		− ·48128	+ ·00024	·00000	+ ·17582
																	[+ ·17580]
ψ_0 . . .	+ ·01161	+ ·00065	− ·00205	− ·00217	+ ·00973	+ ·00054	− ·00172	− ·00182	+1·82012	+ ·10144	− ·32136	− ·34062	+1·52556	+ ·08502	− ·26935	− ·28549	− 1·03694
ψ_2 . . .	− ·00830	− ·02999	+ ·02448	− ·00355	+ ·00157	+ ·00567	− ·00463	+ ·00067	−3·39694	−12·27314	+10·01975	−1·45427	+ ·64137	+2·31726	−1·89180	+ ·27458	− 3·01498
ψ_4 . . .	− ·02057	+ ·03045	− ·02600	+ ·00386	+ ·00393	− ·00582	+ ·00497	− ·00074	−8·41708	+12·45997	−10·64028	+1·57795	+1·60793	−2·38025	+2·03263	− ·30144	+ 2·75530
ψ_6 . . .	*	*	*	*	*	*	*	*	−1·05780	− ·63978	+ 1·30884	− ·53949	+ ·60536	+ ·36613	− ·74902	+ ·30874	+ ·05542
		+ ·00112	− ·00357	− ·00186		+ ·00039	− ·00138	− ·00189		− ·35151	+ ·36695	− ·75643		+ ·38816	− ·87754	− ·00361	− 1·24120
																	[− 1·24117]
Totals		+ ·20722	− ·00526	− ·00188		+ ·31491	+ ·00029	− ·00188		− ·21613	+ ·37086	− ·75647		− ·09612	− ·87730	− ·00361	
		$= \frac{1}{2}\delta_1 G$	$= \delta_2 G$	$= \frac{1}{2}\delta_3 G$		$= \frac{1}{2}\delta_1 H$	$= \delta_2 H$	$= \frac{1}{2}\delta_3 H$		$= \frac{1}{2}\delta_1 K$	$= \delta_2 K$	$= \frac{1}{2}\delta_3 K$		$= \frac{1}{2}\delta_1 L$	$= \delta_2 L$	$= \frac{1}{2}\delta_3 L$	

The multiplications in any line may be checked by multiplying, *e.g.*, the sum of the coefficients of ω_2 in δG, δH, δK, δL into the sum of coefficients of ω_2, as given already, thus

$$+1{\cdot}14882 - {\cdot}21691 + 4{\cdot}90603 - {\cdot}92630 = +4{\cdot}91164, \qquad +4{\cdot}91164 \times -2{\cdot}38174 = -11{\cdot}69825.$$

The additions are to be checked by adding across, when they will give the same sums as the totals of the last column; the actual comparison is shown in [ ].

We conclude from this calculation that the aberrational terms in the emergent ray are

$$\begin{aligned}\delta b' &= b_0[+{\cdot}20722\,(b_0^2+c_0^2)-{\cdot}00526\,(b_0\beta_0+c_0\gamma_0)-{\cdot}00188\,(\beta_0^2+\gamma_0^2)]\\ &\quad+\beta_0[+{\cdot}31491\,(b_0^2+c_0^2)+{\cdot}00029\,(b_0\beta_0+c_0\gamma_0)-{\cdot}00188\,(\beta_0^2+\gamma_0^2)],\\ \delta\beta' &= b_0[-{\cdot}21613\,(b_0^2+c_0^2)+{\cdot}37086\,(b_0\beta_0+c_0\gamma_0)-{\cdot}75647\,(\beta_0^2+\gamma_0^2)]\\ &\quad+\beta_0[-{\cdot}09612\,(b_0^2+c_0^2)-{\cdot}87730\,(b_0\beta_0+c_0\gamma_0)-{\cdot}00361\,(\beta_0^2+\gamma_0^2)]\quad.\qquad(27),\end{aligned}$$

with similar expressions for $\delta c'$, $\delta\gamma'$ if we replace b_0, β_0 outside the brackets by c_0, γ_0.

We may without loss of generality put $\gamma_0 = 0$, and in what follows this shall be done.

The twelve coefficients above are not independent. We have seen that they must satisfy seven relations, and we shall now verify that they do so.

We have, from p. 161,

$$\mathfrak{P} = k_0+nk_2+k_4+mk_6.$$

k	Term in $\mathfrak{P}$.
$-\ {\cdot}41285$	$-\ {\cdot}41285$
$-1{\cdot}58532$	$-1{\cdot}03675$
$+1{\cdot}14501$	$+1{\cdot}14501$
$-\ {\cdot}54509$	$-\ {\cdot}33255$
	$-\ {\cdot}63714 = \mathfrak{P}$

and thus

$$\begin{aligned}\delta_2\mathrm{G}-\delta_1\mathrm{H} &= -\ {\cdot}00526-{\cdot}62982 = -{\cdot}63508 &\qquad \mathfrak{P}\mathrm{G} &= -{\cdot}63503\\ \delta_3\mathrm{G}-\delta_2\mathrm{H} &= -\ {\cdot}00376-{\cdot}00029 = -{\cdot}00405 & \mathfrak{P}\mathrm{H} &= -{\cdot}00406\\ \delta_2\mathrm{K}-\delta_1\mathrm{L} &= +\ {\cdot}37086+{\cdot}19224 = +{\cdot}56310 & \mathfrak{P}\mathrm{K} &= +{\cdot}56312\\ \delta_3\mathrm{K}-\delta_2\mathrm{L} &= -1{\cdot}51294+{\cdot}87730 = -{\cdot}63564 & \mathfrak{P}\mathrm{L} &= -{\cdot}63566\end{aligned}$$

Next for the relations (20); we have, noting that $\mathrm{N} = 1$,

s.	$+\mathrm{L}\delta_s\mathrm{G}$.	$-\mathrm{K}\delta_s\mathrm{H}$.	$-\mathrm{H}\delta_s\mathrm{K}$.	$+\mathrm{G}\delta_s\mathrm{L}$.	$=\delta_s\mathrm{N}$.	
1	$+{\cdot}41347$	$+{\cdot}55665$	$+{\cdot}00275$	$-{\cdot}19160$	$+{\cdot}78127$	$\mathrm{NK}^2 = +{\cdot}78113$
2	$-{\cdot}00525$	$+{\cdot}00026$	$-{\cdot}00236$	$-{\cdot}87440$	$-{\cdot}88175$	$\mathrm{NKL} = -{\cdot}88176$
3	$-{\cdot}00376$	$-{\cdot}00332$	$+{\cdot}00963$	$-{\cdot}00720$	$-{\cdot}00465$	$\mathrm{N}(\mathrm{L}^2-1) = -{\cdot}00465$

The comparisons seem to point to a small accumulated error in $\delta_1\mathrm{H}$.

If we transfer the origin for emergent rays to the focal plane, $x' = +1{\cdot}12771$, we have finally

$$\begin{aligned}\delta b' &= b[-{\cdot}03651\,d^2+{\cdot}41296\,d\beta\cos\phi-{\cdot}85496\beta^2]\\ &\qquad\qquad+\beta[+{\cdot}20651\,d^2-{\cdot}98905\,d\beta\cos\phi-{\cdot}00595\beta^2]\\ \delta c' &= c[-{\cdot}03651\,d^2+{\cdot}41296\,d\beta\cos\phi-{\cdot}85496\beta^2]\\ &\qquad\qquad+\qquad\qquad\qquad *\qquad\qquad\qquad .\qquad(28),\end{aligned}$$

where the subscript (0) is dropped, γ is taken as zero, and $b = d \cos \phi$, $c = d \sin \phi$, as on p. 165.

These give the aberrations of the lens at its principal focus.

The corresponding normal scheme is

$$\begin{aligned} b' &= \quad * \quad + 1{\cdot}131453\beta, \\ \beta' &= -{\cdot}883818b + {\cdot}997671\beta. \end{aligned} \qquad (29)$$

In order to fix ideas, compare (28) with the case of a parabolic reflector of the same focal length, given on p. 167, for which we get

$$\delta b' = b[\ * \ + {\cdot}44191b\beta + \ * \ ] + \beta[+ {\cdot}22095d^2 - 1{\cdot}00000b\beta + \ * \ ];$$

we see that there is a close resemblance, except for the value of δ_3G, so that the two hardly differ in any sensible way, except in the curvatures of the fields. It will then cause some surprise that SEIDEL concluded that the Fraunhofer glass was free from coma which is so marked in the reflector. It was, in fact, a misapprehension, as the diagrams given by STEINHEIL and by FINSTERWALDER sufficiently demonstrate. SEIDEL'S argument presents an interesting feature.[†] He puts together the four components of his sum S (2),

$$\begin{array}{r} +\ 0{,}412 \\ -12{,}672 \\ +13{,}454 \\ -\ 1{,}662 \\ \hline \mathrm{S}\,(2) = -\ 0{,}468 \end{array}$$

and draws his conclusion from the approximate balance, within one-thirtieth, of the large positive and negative members. It is evident, however, that this amounts to no more than saying that the two internal surfaces nearly annul one another. But the point I wish to make is that these numbers are in fact the same as those found on p. 178 above. If we transfer to the principal focus by adding $f'\delta$K to δG, we have for δ_2G

ω.	ψ.		δ_2G.	δ_2G $\times f$.
*	− ·36445	=	− ·36445	+ ·4125
−·12406	+11·32385		+11·19979	−12·6721
+·13396	−12·02515		−11·89119	+13·4543
−·00718	+ 1·47599		+ 1·46881	− 1·6619
			+ ·41296	+ 0·4672

The connection does not appear to be so close in the case of others of SEIDEL'S sums, but it is interesting to notice this common ground.

Let us now compare my calculations with those of STEINHEIL. First as to

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[†] 'Ast. Nach.,' No. 1029, 326.

spherical aberration. Take rays parallel to the axis, that is, $\beta = 0$, and consider the focus where they unite for impact upon the original plane at fractions 0, 1/3, 2/3, and 1 of the semiaperture, *i.e.*, for

$$d = 0{\cdot}00000, \qquad 0{\cdot}01170, \qquad 0{\cdot}02340, \qquad 0{\cdot}03510.$$

For any of these the distance of the point from the last surface (6) is

$$-(\mathrm{G}+\tfrac{1}{2}\delta_1\mathrm{G}d^2)/(\mathrm{K}+\tfrac{1}{2}\delta_1\mathrm{K}d^2)$$

or

$$-\mathrm{G}/\mathrm{K}\,[1+\tfrac{1}{2}d^2(\delta_1\mathrm{G}/\mathrm{G}-\delta_1\mathrm{K}/\mathrm{K})], \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (30)$$

and

$$\mathrm{G} = +{\cdot}996692, \qquad \mathrm{K} = -{\cdot}883818, \qquad \tfrac{1}{2}\delta_1\mathrm{G} = +{\cdot}20722, \qquad \tfrac{1}{2}\delta_1\mathrm{K} = -{\cdot}21613.$$

$$\therefore \tfrac{1}{2}[\delta_1\mathrm{G}/\mathrm{G}-\delta_1\mathrm{K}/\mathrm{K}] = +{\cdot}20791-{\cdot}24454 = -{\cdot}03663.$$

Hence the rays meet at the following points along the axis :—

		STEINHEIL, p. 417.	
Axial	$1127^{l}{\cdot}712$	$1127^{l}{\cdot}712$	
1/3 semiaperture . .	·706	·706	
2/3 ,, . .	·689	·687	
1 ,, . .	·662	·659.	. . . (31)

In these and the following comparisons the unit of length has been brought back to 1 line by multiplying by 1000, to preserve STEINHEIL'S numbers unchanged.

In consequence of this residue of spherical aberration the best setting for focus at the middle of the field is not the axial focus but a point within it. STEINHEIL takes this point at 1127·670, following presumably the theory of BESSEL, which gives a position for the greatest apparent concentration of light that is slightly within the least circle of aberration (1127·672).*

Adopting the corresponding point, which allows for the slightly smaller aberration shown by my numbers, and multiplying by 10^{-3} to bring the units into agreement with formula (28), we see, in accordance with p. 165, we must include with $\delta b'$ of p. 179 the term

$$+\mathrm{K}\delta f' \,.\, b = -{\cdot}8838\times-{\cdot}0000400\times b = +{\cdot}000035356,$$

with a corresponding term for $\delta c'$ in terms of c.

The diameters of the image-disc in the focal plane and at this setting are respectively the corresponding extreme values of $\delta b'$, doubled, or

	STEINHEIL.
$0^{l}{\cdot}00316$	—
$0^{l}{\cdot}00067$	$0^{l}{\cdot}00071$.

---

* BESSEL, *loc. cit.*, p. 104.

We take next the oblique rays in a plane through the axis, that is, we take $c = 0$. The rays considered are taken at an angle of 48′ with the axis, following BESSEL and STEINHEIL; hence $\beta = \tan 48' = \cdot 01396353$, and we take in succession $b = d = +\cdot 03510$, $+\cdot 02340$, $+\cdot 01170$, $-\cdot 01170$, $-\cdot 02340$, $-\cdot 03510$. The final numbers given below have been multiplied by 1000 in order to compare with STEINHEIL.

The central ray meets the chosen plane at a distance from the axis

$$(\mathrm{H}+\mathrm{L}\delta f')\,\beta = (+1\cdot 131453-\cdot 000040)\times\beta = \cdot 01579852.$$

Giving as before the calculations in full, the formulæ (28), supplemented by the term $\mathrm{K}\delta f' \,.\, b$, give the following:—

$\delta b'$—

b.	$+\mathrm{K}\delta f'$.	$+\frac{1}{2}\delta_1\mathrm{G}d^2$.	$+\delta_2\mathrm{G}b\beta$.	$+\frac{1}{2}\delta_3\mathrm{G}\beta^2$.	Coeff. b.	$+\frac{1}{2}\delta_1\mathrm{H}d^2$.	$+\delta_2\mathrm{H}b\beta$.	$+\frac{1}{2}\delta_3\mathrm{H}\beta^2$.	Coeff. β.
+ ·03510	+ 353,5	– 449,8	+ 2023,9	– 1667,2	+ 260,4	+ 2544,2	– 4847,3	– 11,6	– 2314,7
·02340	*ibid.*	– 199,9	+ 1349,3	*ibid.*	– 164,3	+ 1130,8	– 3231,5	*ibid.*	– 2112,3
+ ·01170	*ibid.*	– 50,0	+ 674,6	*ibid.*	– 689,1	+ 282,7	– 1615,8	*ibid.*	– 1344,7
– ·01170	*ibid.*	– 50,0	– 674,6	*ibid.*	– 2038,3	+ 282,7	+ 1615,8	*ibid.*	+ 1886,9
·02340	*ibid.*	– 199,9	– 1349,3	*ibid.*	– 2862,9	+ 1130,8	+ 3231,5	*ibid.*	+ 4350,7
– ·03510	*ibid.*	– 449,8	– 2023,9	*ibid.*	– 3787,4	+ 2544,2	+ 4847,3	*ibid.*	+ 7379,9

The comma is placed between the 7th and 8th decimals.

Hence we have the following, with unit 1 line:—

b.	$\delta b'$.	$b' + \delta b'$.	STEINHEIL, p. 419.
+ 35^l·1	+ 91 – 323 = – ·00232	15^l·79628	15^l·79622
23 ·4	– 38 – 295 – 333	·79519	·79528
+ 11 ·7	– 81 – 188 – 269	·79583	·79587
0 ·0	0 – 2 – 2	·79850	·79852
– 11 ·7	+ 238 + 263 + 501	·80353	·80349
23 ·4	+ 669 + 608 + 1277	·81129	·81130
– 35 ·1	+ 1329 + 1031 + 2360	·82216	·82212

. (32)

There is a slight discrepancy for $b = +23\cdot 4$.

STEINHEIL now considers the rays which do not meet the axis. Fig. 6 is taken from his memoir and shows the object-glass on reduced linear scale. He divides the object-glass into three rings, and computes all the rays which impinge upon it at an angle of 48′ with the axis, at the points indicated in the figure. The rays 2, 10, 18, 1, 22, 14, 6 are those just given; of the remainder, those upon the left may be written down from symmetry from those upon the right, so that he computes in all nine independent rays which do not meet the axis.

We derive these as follows. We have throughout β unchanged :—

For the rays (4), (12), (20), $b = 0$, $c = d$;
,, ,, (3), (11), (19), $b = c = d \sin 45^\circ = d \times {\cdot}70711$,
,, ,, (5), (13), (21), $-b = c = d \sin 45^\circ = d \times {\cdot}70711$.

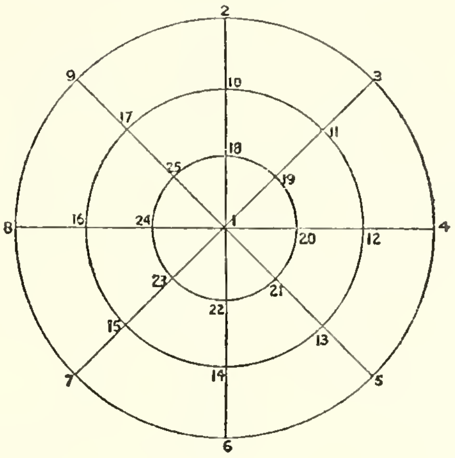

Fig. 6.

Hence the additional calculations required run as follows.

In the calculation of the coefficients replace the columns $\delta_2 \mathrm{G} b \beta$, $d_2 \mathrm{H} b \beta$ by the following :—

Ray.	$\delta_2 \mathrm{G} b \beta$.	$\delta_2 \mathrm{H} b \beta$.
3	+ 1431,1	− 3427,6
11	+ 954,1	− 2285,0
19	+ 477,0	− 1142,5
21	− 477,0	+ 1142,5
13	− 954,1	+ 2285,0
5	− 1431,1	+ 3427,6

In the rays (4), (12), (20) replace these by zero.

Therefore

					Steinheil.	
Ray.	Coefficient b or c.	Coefficient β.	$= \delta b'$.	$\delta c'$.	$\delta b'$.	$\delta c'$.
3	− 332,4	− 895,0	$-\ 82 - 125 = -{}^{l}{\cdot}00207$	$-{}^{l}{\cdot}00082$	$-{}^{l}{\cdot}00204$	$-{}^{l}{\cdot}00080$
11	− 559,5	− 1165,8	$-\ 93 - 163 = -\ {\cdot}00256$	$-\ {\cdot}00093$	$-\ {\cdot}00251$	$-\ {\cdot}00092$
19	− 886,7	− 871,4	$-\ 73 - 122 = -\ {\cdot}00195$	$-\ {\cdot}00073$	$-\ {\cdot}00191$	$-\ {\cdot}00070$
21	− 1840,7	+ 1413,6	$+152+197 = +\ {\cdot}00349$	$-\ {\cdot}00152$	$+\ {\cdot}00351$	$-\ {\cdot}00151$
13	− 2467,7	+ 3404,2	$+408+475 = +\ {\cdot}00883$	$-\ {\cdot}00408$	$+\ {\cdot}00879$	$-\ {\cdot}00410$
5	− 3194,6	+ 5960,2	$+793+832 = +\ {\cdot}01625$	$-\ {\cdot}00793$	$+\ {\cdot}01605$	$-\ {\cdot}00758$
4	− 1763,5	+ 2532,6	$+\ *\ +354 = +\ {\cdot}00354$	$-\ {\cdot}00618$	$+\ {\cdot}00357$	$-\ {\cdot}00627$
12	− 1513,6	+ 1119,2	$+\ *\ +156 = +\ {\cdot}00156$	$-\ {\cdot}00354$	$+\ {\cdot}00160$	$-\ {\cdot}00353$
20	− 1363,7	+ 271,1	$+\ *\ +038 = +\ {\cdot}00038$	$-\ {\cdot}00160$	$+\ {\cdot}00041$	$-\ {\cdot}00162$

. (33)

There is a slight discrepancy in the ray (5).

In considering what discrepancies may be expected, we have to recall that the method developed in the preceding pages omits terms of the fifth order, which may amount to, say,

$$coeff. \times d \times \cdot 000001.$$

Taking $d = 35^{l}\cdot 1$, for unity as coefficient, we should have an error of 4 units in the last place retained above. We have no means of saying what the coefficient may be, but it is clear that it may affect the last digit. Yet I believe that these calculations are not only very much easier, but also more correct than the trigonometrical ones, for though the formulæ for the latter are exact, the number of operations they require is very large. Thus, for each ray which meets the axis, there are fully 50 operations of which at least one-half consist in taking out a logarithm or an antilogarithm with seven decimal places ; for each ray which does not meet the axis the work is rather more than four times as great.

STEINHEIL has calculated seven of the former rays and nine of the latter.

The controls that exist are of the most meagre description and give little help in locating an error. But, even if the whole is done in strictest accordance with the tables, at any step an error may be introduced which falls only short of half a unit in the last place. Thus, in the rays which do not meet the axis, an irremovable accumulated error of 10 or more units could cause no surprise, and for this reason the trigonometrical method loses any advantage over the formulæ given above which it might claim from resting upon exact formulæ. The differences under discussion are, however, minimal, since 550 units in the last decimal place only amount to 1 second of arc.

But pursuing the question a little further I believe, in spite of the evident care with which the whole of STEINHEIL'S calculations have been carried through, that the comparison above shows that a small error has crept in in respect to ray (5).

If we take the general agreement as showing that the trigonometrical calculation does in fact bring in no terms of the aberrations beyond the 3rd order, we can readily analyse STEINHEIL'S numbers in more than one way so as to derive the coefficients $\delta_1 G$, ... from them.

Take the formulæ (24); on the outer ring $\phi = 0, 45°, 90°, 135°, 180°$, correspond respectively to the rays 2, 3, 4, 5, 6 ; thus we have

$$\begin{aligned}
d^2\beta\delta_2 G &= \delta c'_3 - \delta c'_5 = \tfrac{1}{2}(\delta b'_2 + \delta b'_6) - \delta b'_4 \\
Kd\delta f + \tfrac{1}{2}d^3\delta_1 G + \tfrac{1}{2}d\beta^2\delta_3 G &= \qquad = \frac{1}{\sqrt{2}}(\delta c'_3 + \delta c'_5) = \delta c'_4 \\
Kd\delta f + \tfrac{1}{2}d^3\delta_1 G + \tfrac{1}{2}d\beta^2(\delta_3 G + 2\delta_2 H) &= \qquad = \frac{1}{\sqrt{2}}(\delta b'_3 - \delta b'_5) = \tfrac{1}{2}(\delta b'_2 - \delta b'_6) \\
d^2\beta(\delta_1 H + \delta_2 G) + \beta^3\delta_3 H &= \delta b'_3 + \delta b'_5 = \tfrac{1}{2}(\delta b'_2 + \delta b'_6) + \delta b'_4 \\
\beta^3\delta_3 H &= \delta b'_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)
\end{aligned}$$

From these we get at once

$$d^2\beta\delta_2\mathrm{G},\quad \beta^3\delta_3\mathrm{H},\quad \text{and}\quad d\beta^2\delta_2\mathrm{H},$$

and thence

$$\mathrm{K}d\delta f+\tfrac{1}{2}d^3\delta_1\mathrm{G}+\tfrac{1}{2}d\beta^2\delta_3\mathrm{G}\quad \text{and}\quad d^2\beta\delta_1\mathrm{H}.$$

Also for the case $\beta = 0$,

$$\delta b'_2 = \mathrm{K}d\delta f'+\tfrac{1}{2}d^3\delta_1\mathrm{G}\,;$$

thus we get $d\beta^2\delta_3\mathrm{G}$, and when the adopted value of $\delta f'$ is used, $d^3\delta_1\mathrm{G}$ also, which completes the solution.

We see that we can use the rays (A)—3, 5 exclusively, or (B)—2, 4, 6 exclusively. Making separate determinations by these roads,

	(A.)	(B.)
$d^2\beta\delta_2\mathrm{G}$	+·00678	+·00709
$\mathrm{K}d\delta f'+\frac{1}{2}d^3\delta_1\mathrm{G}+\frac{1}{2}d\beta^2\delta_3\mathrm{G}$	−·00593	−·00627
$\mathrm{K}d\delta f'+\frac{1}{2}d^3\delta_1\mathrm{G}+\frac{1}{2}d\beta^2(\delta_3\mathrm{G}+2\delta_2\mathrm{H})$	−·01279	−·01295
$d^2\beta(\delta_1\mathrm{H}+\delta_2\mathrm{G})+\beta^3\delta_3\mathrm{H}$	+·01401	+·01422

$\beta^3\delta_3\mathrm{H}$	·00000
$2\mathrm{K}d\delta f'+d^3\delta_1\mathrm{G}$	−·00071
$2\mathrm{K}d\delta f'$	+·00260

Hence

	(A.)	(B.)		(A.)	(B.)	p. 179.
$d^3\delta_1\mathrm{G}$	−·00331		$\delta_1\mathrm{G}$	−·0766		− ·0730
$d^2\beta\delta_2\mathrm{G}$	+·00678	+·00709	$\delta_2\mathrm{G}$	+ ·3941	+ ·4121	+ ·4130
$d\beta^2\delta_3\mathrm{G}$	−·01115	−·01183	$\delta_3\mathrm{G}$	−1·6292	−1·7285	−1·7099
$d^2\beta\delta_1\mathrm{H}$	+·00723	+·00713	$\delta_1\mathrm{H}$	+ ·4202	+ ·4144	+ ·4130
$d\beta^2\delta_2\mathrm{H}$	−·00686	−·00668	$\delta_2\mathrm{H}$	−1·0023	− ·9760	− ·9891
$\beta^3\delta_3\mathrm{H}$	·00000		$\delta_3\mathrm{H}$	·0000		− ·0060

There is no doubt, from the checks on p. 179, that the numbers put in the last column for comparison are correct to the last digit, and we see that the numbers (A) which rest upon the ray (5) are decidedly less consistent with them than the numbers (B) which do not.

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VI. *On the Variation with Temperature of the Rate of a Chemical Change.*

By A. Vernon Harcourt, *M.A., Hon. D.Sc. Oxon, F.R.S.*

With an Appendix

by William Esson, *M.A., F.R.S., Savilian Professor of Geometry in the University of Oxford.*

Received April 15,—Read May 9, 1912.

In a study of the laws of connexion between the conditions of a chemical change and its amount, whose results have been communicated at intervals to the Royal Society, one of the conditions varied was the temperature of the solution in which the change took place.*

On considering the numerical results, our first observation was that the increase of rate due to increase of temperature could be nearly represented for equal increments of temperature by a geometric progression. The rate was approximately doubled by each rise of ten degrees in the temperature of the solution. But the ratio of the series gradually diminished as the temperature rose, and a formula had to be found giving a series of this kind. For the way in which such a formula was found, see 'Phil. Trans.,' Series A, vol. 186, pp. 855–866.

Using for the rate of change the symbol k, recently adopted by a committee of the Chemical Society, the formula was

$$\log k_t = \log k_0 + m \log \frac{273+t}{273}, \quad \text{or} \quad \frac{k_t}{k_0} = \left(\frac{273+t}{273}\right)^m,$$

where k_0 is the rate at 0° C., k_t the rate at any other temperature t, and m a constant for each particular case of chemical change.

This equation implies that at $-273°$ C. the rate of change is nil. It has long been accepted that at this point, which is the zero of temperature, gases have no tension because molecules are at rest; and from our observations it appears that at the same point atoms are at rest and no contact between any kinds of matter brings about chemical change.

The discovery by Esson of this natural law seems, as has happened in other cases,

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* 'Phil. Trans.,' vol. 156 (1865), p. 193; vol. 157, p. 117; and series A, vol. 186 (1895), p. 817.

Published separately, August 10, 1912.

to have attracted less attention than it deserves, for, as will be seen in the Appendix, most of the Chemists who have made observations on the variation with temperature of the rate of chemical change have calculated from other formulæ which give numbers agreeing less well with their experimental results.

The following account of work done relates to an attempt to measure the influence of temperature in another case of gradual chemical change.

When solutions of ferric chloride and stannous chloride are mixed, ferrous chloride and stannic chloride are formed more or less gradually according to the concentration and temperature of the solution. Stannic chloride is decomposed by water, hydrogen chloride and a gelatinous precipitate of stannic hydroxide being formed; but if hydrogen chloride has been added in sufficient quantity the liquid remains clear. If the liquid is hot, a larger proportion of hydrogen chloride is needed to resist the action of water than when it is cold. For the observation of a colour change, it is necessary that the liquid should remain clear. A ferric salt loses its colour when it is reduced, but the colour is too pale, and therefore the change of colour too little, to serve for observation; but when a sulphocyanide has been added the fading of the blood-red colour can be followed by the eye from minute to minute, or at less intervals of time when the rate of change is greater.

With stannous chloride in excess the whole of the ferric salt is reduced and the liquid becomes colourless; but it is not possible to fix with any approach to accuracy the time when this final stage is reached, for the rate of change continually decreases as the residue of ferric chloride grows less and less, becoming at last indefinitely slow. The plan followed was, therefore, that of the police-trap, namely, to have two fixed stations or standards and to take as accurately as possible the time at which the change passed each of these. Glass cylinders were used of about 100 c.c. capacity, as similar as possible; one was the reagent glass, two served as standards, filled with a darker and with a paler red liquid. Into the reagent glass, for each observation, water with a small proportion of hydrogen chloride, solutions of ferric chloride and of potassium sulphocyanide, were delivered from pipettes, making up a total volume of 75 c.c., and lastly, when the liquid had been brought to the desired temperature, 5 c.c. of an acid solution of stannous chloride. Exactly the same routine was followed for each observation, the only difference being of the temperature of the liquid.

The darker standard was made by filling one of the glasses to the level at which 80 c.c. stood in the reagent glass, with a mixture of a few drops of ferric chloride with a large proportion of hydrogen chloride and potassium sulphocyanide, such as to produce a colour sufficiently translucent to be well distinguished, and considerably less deep than that of the mixture in the reagent glass. In the absence of an excess of hydrogen chloride and potassium sulphocyanide, ferric sulphocyanide is gradually bleached when exposed to sunlight, but the presence of an excess of one or other or both of these substances seems to increase its stability. If the conditions of this action of light have not been investigated that would be worth doing. Many attractive by-paths have to be left unexplored. For the purpose of these observations it was only necessary to make sure that the dark standard, made in the manner described, would not change appreciably, the tube being corked and kept in the dark except when in use, by exposure to diffused daylight. A set of observations only occupied five or six hours, and the same standard was in use for several weeks without any noticeable change.

The pale standard made by diluting some of the dark standard was less constant, and differed in colour from the liquid in the reagent tube which had faded to a similar depth of colour. This difference of colour made the observations less easy, and therefore less exact, than they would otherwise have been. The cause was found to be that the constancy and precise tint of ferric sulphocyanide, which in dilute solutions varies between pink and orange, depends not only upon the relative proportions of iron, sulphocyanide, and acid, which dilution leaves unaltered, but also upon the concentration of the latter two. In the reagent tube the concentration of these two influential bystanders is practically if not wholly unchanged.

By several preliminary testings a degree of concentration of hydrogen chloride was found which would prevent the formation of a cloudiness by hydrolysis of stannic chloride without increasing unduly the rate of change. The margin is rather narrow.

To maintain a constant temperature the reagent tube was placed on an iron tray covered by white paper, which was heated beneath at one end by a small gas flame, while the liquid was stirred by the passage of large bubbles of carbonic acid from an inverted thistle-funnel. By moving the tube nearer to or further from the heated end of the tray, or by moving the gas burner, the mean temperature of the liquid was regulated during intervals varying from five minutes to three-quarters of an hour within about 0°·05 C. Four or five bubbles a minute stirred the liquid sufficiently when the desired temperature was near that of the room, but for temperatures above 20° C., and during the delivery of stannous chloride from a pipette, a more rapid stream was used.

The colour on mixing was very deep, the excess of ferric chloride being such as to allow at least two or three minutes for adjustment of temperature before the depth of colour approached that of the dark standard. To make the comparison, the cork holding the thermometer and thistle-funnel was replaced by a plain cork, and the dark standard was placed close alongside the reagent tube. The observer looked at the two, watch in hand, closing his eyes at intervals for a few seconds to get a fresh impression, till the colours seemed undistinguishable, made a mental note of the time, and continued to watch till the contents of the reagent tube seemed the paler of the two. Then thermometer and thistle-funnel were quickly replaced, and any disturbance of temperature estimated as having prevailed after the time of agreement, which is the start of the race, was compensated by causing a similar divergence on the opposite side of the thermometer line.

By and by the contents of the reagent tube were only a little darker than the pale standard, then the second observation was made in the same way. The comparison was more difficult because the rate of change was less. It was found helpful to have two similar standard tubes, one on each side of the reagent tube. Generally speaking, the first observation was not liable to an uncertainty of more than 10 seconds; but when the rate was slow the uncertainty attaching to the second observation extended over a minute or more. By a repetition of a set of observations or of a particular observation, and taking the mean of the intervals observed, the error is lessened; but the method does not admit of an accuracy approaching that of observing the appearance in a colourless liquid of the intense colour of the iodide of starch, whose results led to the discovery of what we believe to be a general law. The present observations furnish only another case of agreement within the limits of experimental error with numbers calculated from the formula already established.

The following are the times in which at different temperatures the depth of colour changed from that of the dark to that of the pale standard, that is to say, in which a definite piece of chemical work was done:—

	Temperatures . . .	9°	12°	15°	18°	21°	24°	27°	30°
Time in minutes	Set I.	50·0	37·25	27·75	20·5	15·17	11·1	8·62	6·5
	Set II. . . .	44·7	34·2	26·2	18·2	14·5	10·83	7·83	5·8
	Set III. . . .	47·0	33·3	23·7	18·67	14·0	10·33	7·5	5·92
	Mean . . .	47·2	34·9	25·9	19·1	14·6	10·8	8·0	6·1

The corresponding numbers calculated by the method explained below, and set forth in the following table, are

47·2 34·9 25·9 19·3 14·4 10·8 8·1 6·1.

Using the formula $x/x' = (\mathrm{T}'/\mathrm{T})^m$, x, x' being consecutive observed values of the times at temperatures T, $= 273+t$, and T′, $= 273+t'$, a value of $\log m$ is calculated from the derived formula

$$\log\log x/x' - \log\log \mathrm{T}'/\mathrm{T} = \log m.$$

In the table, column 7 contains the values of $\log m$ calculated by subtracting the values of $\log\log \mathrm{T}'/\mathrm{T}$ in column 6 from the corresponding values of $\log\log x/x'$ in column 5. The mean of these values of $\log m$ is taken to be the true value of $\log m$. Assuming this value of $\log m$, values of $\log\log x/x'$ are calculated from the formula

$$\log\log x/x' = \log\log \mathrm{T}'/\mathrm{T} + \log m.$$

Column 8 in the table contains the values of $\log\log x/x'$ calculated by adding the corresponding values of log log T′/T in column 6 to the constant mean value of log m at the foot of column 7. From these values of log log x/x' are derived the values of log x/x' in column 9. If the times of the first, second, ... observations are x_1, x_2, ..., values of log x_1/x are obtained as the sum of the values of log x_1/x_2, log x_2/x_3, ...

Column 10 in the table contains these values of log x_1/x, as the sum of the values of log x/x' in column 9. Values of log x_1 are obtained by adding to the values of log x_1/x the values of log x. These values of log x_1 in column 11 of the table are calculated by adding the values of log x_1/x in column 10 to the corresponding values of log x in column 3. The mean of these values of log x is taken to be the true value of log x_1, which is given at the foot of column 11.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
t.	x.	log x.	log x/x'.	log log x/x'.	log log T′/T.	log m.	log log x/x'.	log x/x'.	log x_1/x.	log x_1.	log x.	x.
° C.												
9	47·2	674	—	—	—	—	—	—	—	674	674	47·2
12	34·9	543	131	117	662	455	117	131	131	674	543	34·9
15	25·9	413	130	114	658	456	113	130	261	674	413	25·9
18	19·1	281	132	121	653	468	108	128	389	670	285	19·3
21	14·6	164	117	068	649	419	104	127	516	680	158	14·4
24	10·8	033	131	117	644	473	099	126	642	675	032	10·8
27	8·0	903	130	114	639	475	094	124	766	669	908	8·1
30	6·1	785	118	072	635	437	090	123	889	674	785	6·1
log m (mean) . . .						1·455	log x_1 (mean) . . .			674		
m (mean) . . .						28·5						

Assuming this value of log x_1, the values of log x in column 12 of the table are calculated by subtracting from this constant value of log x_1 the corresponding values of log x_1/x in column 10; and from these values of log x are derived the values of x in column 13 of the table. Thus x is calculated from the formula $x = x_1 (\mathrm{T}_1/\mathrm{T})^m$, m and x_1 being the means of values obtained from the observations, namely, $m = 28{\cdot}5$, $x_1 = 47{\cdot}2$.

The following is another way of presenting the fundamental equation. Reckoning the time required at 0° C., x_0, from the observed times at other temperatures, it is found to be 118·3 minutes. The relation between this time and that at any other temperature, x_t, is $\dfrac{x_0}{x_t} = \left(\dfrac{273+t}{273}\right)^{28\cdot5}$, whence $x_t = x_0 \times \left(\dfrac{273}{273+t}\right)^{28\cdot5}$.

The mixture made for each observation was an aqueous solution, 80 c.c. in volume, of four substances, in the following masses and molecular proportions :—

	Gram.	Mol. props.
Ferric chloride, $FeCl^3$	·0145	1·0
Potassium sulphocyanide, KCNS	·312	36·1
Stannous chloride, $SnCl^2$	·106	6·3
Hydrogen chloride, HCl	·289	88·8

No simple numerical relations were aimed at. A large excess of sulphocyanide was taken in order to increase the depth of colour, Dr. GLADSTONE having shown that this increase extends to a proportion thirty or more times that of the ferric salt. The proportions of hydrogen chloride and of stannous chloride were chosen, after many trials, such as to avoid separation of a stannic compound, and to give rates convenient over the whole range of temperatures. The stannous chloride was taken in large proportion relatively to the ferric chloride, so that the rate of decrease of depth of colour when the change was passing the pale standard might be mainly that due to the diminution of one only of the acting substances.

The conditions were now varied by increasing the amount of hydrogen chloride ; the rate was nearly trebled. The short-time observations were made by removing the cork and thistle-funnel and stirring with the thermometer. One set only was made, and gave the following times of change at the same series of temperatures as before :—

Temperatures . . .	9°	12°	15°	18°	21°	24°	27°	30°
Minutes	15·8	12·2	8·8	6·8	5·0	4·1	2·8	2·2
(Calculated) . . .	16·35	12·26	8·99	6·82	5·02	3·83	2·91	2·19

The numbers in the lower line are calculated from the equation

$$x_t = 40{\cdot}14 \times \left(\frac{273}{273+t}\right)^{28},$$

40·14 being the estimated number of minutes in which the portion of change would be completed at 0° C.

A few further observations were made upon the influence on the rate of change of other acids.

Phosphoric acid changes the colour of the liquid to a pale yellow. Sulphuric and nitric acids can be used, and have curiously different effects upon the rate of change. The former, instead of increasing the rate, as an addition of hydrogen chloride does, diminishes it greatly. The times of reduction of the same amount of ferric chloride by the same amount of stannous chloride (1) in the mixture, whose composition is given above ; (2) in the same mixture with an additional quantity of hydrogen chloride ;

(3) in the same mixture with the addition of a corresponding quantity of hydrogen sulphate, were as follows:—

Temperatures . .	12°	15°	18°	21°	24°	27°	30°
Minutes (1) . . .	34·9	25·9	19·1	14·6	10·8	8·0	6·1
,, (2) . . .	12·2	8·8	6·8	5·0	4·1	2·8	2·2
,, (3) . . .	60·0	45·0	36·0	26·8	19·3	16·2	10·7

At each temperature the times in the third set are approximately 1·8 times those in the first set, and 5 times those in the second set.

No complete set has been made with hydrogen nitrate, but enough observations to show that it has an influence on the rate of change quite as unexpected as that of hydrogen sulphate, namely, that its addition makes little if any difference.

The times required for doing the fixed amount of chemical work at 21°, with (*a*) no addition, and then with the addition of equivalent quantities of (*b*) hydrogen chloride, (*c*) hydrogen sulphate, and (*d*) hydrogen nitrate, were as follows:—

a.	*b.*	*c.*	*d.*
14·6	5·0	26·2	13·7 minutes.

Having carried thus far an experimental inquiry which is suggestive of much further work, the author ventures to express a hope that it may attract the attention and pass into the hands of some younger chemist. The mode of working adds to the usual interest of research the particular excitement which attaches to all observations and predictions of time, sporting or scientific, whether it be of the time of a race or of the moment of an occultation.

Lastly, he desires to express his thanks to Dr. Baker and to Christ Church for the welcome and the opportunity of work and the help which he has received.

APPENDIX. *By Prof.* W. Esson, *F.R.S.*

I. The observations recorded in the preceding pages follow the law of connexion between chemical change and temperature with great exactness. This law, first enunciated in the Bakerian Lecture delivered to the Royal Society in 1895, is expressed by the relation

$$k/k' = (\mathrm{T}/\mathrm{T}')^m,$$

k, k' being the rates of chemical change at absolute temperatures T, T$'$ respectively. This relation is independent of the units of measurement of k and T, and m is a pure number which expresses the ratio of dk/k to $d\mathrm{T}/\mathrm{T}$. This implies that if at a temperature T a small change is made in each unit of temperature, and this change produces a corresponding small change in each unit of chemical change, the latter change is m times the former change. The number m may be regarded as the measure of the effect of heat energy upon chemical energy.

In the Bakerian Lecture it was shown that m is constant for all the temperatures at which the experiments were made, but varies with the medium in which the chemical change takes place. The constancy of m for each medium is secured by making one of the constituents of the medium predominant; m has different values for different predominant constituents in the medium in which the same chemical change occurs; m has also different values for different chemical changes. On p. 879 of the Lecture the values of m are 10, 20·4, 21·2, 24·1 for the predominant constituents $NaHCO^3$, H^2SO^4, HCl, HI respectively in the medium in which the reaction between hydrogen peroxide and hydrogen iodide is taking place. The value of m is 40·5 in the case of the reaction between hydrogen chlorate and potassium iodide, studied by PENDLEBURY and SEWARD, and quoted on the same page of the Lecture.

If the conditions for a stable communication of heat energy to chemical energy are not satisfied the value of m is different at different temperatures. For instance, the predominant constituent of the medium may change its character with a change of temperature, or the nature of the reaction between the substances undergoing change may vary. Examples of this variation of m with temperature are given later. But even when m varies with temperature it is still to be regarded as the measure of the effect of heat energy upon chemical energy at a given temperature, and the value of m is obtained from the experiments by calculating the ratio of dk/k to $d\mathrm{T}/\mathrm{T}$ at each temperature. In the experiments recorded in the preceding pages there are no such disturbing conditions, and m is constant at all the temperatures at which these experiments were made.

In the experiments recorded in the preceding pages the expression for the progress of the chemical change is, by the law of mass action, of the form

$$f'(y)\,dy/dx = -k,$$

y being the concentration of one of the substances undergoing change, and x the time during which the change takes place. This expression leads to the relation

$$f(y_2) - f(y_1) = kx.$$

The time x is the observed time during which the potential chemical energy expressed by $f(y_1)$ had changed to the potential chemical energy expressed by $f(y_2)$. In the above experiments this change of energy is indicated by the passage of the solution from one given colour to another. At different temperatures this change of energy is constant. Thus if k, k' are the rates of change at temperatures T, T′ respectively, and x, x' are the corresponding observed times,

$$f(y_2) - f(y_1) = kx = k'x'.$$

The relation $kx = k'x'$ is thus independent of the form of the function $f'(y)$, and the method of observation is alike applicable to unimolecular and multimolecular reactions. When this method is used the relation $k'/k = (T'/T)^m$ becomes $x/x' = (T'/T)^m$.

The following table exhibits the agreement of the times calculated from the above relation, the value of m being 28·5 :—

t.	T.	*x.* Found.	*x.* Calculated.
9	282	47·2	47·2
12	285	34·9	34·9
15	288	25·9	25·9
18	291	19·1	19·3
21	294	14·6	14·4
24	297	10·8	10·8
27	300	8·0	8·1
30	303	6·1	6·1

The experimental and calculated numbers agree as well as those recorded in the Bakerian Lecture, and show that the method of experiment gives very accurate results.

If the rate of the reaction at zero centigrade is taken to be unity, the following are the rates at the temperatures of the experiments :—

t.	*k.*	*t.*	*k.*
0	1	21	8·17
9	2·51	24	10·96
12	3·37	27	14·59
15	4·56	30	19·28
18	6·12		

At temperatures increasing by 10° the rates are

t.	*k.*	*t.*	*k.*
0	1	20	7·46
10	2·78	30	19·28

The rate at zero centigrade is doubled at 6°·7.

A few experiments made by various authors are appended (II.–XIII.). Most of these (II.–IX.) appear to satisfy the conditions for a stable communication of heat energy to chemical energy at the temperatures of the experiments, and confirm the law of connexion between chemical change and temperature assumed in the previous discussion of HARCOURT'S observations. The others (X.–XIII.) show a variation in the value of m which sometimes increases and at other times decreases with temperature. In these cases the values of m are calculated from the formulæ of the authors, which for this calculation are a sufficient approximation to the true values. But the relations thus obtained between m and temperature must be regarded as empirical, and hold good only for the range of temperature of each set of observations. These variations in the values of m are considered to be side effects of temperature which interfere with the main effect of temperatures upon the chemical changes.

II. 'Influence of the Temperature on the Rate of Hydrolysis of Ethyl Acetate by Caustic Soda,' REICHER, quoted by VAN 'T HOFF, translated by EWAN, 1896, p. 130 (4).

The values of k are calculated from the relation $k/k_1 = (T/T_1)^m$, m being 18·9.

t.	k.		
	Found.	Calculated.	Author.
9·4	2·307	2·31	(2·307)
14·4	3·204	3·22	3·2
24·22	6·151	6·10	(6·151)
35·14	12·096	12·00	11·97
44·94	21·648	21·77	(21·648)

The values of k enclosed in brackets are assumed by the author to be correct. The two remaining values of k are calculated from the relation

$$\log k = \cdot 0074T - 1780T^{-1} + 4\cdot 53.$$

The simpler relation

$$\log k = 18\cdot 9 \log (T/T_1) + \cdot 364,$$

in which the constants are calculated by the method of least squares, gives values of k agreeing with those found within the limits of experimental error.

III. 'Influence of the Temperature on the Velocity of the Reaction between Potassium Chlorate and Ferrous Sulphate in presence of Sulphuric Acid,' HOOD, quoted by VAN 'T HOFF, translated by EWAN, 1896, p. 132 (5).

The values of k are calculated from the relation $k/k_1 = (T/T_1)^m$, m being 26·18.

t.	*k.*		
	Found.	Calculated.	Author.
10	1·00	1·00	1·00
12	1·21	1·21	1·21
14	1·46	1·45	(1·46)
16	1·73	1·74	1·76
18	2·11	2·08	2·11
20	2·51	2·49	2·54
22	2·96	2·98	3·02
24	3·59	3·56	3·62
28	5·08	5·05	(5·08)
30	6·04	6·00	6·04
32	7·15	7·13	7·11

The author's values of k were calculated from the relation

$$\log_e k = 27{\cdot}189 - 7695\mathrm{T}^{-1}$$

or

$$\log k = 11{\cdot}81 - 3342\mathrm{T}^{-1}.$$

The constants were found by assuming the observed values of k enclosed in brackets to be correct. The relation

$$\log k = 26{\cdot}18 \log (\mathrm{T}/\mathrm{T}_1) + {\cdot}002$$

gives values of k which agree with those found within the limits of experimental error.

IV. "On the Dissolution of Metals in Acids," Veley, 'Journal of the Chemical Society,' LV., p. 361.

The values of k are calculated from the relation $k/k_1 = (\mathrm{T}/\mathrm{T}_1)^m$, m being 7·28.

t.	*k.*		
	Found.	Calculated.	Author.
21	8·15	8·18	8·15
31	10·38	10·43	10·4
36	12·04	11·76	11·84
41	13·03	13·21	13·4

The author's formula is

$$\log k = {\cdot}685 + {\cdot}0108t.$$

The values of k are calculated from

$$\log k = 7{\cdot}28 \log (\mathrm{T}/\mathrm{T}_1) + {\cdot}913.$$

In his subsequent experiments VELEY uses the relation $k/k_1 = (T/T_1)^m$, from which he obtains values of k agreeing with those found within the limits of experimental error.

V. In the observations on "The Rate of Action of Drugs upon Muscle as a Function of Temperature," VELEY and WALLER, 'Roy. Soc. Proc.,' B, vol. 82, 1910, values of m were found to be 26·7, 20·8, 14·3 in experiments with different drugs.

VI. "The Affinity Constants of Bases as determined by the aid of Methyl Orange," VELEY, 'Journal of the Chemical Society,' XCIII., 2, pp. 2122–2144.

In this paper VELEY uses the formula $k/k_1 = (T/T_1)^m$ for his own experiments and applies it to experiments of the same kind by other chemists. Values of m in different experiments were found to be

2, 9, 11, 13, 14, 15, 22·5.

VII. 'Decomposition of Phosphine,' KOOY. These experiments are quoted by VAN 'T HOFF, p. 135 (b), who calculated values of k from the formulæ

$$(a)\ m = (k^{-1}\,dk)/(T^{-1}\,dT) = AT^{-1},$$

$$(b)\ m = (k^{-1}\,dk)/(T^{-1}\,dT) = AT^{-1}+B,$$

$$(c)\ m = (k^{-1}\,dk)/(T^{-1}\,dT) = C.$$

For (a) and (c) he assumes as correct the first and last observation, and for (b) he assumes all the observations except the second. The value of m in (c) is 12·3. The values of k are calculated from the formula

$$\log k = 12{\cdot}3 \log (T/T_1) + \bar{4}{\cdot}681.$$

VIII. "Action of Bromine on Acetaldehyde in Aqueous Solution," BUGARSZKY, 'Zeit. Physikal. Chem.,' 1904, 48, 63–86.

The values of k are calculated from the relation $k/k_1 = (T/T_1)^m$, m being 26·7.

t.	k.		
	Found.	Calculated.	Author.
0	·117	·117	·119
10	·308	·307	·303
20	·790	·777	·772
25	1·205	1·222	1·234

The author's formula is

$$\log k = {\cdot}04068t - {\cdot}9257.$$

This form of relation was rejected by HARCOURT and ESSON for the reasons given in the Bakerian Lecture, p. 859.

The relation

$$\log k = 26{\cdot}7 \log (T/T_1) + \bar{1}{\cdot}07$$

gives values of k agreeing better with those found than the values given by the author.

IX. "On the Decomposition of Ozone by Heat," PERMAN and GRAVES, 'Roy. Soc. Proc.,' A, vol. 80, p. 366. The values of k are calculated from the relation $k/k_1 = (T/T_1)^m$, m being 39·6.

t.	log k.		
	Found.	Calculated.	Author.
40	2·86	2·85	2·86
60	3·95	3·91	3·86
80	4·91	4·92	4·86
100	5·74	5·87	5·86
120	6·86	6·77	6·86

The authors' formula is

$$\log k = {\cdot}05t + {\cdot}86,$$

which is of the same form as the authors' formula in V.

The relation

$$\log k = 39{\cdot}6 \log (T/T_1) + 2{\cdot}85$$

gives values of log k agreeing better with those found than the values given by the authors.

The values of m found from the experiments I.–IX. and those given in the Bakerian Lecture (B) arranged in ascending order of magnitude are given in the following table, with the range of temperature for which m has a constant value :—

	m.	t.		m.	t.
VI.	2	10–40	B.	20·4	0–50
IV.	7·3	21–41	V.	20·8	7–24
VI.	9	10–50	B.	21·2	0–40
B.	10	15–19	VI.	22·5	0–60
VI.	11	10–60	B.	24·1	20–30
VII.	12·3	310–512	III.	26·2	10–32
VI.	13	10–60	V.	26·7	7–25
VI.	14	10–60	VIII.	26·7	0–25
V.	14·3	7–24	I.	28·5	9–30
VI.	15	15–60	IX.	39·6	40–120
II.	18·9	9–45	B.	40·5	4–30

The experiments (X.–XIII.) do not satisfy the conditions for the constancy of m. They are quoted by VAN 'T HOFF, translated by EWAN, 1896, pp. 127–135, and are numbered (1), (2), (3), (6). The values of m, the ratio of dk/k to dT/T are calculated at each temperature from the formulæ given by the authors.

X. (1) 'Influence of the Temperature on the Rate of Decomposition of Dibromosuccinic Acid.'

The author's formula is

$$\log k = \cdot 0412t - a$$

or

$$\log k = \cdot 0412\mathrm{T} - b\,;$$

hence

$$\log_e k = \cdot 09462\mathrm{T} - c,$$

and

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}) = \cdot 09462\mathrm{T}.$$

t.	m.	t.	m.
15	27·2	70·1	32·4
40	29·6	80	33·4
50	30·5	89·4	34·3
60·2	31·5	101	35·4

XI. (2) 'Influence of the Temperature on the Rate of the Reaction between Sodium Chloracetate and Caustic Soda,' SCHWAB.

The author's formula is

$$\log k = \cdot 0404t - a,$$

or

$$\log_e k = \cdot 093\mathrm{T} - b\,;$$

hence

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}) = \cdot 093\mathrm{T}.$$

t.	m.	t.	m.
70	31·9	110	35·6
80	32·8	120	36·5
90	33·7	130	37·5
100	34·7		

XII. (3) 'Influence of the Temperature on the Rate of Change of Chloracetic Acid in Aqueous Solution,' SCHWAB.

The author's formula is

$$\log k = a - 5202\mathrm{T}^{-1},$$

or

$$\log_e k = b - 13280\mathrm{T}^{-1}\,;$$

hence

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}) = 13280\mathrm{T}^{-1}.$$

t.	m.	t.	m.
80	37·6	110	34·7
90	36·5	120	33·8
100	35·6	130	33·0

XIII. (6) 'Influence of the Temperature on the Rate of Hydrolysis of Ethyl Acetate by Caustic Soda,' WARDER.

The author's formula is

$$\log_e k = a - 5579\mathrm{T}^{-1};$$

hence

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}) = 5579\mathrm{T}^{-1}.$$

t.	m.	t.	m.
3·6	20·2	27·0	18·6
5·5	20·0	28·4	18·5
7·2	19·9	30·4	18·4
11·0	19·6	32·9	18·2
12·7	19·5	34·0	18·2
19·3	19·1	35·0	18·1
20·9	19·0	37·7	17·9
23·6	18·8		

In X. and XI. m increases with the temperature: in X. from 27·2 at 15° C. to 35·4 at 101° C.; in XI. from 31·9 at 70° C. to 37·5 at 130° C. In XII. and XIII. m decreases with the temperature: in XII. from 37·6 at 80° C. to 33 at 130° C.; in XIII. from 20·2 at 3°·6 C. to 17·9 at 37°·7 C. It is remarkable that in the experiments by SCHWAB, XI., XII., the sum of the values of m at each temperature from 80° C. to 130° C. is very nearly constant, having a mean value 70·3. The two experiments taken together give a mean value of $m = 35·17$.

The value of m is the same at the temperature given by $·093\mathrm{T} = 13280\mathrm{T}^{-1}$, *i.e.*, at $\mathrm{T} = 377·9$ or $t = 104·9$. At this temperature $m = 35·14$. It would appear from this that if the conditions for a stable communication of heat energy to chemical energy had been secured in each set of experiments the constant value of m would have been 35·1.

The relation of m to temperature is in X. and XI. $m = c\mathrm{T}$, and in XII. and XIII. $m = b\mathrm{T}^{-1}$. These relations are probably merely empirical, and are used in this paper to obtain approximate values of m at each temperature. VAN 'T HOFF'S formula for m is

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}) = b\mathrm{T}^{-1} + a + c\mathrm{T},$$

which he deduces from the principles of thermodynamics. In the experiments discussed by him, a, b, c are made equal to zero in succession, but no reason is given for this process. In the discussion of the experiments, I.–IX., b and c are considered to be both zero, and a is the constant value of m deduced from the observations.

In the series of experiments II.–XII. taken at random from a number of experiments by other authors on the effect of temperature upon chemical change it has been shown that in the majority of cases II.–IX. m has a constant value. The reason for the variation of m with temperature in X.–XIII. has yet to be discovered. The writer intends to discuss at some future time all the experiments upon the subject, and hopes with the aid of HARCOURT to discover an explanation of the variation.

The experiments recorded in the Bakerian Lecture were made upon a simple unimolecular reaction, and the utmost care was taken to eliminate all possible sources of error in the determination of the effect of temperature upon the reaction. On p. 860 the assumption is made that the relation is of the form

$$k/k_1 = \{(c+t)/(c+t_1)\}^m.$$

The value of c, the temperature of no action, is determined from the experiments to be $-272°{\cdot}6$ C. This agrees closely with the zero of absolute temperature, $-273°$ C. In the subsequent experiments of the Lecture, in HARCOURT'S recent experiments, and in the experiments of other authors, the relation is for this reason assumed to be

$$k/k_1 = (\mathrm{T}/\mathrm{T}_1)^m,$$

with the consequent relation

$$m = (k^{-1}dk)/(\mathrm{T}^{-1}d\mathrm{T}).$$

In studying the effect of one phenomenon, A, upon another phenomenon, B, which mutually influence each other, it often happens that the chain of processes from A to B which cause the influence is unknown. It would seem reasonable, in our ignorance of these processes, to assume that when the chain is uniform the ratio of the increase per cent. in B to the increase per cent. in A is constant, and further to assume that if the chain is not uniform, and this ratio, therefore, is no longer constant, the ratio will still be a measure of the effect of A upon B.

In the present case the phenomenon A is the molecular energy of heat, and the phenomenon B is the chemical energy of a reaction which may be energy of atoms or electrons. The mode of influence of the one kind of energy upon the other is unknown, and the measure m of the influence is taken to be

$$m = (\mathrm{B}^{-1}d\mathrm{B})/(\mathrm{A}^{-1}d\mathrm{A}).$$

If A is of the form $\frac{1}{2}mu^2$ and B of the form $\frac{1}{2}nv^2$ another form of the measure is

$$m = (v^{-1}dv)/(u^{-1}du),$$

and m is the ratio of the percentage increase of the average velocity of atoms or electrons to the percentage increase of the average velocity of molecules.

It is possible that this mode of measuring the effect of one phenomenon upon another may have a wider application. In studying the relation between unemployment and pauperism, the proper course might be to take the ratio of the increase per cent. of pauperism to the increase per cent. of unemployment as the measure of the effect of one upon the other. The ratio of the increase per cent. of coal or oil consumed in a ship to the increase per cent. in the number of knots attained by the vessel might be used with advantage in comparing the merits of coal and oil.

[*June* 15.—The referees of this paper have asked the author to discuss, with reference to the law here advocated, the experiments of TRAUTZ and VOLKMANN "On the Saponification of Esters," 'Zeit. Phys. Chem.,' 1908, 64, pp. 53–88; 1909, 66, p. 496; 67, p. 93; 68, p. 295.*

TRAUTZ calls the ratio $n = k_{t+10}/k_t$ the temperature coefficient of the rate of chemical change; and he discusses the effect of temperature on the value of n, which is a constant when the rate increases in geometrical progression as the temperature increases in arithmetical progression. This relation has been often used since its first use by BERTHELOT in 1862. In most experiments n has been found to decrease with temperature, but in the cases of saponification of esters it first increases and then decreases, having a maximum value between 10° C. and 20° C. TRAUTZ connects this with a similar maximum of viscosity in the medium in which the chemical action is taking place.

The value of $m = (k^{-1}\,dk)/(\mathrm{T}^{-1}\,d\mathrm{T})$ also shows a maximum value at the same point. The following table exhibits the values of m and n in the experiments with methyl acetate, vol. 64, p. 83:—

t.	m.	n.	$\dfrac{m = 20}{n}$.
0	—	—	—
10	17·9	1·85	2·05
20	23·5	2·26	2·00
30	19·0	1·87	1·96
40	18·2	1·81	1·91
50	17·7	1·75	1·87

[* It appears from the results of several experimentalists that the saponification of esters at different temperatures does not give, for the change of rate with temperature, interpretable results. This may be owing to a complication in the reaction or a liability to error in the subsequent analysis. VOLKMANN does not describe his *modus operandi* fully enough for any judgment to be formed. Nor does he interpret his results. See p. 88.

Both he and TRAUTZ, who is the sole author of the three subsequent papers in vols. 66, 67, and 68 of the 'Zeitschrift für Phys. Chem.' (in which there is no experimental work), give lists of the literature of the subject which do not include ESSON's and my papers. Our formula is given, vol. 64, p. 57, but is not referred to elsewhere or discussed. Nothing in VOLKMANN and TRAUTZ's papers leads me to doubt of anything we have written.—A. V. H.]

When m has the constant value 20, the values of n in the fourth column of the table diminish regularly.

The conditions of these experiments are such that no definite measure of the effect of heat energy upon chemical energy can be deduced from them.

In the next paper, vol. 66, pp. 496–510, Trautz obtains a formula for n of a complicated character based on thermodynamical principles and containing expressions involving atomic heat, vapour pressure, and molecular heat of combination. The fundamental theorem of the investigation is open to criticism, and has been shown to be erroneous by Sackur in a paper in 'Zeit. für Electrochemie,' Nov. 15, 1909, 15, 22, p. 865. Trautz uses his expression to calculate the values of k in several experiments, but the values found and calculated do not agree sufficiently to render the expression probable.

In any experiments upon the effect of temperature on chemical change which are affected by the variation of the side effects of temperature enumerated above, the main effect is inevitably masked, because more than one condition is varied at the same time. In the experiments by Harcourt and the author, recorded in the Bakerian Lecture, 1895, and in the experiments by Harcourt set forth in the present paper, 1912, these complications have been avoided and the true relation between temperature and chemical change has been established.]

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ON THE EMISSION VELOCITIES OF PHOTO-ELECTRONS.

BY

A. LL. HUGHES, M.Sc., B.A.,
RESEARCH SCHOLAR OF EMMANUEL COLLEGE, CAMBRIDGE.

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VII. *On the Emission Velocities of Photo-Electrons.*

By A. Ll. Hughes, *M.Sc., B.A., Research Scholar of Emmanuel College, Cambridge.*

(*Communicated by Prof. Sir* J. J. Thomson, *O.M., F.R.S.*)

Received May 21,—Read June 13, 1912.

Contents.

1. *Introduction.*—Since the discovery of the photo-electric effect by Hertz, many experiments have been made on the emission of negative electricity from metallic surfaces when illuminated by light. Yet with regard to many important points the results are often indefinite and contradictory. Most theories of the photo-electric effect indicate definite relations between the velocity of emission of the electrons and (a) the nature of the metal from which they are emitted, and (b) the wave-length of the incident light. Up to the present, however, the experimental evidence as to these two relations must be regarded as quite inadequate to afford any decisive test between rival theories. This research was undertaken to obtain, among other things, quantitative evidence on these two relations.

2. *Previous Work.*—Ladenburg[*] made some valuable experiments on the velocity with which electrons are emitted from metals when illuminated by ultra-violet light. He concluded that the maximum emission velocity was inversely proportional to the wave-length. The velocity varied from metal to metal; thus, for light of wave-length λ 2010, the maximum emission velocity (measured in volts) for platinum was

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[*] Ladenburg, 'Phys. Zeits.,' VIII., p. 590, 1907.

Published separately, August 12, 1912.

1·86 volts, and for zinc 1·12 volts. The source of light used by LADENBURG was a mercury arc. His metals were polished with emery and oil, and were exposed to the atmosphere for some time before the apparatus for measuring the velocity could be exhausted.

MILLIKAN and WINCHESTER[*] in their investigations on the photo-electric effect found enormous differences in the emission velocities from different metals. The values range from 1·34 volts for silver down to 0 volt for lead. Their apparatus was much more complicated than the type of apparatus usually used for measuring the velocities, and the interpretation of their results is correspondingly more open to doubt. As in LADENBURG'S experiments, the newly polished surfaces were unavoidably in contact with the atmosphere for some time before the apparatus was exhausted. These experiments and others show that the state of the surface is of great importance in photo-electric investigations.

Such results led to a search for methods of preparing surfaces which would show greater regularity in their photo-electric behaviour. A promising way of obtaining a clean uncontaminated surface seemed to be to sputter away the surface-layer of a metal *in vacuo*. v. BAEYER and GEHRTS[†] found that the emission velocities from such surfaces were much increased, and concluded that the velocities were the true velocities with which the electrons left the metal. Later experiments[‡] showed that this view was incorrect, and that the electric discharge polarised the surface of the metal in such a way that the electrons were accelerated on passing through the surface film.

New surfaces of liquids can easily be prepared *in vacuo*. It seems very probable that such surfaces are (at all events initially) free from gaseous films which may retard or accelerate the electrons passing through. KLAGES[§] used surfaces of mercury formed *in vacuo*, and KUNZ[||] used similar surfaces of sodium-potassium alloy and of caesium. Surfaces of metals distilled *in vacuo* were used by the author,[‡] and far more consistent results were obtained with them than with the surfaces treated as electrodes.

The law connecting the maximum emission velocity of the photo-electrons with the wave-length has been investigated by LADENBURG[¶] for Cu, Zn and Pt, and by KUNZ[**] for Na-K alloy and Cs. LADENBURG concluded that the velocity of the electron was proportional to the frequency. JOFFÉ[††] pointed out that the experimental results

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[*] MILLIKAN and WINCHESTER, 'Phil. Mag.,' XIV., p. 188, 1907.

[†] v. BAEYER and GEHRTS, 'Verh. d. D. Phys. Ges.,' p. 870, 1910.

[‡] HUGHES, 'Proc. Camb. Phil. Soc.,' XVI., p. 167, 1911; v. BAEYER and TOOL, 'Verh. d. D. Phys. Ges.,' p. 569, 1911.

[§] KLAGES, 'Ann. d. Phys.,' XXXI., p. 343, 1910.

[||] KUNZ, 'Phys. Rev.,' XXXIII., p. 208, 1911.

[¶] LADENBURG, *loc. cit.*

[**] KUNZ, *loc. cit.*

[††] JOFFÉ, 'Ann. d. Phys.,' XXIV., p. 939, 1907.

would satisfy equally well the law that the energy (or the square of the velocity) was proportional to the frequency. The reason for this is that Ladenburg had only a short range of wave-lengths available for producing photo-electrons. One has to decide whether the experimental results lie on a straight line or on a short piece of a parabola some distance away from its vertex. Kunz concluded that his results supported Ladenburg's law. They are, however, in good agreement with the energy law, except in the red end of the spectrum.

3. *Experiments with Surfaces Formed* in vacuo.—It was shown in an earlier experiment that the maximum emission velocities of photo-electrons from surfaces of Zn, Cd and Hg, all distilled *in vacuo*, were approximately the same. It was thought advisable to investigate the velocities of the photo-electrons from a surface of mercury prepared *in vacuo* by the method described below.

The mercury, on which the light[*] fell, was contained in the shallow iron dish C (fig. 1) which was 2 cm. in diameter and 1 mm. deep. (The scale of the reservoir D is ten times less than that of the rest of the apparatus.) New surfaces could be formed by opening the tap T and allowing the mercury to overflow at C. The apparatus was evacuated before this was done, and the vacuum was maintained by the liquid air method. The maximum emission velocity was measured by the minimum potential between B and C necessary to prevent electrons leaving C, and passing through the gauze to A. The brass cylinder E and B were kept at a potential of −2 volts relative to A, in order to prevent the escape of electrons from A due to reflected light. The gauze B was symmetrically situated with respect to A and C, and as a potential difference of about 2·15 volts between C and B was sufficient to stop all the electrons passing from C to B, this potential could be taken as a measure of the velocity without any correction for the "streufeld."

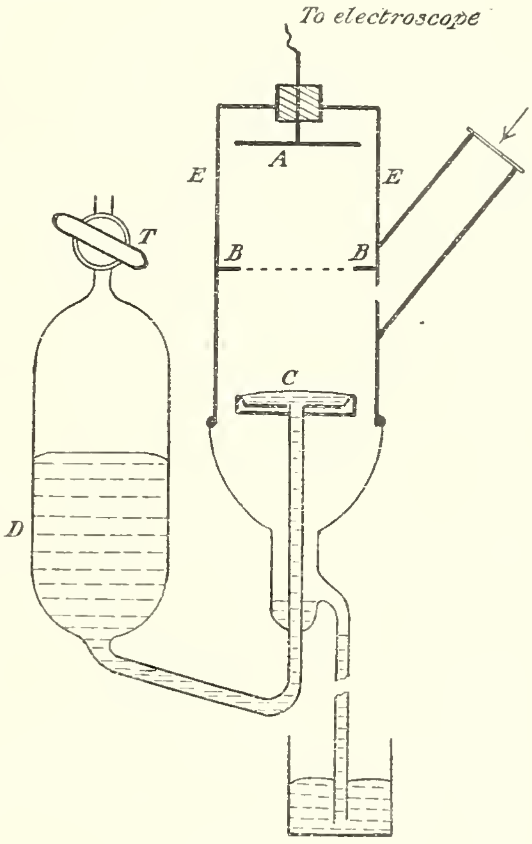

Fig. 1.

Several new surfaces were formed, and the maximum emission velocity was found to be 2·15 volts. The arrangement used by Klages was not suitable for the accurate measurement of the velocities; one can only say from his tables that the maximum emission velocity is somewhere between 2·0 and 2·6 volts. It might be urged that a surface

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[*] The unresolved light from the mercury arc was used in this experiment. The shortest wave-length was therefore λ 1849.

film of gas could be formed, even *in vacuo*, in a few seconds after the exposure of a new surface. To meet this objection a more drastic treatment was devised. Velocity measurements were made while the mercury was in motion. The tap T was adjusted so that the mercury overflowed at C at the rate of about 3 c.c. per second. On considering this, together with the dimensions of the dish, it is clear that no part of the surface exists for more than a small fraction of a second. Owing to the fact that the mercury in D was soon exhausted, accurate measurements could not be made. However, it can be said that the maximum emission velocity from the continuously forming mercury surface was 2·15 ± ·05 volts. This is practically the same value as that obtained for distilled Zn, Cd, and Hg. It seems extremely unlikely that any retarding film could be formed on the Hg surface in this experiment, hence it is concluded that 2·15 volts represents the actual emission velocity from Hg. The agreement with the distillation experiments supports the view that metals prepared by distillation *in vacuo* are also free from surface films.

In the course of this experiment evidence was obtained which indicates that photo-electrons are emitted nearly equally in all directions. The photo-electric current from C to A was measured in the absence of an electric field between C and B—(1) with, (2) without, a strong magnetic field along the axis of the cylinder. In the first case, when the electrons were compelled to follow the lines of magnetic force, the current was 33 times larger than when the electrons were not constrained to follow any path. The ratio of the solid angle subtended by the gauze B at the mercury surface to 2π, was about 1 to 38. This indicates that the ratio of the electrons emitted inside the cone to those emitted outside is of the order of the respective solid angles.

From the experiments described and discussed in this section, it was concluded that the most satisfactory surfaces to use in the investigation on the velocities of the photo-electrons were those prepared by distillation *in vacuo*.

4. *The Source of Light.*—The mercury arc in quartz glass was used as the source of light in this research. In the early stages of the work a very intense spark between Al terminals, produced by the primary transformer of a Tesla apparatus, was used in order to get very short wave-lengths of appreciable intensity. The results obtained with this intense spark were most irregular, frequently emission velocities as high as 10 or 12 volts were obtained. Direct experiment showed that this was not an effect due to electric waves. The spark was finally abandoned in favour of the mercury arc which gave very regular results, although the energy available in the short wave-lengths was far less.

To produce monochromatic light, a Hilger quartz spectrograph was adapted for the purpose. A sliding slit was arranged to pass over the focal plane of the camera side of the instrument. The slit having been set so as to transmit any desired wave-length, the mercury arc was placed close to it and monochromatic light emerged from the collimator. The aperture of the slit was 14 mm. by 2 mm., the collimator lens was 2 cm. in diameter, and of 20 cm. focal length. Hence the amount of light which passed through the monochromator was a very small fraction of that emitted by the lamp.

Some anomalous results in the earlier experiments led to the discovery that the monochromator did not isolate the wave-lengths perfectly. It was set so as to isolate one wave-length, and the light which emerged was analysed by means of a second quartz spectrograph. It was found that, in addition to the isolated line, all the other wave-lengths were present though much weaker. This effect leads to spurious results when working with the longer wave-lengths which are made to appear photo-electrically active when they are not. This error only becomes appreciable when using wave-lengths longer than λ 3000. Sheets of mica of different qualities were found to cut off wave-lengths shorter than λ 2967 and λ 3125, thick glass transmitted down to λ 3340, and a solution of chromium chloride absorbed all wave-lengths shorter than λ 3665. During the course of the investigation, a new wave-length λ 1849 in the mercury arc spectrum was discovered.*

5. *The Apparatus.*—The amount of energy which is transmitted by the monochromator when set to isolate any one wave-length is exceedingly small. The small photo-electric effect which would result from this feebleness in the light determined that great sensitiveness to electrical changes must be an important feature of the apparatus. Hence it is that, in the apparatus which was finally adopted, the electrical capacity is very small. The apparatus is shown approximately to scale in fig. 2.

The plate on which the light is incident is a disc, N, of nickel, 3 cm. in diameter. The disc is suspended by a thin wire from a slide, S, which runs in grooves in the tube T. The disc and wire are insulated from S by the quartz rod Q. This system can be raised or lowered by means of the winch, E, which is a glass tap with a groove cut round the barrel. S is suspended from the winch by a silk thread. The metal to be distilled is heated in a little furnace, F. This is a quartz-ignition spoon into which fits a thin quartz cup containing the metal. Between the cup and the quartz spoon there is a thin sheet of Pt or Ni, which can be heated to redness by a current. As the vacuum forms a good heat insulator, the metals can be raised to a high temperature. To get rid of occluded gases the quartz furnace containing the metal is heated for a long time in an auxiliary vacuum, until little or no gas is evolved during distillation. In this way surfaces of Ca, Bi, Sb, Zn, Cd, Se, Pb, Mg, and As were deposited on the disc, the whole process being carried out in a liquid air vacuum. When the distillation is finished the disc is raised to the position shown in the diagram.

Contact with the tilted electroscope is made by means of a spring, S′, which rests on a short cross wire behind the disc. The electroscope is placed close to the apparatus. To keep the capacity as low as possible thin connecting wires are used. The capacity of the insulated system is probably below 10 cm.

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* HUGHES, 'Proc. Camb. Phil. Soc.,' XVI., p. 428, 1912.

The maximum emission velocity is given by the potential to which the disc rises when illuminated. As this frequently exceeds 2 volts there is danger of insulation leak. This is avoided by charging the case of the apparatus to a negative potential slightly less than the maximum emission velocity. The potential of N will then only rise to a fraction of a volt. Hence the ebonite insulation *e* and the sulphur insulation *f* have only to insulate for potential differences of less than ·1 volt. The quartz rod, Q, however, has to insulate the full difference of potential. Fortunately its insulating properties were found to be practically perfect. The potential to which the system rises is always measured by comparison with a potentiometer.

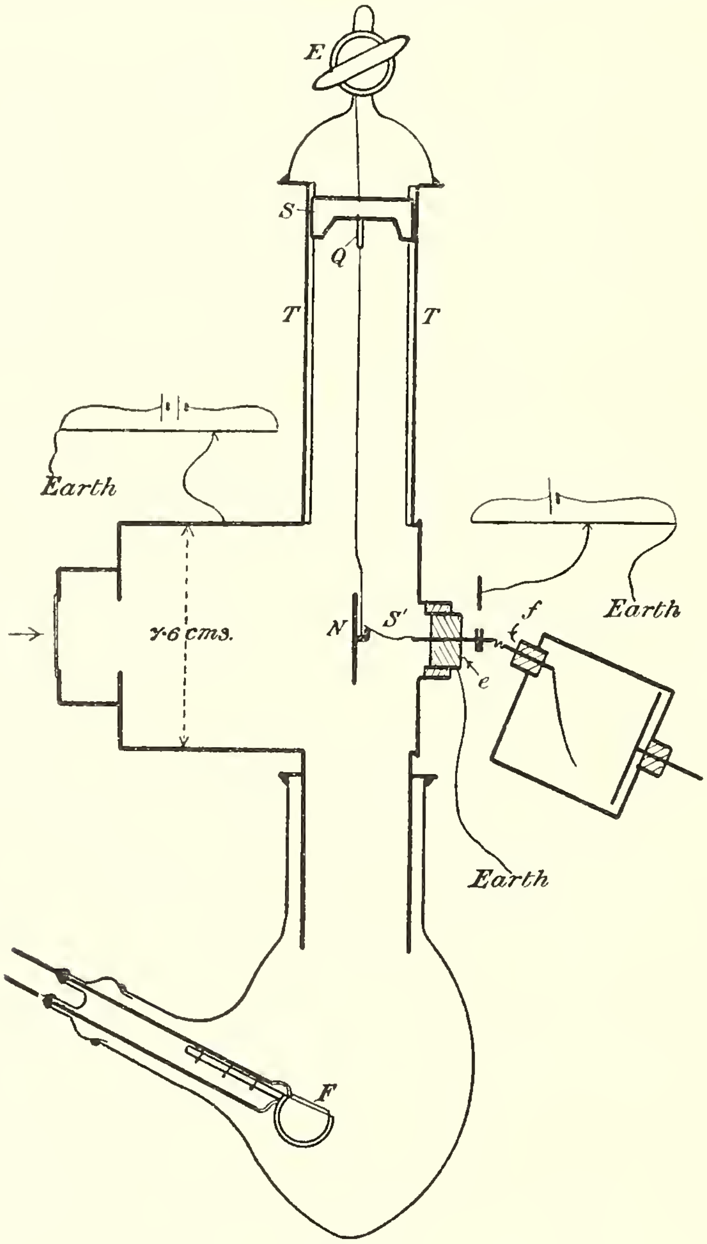

Fig. 2.

In order to produce a very good vacuum, the apparatus is always exhausted by a Toepler pump to a pressure of ·01 mm. before communication with the cooled charcoal tube is made.

6. *Velocity Distribution Curves.*—A curve giving the relation between the photo-

electric current and the potential difference between the illuminated plate and the surrounding case is called a velocity distribution curve. When the potential difference is such as to retard the electrons, then the photo-electric current is usually taken to be a measure of the number of electrons possessing velocities greater than that implied by the potential difference. Curve I., fig. 7, is a typical velocity distribution curve. Electrons whose velocities range from a maximum down to zero appear to be present, while a large number apparently require a small accelerating potential to enable them to get away from the plate. LADENBURG* and v. BAEYER† obtained curves which implied that there was a minimum velocity present as well as a maximum velocity. The majority of curves which have been published show no trace of a minimum velocity. v. BAEYER has shown that the velocity distribution curves are liable to distortion by reflection of electrons, and he says that this effect also apparently reduces the maximum emission velocities. As the accurate determination of the maximum emission velocity is of prime importance in the experiments described later, it is essential to examine very carefully all possible ways in which incorrect values may arise.

(A) *Reflection of Electrons.*—Let us assume that the illuminated plate emits electrons whose velocities range from a maximum down to zero. The distribution curve will be of the form ABC, fig. 3. If reflection of electrons by the surrounding case takes place this curve will be modified. When there is no potential difference between the plate and the case, the part bB represents the number reflected back to the plate, and hence the actual photo-electric current is Ob. A small potential accelerating the electrons from the plate is sufficient to stop all the reflected electrons, and the experimental curve AbC joins the ideal curve ABC. v. BAEYER says that the effect also reduces the maximum emission velocity as measured by the potential to which the plate rises when illuminated. It is difficult to see how this can be so, for before any electrons can be reflected to the plate a larger number must be emitted by the plate, and it should go on charging up (though more slowly) to the same potential whether reflection takes place or not.

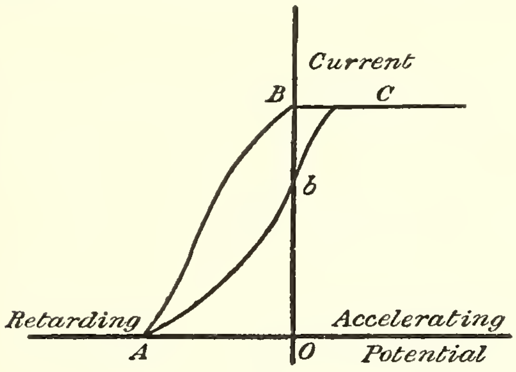

Fig. 3.

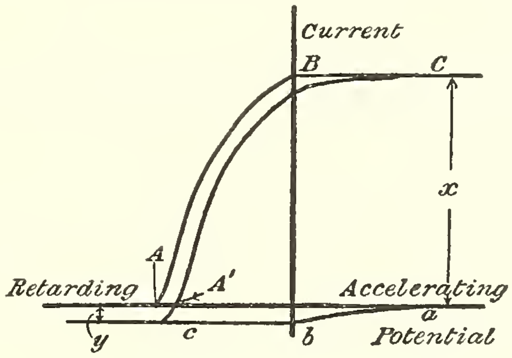

Fig. 4.

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* LADENBURG and MARKAU, 'Verh. d. D. Phys. Ges.,' IX., p. 562, 1908.

† v. BAEYER, *loc. cit.*

(B) *Reflection of Light.*—Let ABC, fig. 4, represent the velocity distribution curve from the illuminated plate. If a little light gets to the inside of the case, by reflection or otherwise, then the curve *abc* will be the velocity distribution curve for the current from the case to the plate. Experimentally the sum of these two curves is observed. A′ is the potential to which the system will charge up, and this is less than the real value A of the maximum velocity. It is clear that the difference AA′ increases as the ratio of the reflected effect y to the direct effect x increases.

(C) *Effect of an Electron approaching the Boundary Obliquely.*—Consider photo-electrons leaving the point P (fig. 5) with equal velocities and in all directions. We shall see that the velocity distribution curve is not ABC (fig. 6) but A*b*C, which implies, on the usual interpretation, that all velocities from A down to zero are present. Let V_0 be the potential required to stop the electrons travelling normally. An electron starting in the direction PN′ will describe a parabola. The potential difference, which will allow this parabola to graze the plane NN′ is $V_0 \cos^2\theta$. If we assume that the electrons are emitted equally in all directions, then the number of electrons emitted between the cones θ and $\theta+d\theta$ is proportional to $\sin\theta$. Hence a number $n\int_0^\theta \sin\theta\, d\theta$ of electrons apparently have a velocity equal to and greater than $V_0 \cos^2\theta$, and therefore the relation between the number possessing velocities above a certain apparent velocity and that velocity is parabolic. The experimental velocity distribution curve would be A*b*DC and not ABDC.

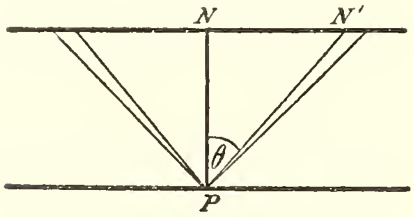

Fig. 5.

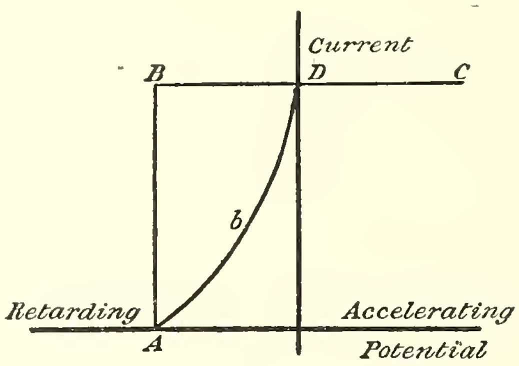

Fig. 6.

The usual experimental arrangements are not so simple as in this case, but it easily follows that whenever an electron approaches a boundary obliquely then the potential difference just necessary to stop it is less than that potential which corresponds to its actual velocity.

(D) *The Effect of Magnetic Fields.*—A weak magnetic field (such as the earth's field) is often sufficient to impose a considerable curvature on the path of a photo-electron. This would cause many electrons to approach the boundary with an increased tangential component of velocity and so give rise to the effect discussed in the last paragraph. Some of the slower electrons would never get away from the illuminated plate, for in the absence of an electric field, they would describe complete circles inside the apparatus. Thus a magnetic field would account for the part B*b*, fig. 3, which is usually attributed entirely to reflection of electrons.

From a consideration of these effects, one must conclude that the velocity distribution curves usually obtained do not give anything like the actual distribution of velocities with which the electrons emerge. Many velocity distribution curves have been given and discussed in various papers, but the complications arising from effects (C) and (D) have been completely overlooked.

Experimental.—Experiments were made to see how the velocity distribution curves could be affected by magnetic fields and the presence of gas. In particular, the corresponding effect on the maximum velocity was investigated. The apparatus used is shown in fig. 2. The disc N was covered with a layer of zinc. The unresolved light from a mercury arc was used.

In column I. the results obtained under normal conditions are given. The vacuum was obtained by the liquid air method, and the pressure was certainly below ·0005 mm. The earth's magnetic field (about ·5 gauss) was approximately parallel to the disc.

In column II. the results are given when an electromagnet was held near the apparatus. The field inside the apparatus was far from uniform, but at the centre it was about 7 gauss.

In column III. the results are given when the magnetic field was increased to 30 gauss.

The results given in column IV. were obtained with air in the apparatus at a pressure of ·03 mm.

The results given in Table I. are plotted in fig. 7.

TABLE I.

Potential.	Photo-electric current.			
	I.	II.	III.	IV.
40 volts	83		86	
30	83		85	
20	82		80	
10	82	82	72	79
4	82	80	54	71
2	82	77	38	63
1	80	72	19	52
0	35·5	22·5	3·5	18
− ·7	17·2	7·0	1·0	5
− 1·0	10·0	4·5	·5	2·5
− 1·3	5·0	2·0	0	·5
− 2·0	0	0	0	0
− 10·0	− 1·5	− 1·0	0	0
Maximum velocity . . .	1·93 volts	1·76 volts		1·86 volts

Let us consider whether reflection of electrons is adequate to explain the part AB in curve I., fig. 7. Let ω be the solid angle subtended by the disc at any part of the case in front of the disc. In the expression for the number of the electrons which get back to the disc there will be a factor $\omega/2\pi$. This is roughly ·1 for this apparatus. The other factor is less than 1, otherwise it would mean complete reflection of electrons. The ratio of AB to AO is therefore much bigger than can be accounted for by reflection of electrons. The earth's magnetic field is more likely to account for this effect. It will be noticed that the maximum velocity is apparently reduced by the magnetic field. This is due to the fact that the paths of the electrons are so curved that none of them strike the case normally. As long as a few electrons impinge on the case normally the correct maximum velocity will be given. This was shown in the following experiment. Two coils were arranged on opposite sides of the apparatus to assist or to oppose the earth's field. Light of wave-length λ 2537 caused the plate to charge up to ·70 volt. This remained the same for all magnetic fields from 0 to 2 gauss. With greater fields the maximum velocity began to diminish slightly. This shows that, for velocities of ·7 volt (and above), the effect of the earth's magnetic field (·5 gauss) can be ignored.

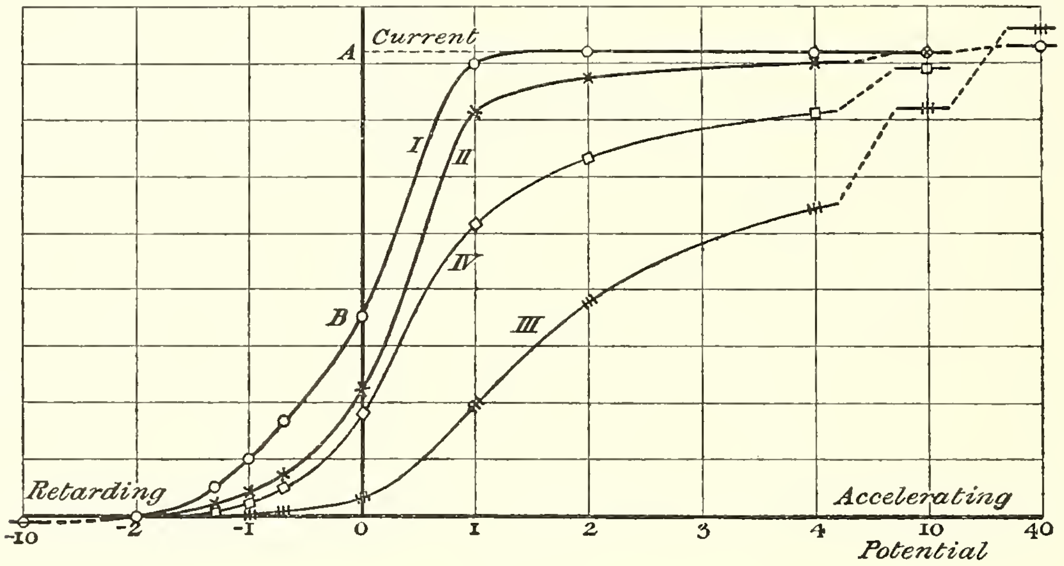

Fig. 7.

Column IV. shows that the presence of enough air to allow the majority of the electrons to collide with air molecules modifies the velocity distribution curves and reduces the maximum velocity from 1·93 volts to 1·86 volts. On opening communication with the cooled charcoal tube, the emission velocity rose to 1·93 volts in five minutes. It would take considerably longer for the pressure of the residual gas to reach its lowest value.

It therefore appears that reflection of electrons, the earth's magnetic field, and the degree of vacuum used in these experiments have no appreciable effect on the maximum emission velocities.

There remains to consider the effect due to reflected light. In column I., Table I., the ratio of the effect due to reflected light to the direct effect is 1·5 to 85. Consider what happens at the point A′ where the curve cuts the axis (fig. 4). Only the shortest wave-length has any tendency to cause the plate to charge up positively, while it receives negative electricity due to the whole range of wave-lengths reflected to the sides. When using monochromatic light the latter effect would be much less. A zinc plate charged up to 2·02 volts when illuminated by the unresolved light from the mercury arc. When the shortest wave-length λ 1849 was isolated and directed to the plate it charged up to 2·06 volts. It is evident therefore that 2·06 volts was very nearly the true velocity with which the fastest electrons were emitted.

From these considerations it seems quite justifiable to take the potential to which the disc rises as being the actual maximum velocity of emission.

7. *Experiments with Monochromatic Light.*—In the following pages experiments are described from which it is concluded that the maximum energy of emission of photo-electrons, and not the maximum velocity, is proportional to the frequency of the incident light. It seemed the best course to work not with a large number of different wave-lengths, but with three selected wave-lengths, and having fixed on these, to determine the corresponding emission velocities with the highest possible accuracy. Observations were sometimes made with other wave-lengths, but the proof rests largely on the experiments made with λ 2537, λ 2257, and λ 1849.

Nearly all the elements distilled in these experiments were pure. In most cases the distilled portion was tested chemically at the end of the experiment.

Cadmium.—The total photo-electric currents from a surface of distilled cadmium corresponding to the lines λ 2537, λ 2257, and λ 1849, were approximately proportional to 40, 20, and 1. The times taken for the disc to attain its final potential were in the inverse order. The rate at which the final potential was attained, when using λ 1849, was so slow that it always required about an hour to determine the final potential, even when the system was initially charged to a value ·1 volt below its final value. It was this excessive feebleness of the light that made the experiments difficult, even when the electrical conditions were at their best.

In Table II. the experimental results are given. The velocities, corresponding to the three wave-lengths, were determined three times each in rotation. For reasons discussed in section 4, the lines λ 2967 and λ 3340 were obtained by the transparency limits of mica and glass. In the fourth and fifth columns the theoretical values are given on the energy law and LADENBURG's law respectively, taking the values for λ 2537 and λ 1849 as standard.

The velocity predicted by the energy law for λ 2257 is in much better agreement with the experimental value than that predicted by LADENBURG's law. The experimental values for λ 2967 and λ 3126 are lower than the theoretical values, on account of the earth's magnetic field curling the paths of the photo-electrons so much that none of them impinge on the case normally. Though the experimental velocity for λ 3126 is given as 0 in the table, a well-marked current was obtained with an

TABLE II.—*Cadmium.*

Wave-length.	Velocities (in volts).			Mean velocities.
λ 2537	·901	·901	·890	·897
λ 2257	1·420	1·431	1·431	1·427
λ 1849	2·480	2·480	2·480	2·480

Wave-length.	Frequency, n.	Experimental velocities.	$V = kn - V_0$.	$\sqrt{V} = k'n - c$.
λ 1849	1623 × 10^{12}	2·480 volts	[2·480]	[2·480]
λ 2257	1329	1·427	1·424	1·339
λ 2537	1182	·897	[·897]	[·897]
λ 2967	1010	·148	·286	·495
λ 3126	960	0	·101	·398
λ 3340	898	No effect.	(− ·12)	·293

$V_0 = 3·347$ volts; $k = 3·590 \times 10^{-15}$.

accelerating potential of ·5 volt. There was no leak due to λ 3340 under the same conditions. In this region, perhaps the best test of the energy law is that there is an emission of electrons with λ 3126, but not with λ 3340, and this is exactly what theory predicts. According to LADENBURG'S law, one might expect an emission of electrons down to λ 4000.

Dry oxygen at 140 mm. was admitted to the apparatus for 15 minutes. This caused a reduction (after evacuating again) in the total leak for each wave-length of about five times. The result of this was that it was impossible to measure the maximum emission velocity corresponding to λ 1849. The velocity changes are:—

λ 1849	effect too small.
λ 2257	·276 volt reduction.
λ 2537	·244 ,, ,,
λ 2967	no effect.

The results of another experiment with a fresh surface of distilled Cd are given in Table III.

As before, there is close agreement between the experimental value for λ 2257 and the value predicted on the energy law. The energy law also predicts that the effect should set in between λ 3126 and λ 3340.

The apparatus was filled with oxygen at 160 mm. for 10 minutes. A reduction in the total effect was again noticed. The velocity changes are:—

λ 1849	effect too small.
λ 2257	·213 volt reduction.
λ 2537	·244 ,, ,,
λ 2967	no effect.

TABLE III.—*Cadmium.*

Wave-length.	Velocities (in volts).			Mean velocities.
λ 2537	·869	·869	·869	·869
λ 2257	1·399	1·389	1·389	1·392
λ 1849	2·459	2·459	2·448	2·455

Wave-length.	Frequency, n.	Experimental velocities.	$V = kn - V_0$.	$\sqrt{V} = k'n - c$.
λ 1849	1623×10^{12}	2·455 volts	[2·455]	[2·455]
λ 2257	1329	1·392	1·396	1·309
λ 2537	1182	·869	[·869]	[·869]
λ 2967	1010	·159	·249	·468
λ 3126	960	·042	·070	·373
λ 3340	898	No effect.	(– ·15)	·274

$V_0 = 3·384$ volts ; $k = 3·597 \times 10^{-15}$.

From these two experiments with oxygen one may conclude that the effect of contact with oxygen is to move the line $V = kn - V_0$ parallel to itself, the value of V_0 being increased.

The results of a third experiment with cadmium are given in Table IV.

TABLE IV.—*Cadmium.*

Wave-length.	Velocities (in volts).				Mean velocities.
λ 2537	·716	·716	·720	·720	·718
λ 2257	1·256	1·282	1·267	1·282	1·270
λ 1849	2·380	2·395	2·385		2·387

Wave-length.	Frequency, n.	Experimental velocities.	$V = kn - V_0$.	$\sqrt{V} = k'n - c$.
λ 1849	1623×10^{12}	2·387 volts	[2·387]	[2·387]
λ 2257	1329	1·270	1·275	1·185
λ 2537	1182	·718	[·718]	[·718]
λ 2967	1010	0	·068	·334
λ 3126	960	No effect.	(– ·12)	·253

$V_0 = 3·754$ volts ; $k = 3·784 \times 10^{-15}$.

With a small accelerating potential there was a decided leak with λ 2967, but not with λ 3126.

From these three experiments with different surfaces of cadmium distilled *in vacuo*, it appears conclusive that the results satisfy the energy law accurately, and that LADENBURG'S law is incorrect. This conclusion is based on the results for λ 2537, λ 2257, and λ 1849. Additional support is derived from the fact that the photo-electric effect sets in at the wave-length predicted by the theory.

Zinc.—Experiments similar to those on cadmium were carried out with surfaces of distilled zinc. The energy law was found to be obeyed as accurately as in the case of cadmium. As the experimental results for zinc (and for all the metals subsequently mentioned) are very similar to those for cadmium, it is unnecessary to reproduce them here. The velocities in any experiment can be calculated from the values of k and V_0 which follow. (Each pair of values for k and V_0 represents a separate distillation and a table similar to Tables II., III., and IV.)

	k.	V_0
	$3 \cdot 70 \times 10^{-15}$	3·72 volts.
	3·82	3·79
	3·83	3·83
	3·79	3·73
Mean . . .	3·79	3·77

Magnesium.—Rather more difficulty was experienced in working with magnesium than with zinc or cadmium. Except in the experiment where $V_0 = 2 \cdot 91$ volts, the effect for λ 1849 was rather smaller than in the other experiments, and it was therefore more difficult to determine the corresponding maximum velocity. The results of the experiments are :—

	k.	V_0.
	$3 \cdot 45 \times 10^{-15}$	2·91 volts.
	3·33	3·25
Mean . . .	3·39	3·08

Bismuth.—The results for bismuth are summarised by the following values for k and V_0 :—

	k.	V_0.
	$3 \cdot 60 \times 10^{-15}$	3·49 volts.
	3·65	3·48
	3·63	3·14
Mean . . .	3·63	3·37

Antimony.—The values for k and V_0 for antimony are :—

	k.	V_0.
	$3·72 \times 10^{-15}$	3·67 volts.
	3·66	3·54
Mean . . .	3·69	3·60

Calcium.—Owing to its high boiling point, calcium was very difficult to distil. Some trouble was experienced in getting the velocity corresponding to λ 1849. In the experiment denoted by $k = 3·01 \times 10^{-15}$ and $V_0 = 2·37$ volts, a slight photo-electric leak was obtained with λ 3650 which (with these constants) is just within the range of wave-lengths capable of producing a photo-electric effect on the energy law. This was the only occasion in the course of the research when λ 3650 was found to produce a photo-electric effect :—

	k.	V_0.
	$3·30 \times 10^{-15}$	2·80 volts.
	3·01	2·37
	3·22	2·55
Mean . . .	3·17	2·57

Lead.—The experiments on lead are represented by the following values of k and V_0 :—

	k.	V_0.
	$3·58 \times 10^{-15}$	3·51 volts.
	3·51	3·33
Mean . . .	3·55	3·42

Selenium.—All the elements that have been tested belong to groups 2, 4, and 5 of the periodic table. They are all metals, and are generally more or less electropositive in character. Selenium, which belongs to group 6, is a non-metal, and is much more electronegative. There is not very much variation in the photo-electric behaviour of the seven metals whose photo-electric behaviour has been investigated, and it is probable that one would not get much variation until one tried an element possessing widely different properties. Selenium might, therefore, be expected to show some difference in its photo-electric properties.

Not the slightest effect was obtained with λ 2537 or with λ 2257, but a well-marked effect was obtained with λ 1849. The total photo-electric effect for this wave-length appeared to be quite as big as for any of the other elements previously tested. A very thin layer of Se was distilled first, and the maximum emission velocity corresponding to λ 1849 was 1·01 volt. Then a much thicker layer was distilled, and the velocity was again 1·01 volt. The selenium was left for about fifty hours in contact with the residual gases which came out from the charcoal ($\simeq$ ·01 mm.). There was no change in the velocity. Then air at 200 mm. was admitted for 15 minutes. There was no change in the velocity even after this. It is clear that the photo-electric properties of selenium are not nearly so much affected by contact with air as those of zinc or cadmium.

As selenium would only emit electrons with λ 1849, it was not possible to find k and V_0 for selenium. If we assume selenium to have approximately the same k as Bi and Sb (which are in the next group), we find that V_0 for selenium is about 4·8 volts.

Arsenic.—Four distillations of arsenic were made. The effects of the first two were so much smaller than the effects with other metals that velocity measurements were not undertaken. Some pure arsenic from another source was obtained, but still the unusually small leak was obtained and so the effect appeared to be real. There was no photo-electric effect with λ 2537. The effect set in between λ 2386 and λ 2330. With λ 2257 the effect was far smaller than with other metals. The effect with λ 1849 was considerably smaller than with other metals, but the difference was nothing like so great as in the case of λ 2257. It was impossible to determine the emission velocities with any accuracy. One distillation gave ·44 volts for λ 2257 and 1·50 volts for λ 1849. The other distillation gave ·33 volts for λ 2257 and 1·40 volts for λ 1849. Even when the greatest precautions were taken, these values could not be determined to within ·1 volt. Hence we can only say that k lies between $3{\cdot}6 \times 10^{-15}$ and $3{\cdot}8 \times 10^{-15}$, and that V_0 is of the order 4·4 – 4·6 volts.

Zinc Chloride.—Zinc chloride was heated in the quartz furnace in the vacuum for some time to drive off moisture. Then the disc was lowered in order to receive a layer of the distilled salt. There was not the slightest trace of any photo-electric leak even when the unresolved light from the mercury arc fell upon the disc. An unexpected effect was then observed. Ordinary undried air was admitted to the apparatus at a pressure of 760 mm. for 15 minutes. On evacuating again, a slight photo-electric leak was obtained. Under similar conditions a zinc plate would emit a current of the order 10^5 times as great. This leak from the zinc chloride after contact with air increased by about 80 per cent. in the course of an hour. The plate charged up to about ·3 volt when the unresolved light from the mercury arc fell upon it. There was not enough effect to use the monochromator. After the exposure to air, the surface of the zinc chloride, previously quite dry, appeared slighly moist.

Quantitative experiments on the total photo-electric effect were not made, but, as far as one could judge from the rate at which the plate charged up, the effect was much the same for all metals except arsenic. The reduction in the total effect for cadmium after the admission of oxygen was certainly far greater than the differences between the effects for the metals distilled *in vacuo*.

8. *Discussion of the Results.*—(i.) It is clear from these experiments that the energy with which the fastest electrons emerge from a plate illuminated by ultra-voilet light

is proportional to the frequency of the light. The evidence is based mainly on observations made with the wave-lengths λ 2537, λ 2257, and λ 1849. The velocity V, measured in volts, is related to the frequency n by the formula $V = kn - V_0$. This implies that the emission of photo-electrons should cease below a certain definite frequency, and this was found to be the case experimentally. We may therefore consider the energy law to be established over the whole range of wave-lengths which are effective in causing the emission of photo-electrons.

(ii.) The great differences between the results of experiments on the photo-electric effect, which have been published from time to time, are no doubt very largely due to more or less tenacious gaseous films covering the surfaces. The method of distillation *in vacuo* was adopted to avoid the presence of these gaseous films, as it is impossible to get rid of them when once they are formed. If a metal distilled *in vacuo* soon became covered with a retarding film, then we should not expect the agreement which was obtained between the experiments on distilled mercury and those on the continuously forming mercury surface, where the surface is exposed to the light as soon as it is formed.

Millikan[*] and Wright[†] have obtained abnormally high values for the emission velocities from metals which were kept in a very good vacuum for several months. During that period the metals were frequently illuminated by intense ultra-violet light. Millikan explains the results by a purification of the surfaces from gaseous films which are considered to have a marked retarding effect on the electrons. They also found that when these abnormally high values were obtained the emission velocity was a maximum (13·5 volts for Al) for the wave-length λ 2166. It is possible that, in Millikan and Wright's experiments, the long-continued exposure to ultra-violet light produces a surface polarisation, for when the metal emits electrons it is acting as a cathode. There certainly seems to be more opportunity for unknown changes to take place, perhaps producing surface polarisation, than in these experiments. Here the measurements were usually complete in about four hours after the distillation had taken place.

(iii.) Do the electrons which emerge from a plate illuminated by ultra-violet light all possess the same velocity, or do their velocities range from a maximum down to zero? The latter would almost certainly be the case if the electrons suffered various amounts of scattering by the molecules in the surface before they emerged. The discussion in section 4 of this paper shows that the so-called velocity distribution curve obtained by plotting the leak against various retarding potentials is mainly a function of the obliquity with which the electrons strike the surrounding boundary. This question cannot therefore be answered from the curves given in fig. 7. In some experiments of Ladenburg, to which this consideration does not apply to the same extent, it appeared that monochromatic light produced electrons all of the same velocity.

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[*] Millikan, 'Phys. Rev.,' XXX., p. 287, 1910.

[†] Wright, 'Phys. Rev.,' XXXIII., p. 43, 1911.

It would follow from this, that only those electrons which do not undergo any scattering (or, more accurately, which do not suffer any reduction in velocity through scattering) can emerge. It is proposed to investigate this important point in further experiments.

(iv.) The values of k and V_0 (Table V.) for the elements investigated in this research change in the same direction, though the changes in V_0 are considerably greater than those in k. The variations in k are a little larger than the possible errors of experiment.

The photo-electric effect was one of the first phenomena to be interpreted on the quantum theory of radiation. If the energy of the photo-electron is equal to that in the quantum, hn, where h is PLANCK'S constant, then we should have

$$Ve = hn.$$

This gives a definite value for our k. The value of h/e is numerically equal to $4 \cdot 19 \times 10^{-15}$. The experimental values of k, which vary from $3 \cdot 17 \times 10^{-15}$ to $3 \cdot 79 \times 10^{-15}$, suggest, on this view, that only a fraction of the energy of the quantum is transferred to the electron. Had the experimental values for k been grouped about the theoretical value h/e, one would almost be compelled to conclude that k was a constant for all metals and equal to the quotient of these two universal constants. However, as the experimental values are well outside the theoretical value, there is no reason on the quantum theory why they should be the same for all elements, as the sharing of the energy between the electron and the parent molecule may depend on the nature of the element.

The view that the quantum is a localised vehicle for radiant energy of dimensions comparable with those of a molecule is not now accepted. The earlier view led to a very simple explanation of photo-electricity. Nevertheless, some new way of considering the phenomena in terms of the quantum theory may explain many of the results. A molecule may have to be in a condition to accumulate energy to the amount hn before it can emit an electron carrying away a definite and, for any one substance, a constant fraction of the energy away with it. In some way such as this the energy law could be accounted for.

(v.) Sir J. J. THOMSON* has given a theory of the photo-electric effect, based on resonance, which leads to the law verified in these experiments, that the energy of the photo-electron is proportional to the frequency of the light. It was shown that if an electron rotates on a certain cone at whose apex there is an electrical doublet, its energy of motion is proportional to the frequency. If light of the same period passes over the system, resonance takes place, and the electron is expelled with about the same energy as it had in its orbit.

(vi.) The experimental relation $V = kn - V_0$ suggests that the electron starts initially

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* Sir J. J. THOMSON, 'Phil. Mag.,' XX., p. 238, 1910.

with an amount of energy $e.kn$ and that $e.V_0$ represents the loss of energy by the time it has emerged from the surface. We may regard this $e.V_0$ as being made up of two parts, $V_1.e$ the loss of energy in passing out of the molecule and $V_2.e$ the loss of energy in passing through the retarding surface layer. It is very probable that V_2 is zero for surfaces prepared by distillation of metals *in vacuo*. The effect of admitting oxygen for a short time to the apparatus, when the disc was covered with a new surface of cadmium, was to increase V_2 from 0 to about ·3 volt. A previous research* showed that oxygen was effective in reducing the emission velocities from Cd and Zn and other metals while hydrogen was ineffective. This is in agreement with a view advanced by Sir OLIVER LODGE and others, that oxygen is mainly responsible for the contact potential. On this theory, however, the oxygen layer is positive with respect to the metal, while to account for the reduction in the velocity the layer should be negatively charged.

V_1e may be identified with the work required to take an electron away from a molecule. Unless the quantity kn exceeds V_1, light is incapable of producing a separation of the electron from the molecule. If the V_0 given by these experiments is equal to V_1, then the smallest frequency capable of exciting the photo-electric effect should be identical with the smallest frequency capable of producing ionisation in the vapour of the metal. An assumption is made here that ionisation in gases by light is essentially the same thing as the photo-electric effect.

An inspection of the values of V_0 in Table V. shows that the work of withdrawing an electron from a molecule is least for calcium, the most electropositive element in the table, and greatest for the more electronegative elements.

(vii.) We may apply these principles to determine the work required to ionise a molecule of oxygen. From my experiments† on the ionisation of the air by ultra-violet light, I concluded that air (or more probably the oxygen in it) is only ionised to an appreciable extent when light of wave-length shorter than about λ 1350 is absorbed in it. An examination of the results given in PALMER'S paper‡ justifies this estimate. What value shall we give to k for oxygen? Fortunately the values of k do not alter much, so a mean may be taken without much error. The mean of all the k's (omitting k for the electropositive calcium) is $3{\cdot}62 \times 10^{-15}$. The mean k for Bi and Sb is $3{\cdot}66 \times 10^{-15}$, and these elements resemble oxygen somewhat more than the other elements. The value of $V_1 (= kn)$ works out to be 8·0 volts. DEMBER§ finds that the work required to ionise a molecule of air is $1{\cdot}26 \times 10^{-11}$ erg. Dividing this by $e = 4{\cdot}65 \times 10^{-10}$ we get the ionising potential to be 8·1 volts.

(viii.) When zinc is in combination with chlorine, which has a strong attraction for the electron, experiment shows that light of wave-length λ 1849 is incapable of

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[*] HUGHES, 'Proc. Camb. Phil. Soc.,' XVI., p. 167, 1911.

[†] HUGHES, 'Proc. Camb. Phil. Soc.,' XV., p. 482, 1910.

[‡] PALMER, 'Phys. Rev.,' XXXII., p. 1, 1911.

[§] FRANCK and HERTZ, 'Verh. d. D. Phys. Ges.,' p. 967, 1911.

producing a photo-electric effect. It was shown in a previous research* that the vapours zinc ethyl, tin tetrachloride, and carbon disulphide, could not be ionised by ultra-violet light,† although all these compounds contain elements which are photo-electric when uncombined. These results are easily interpreted on the view that the valency electron is the electron concerned in the photo-electric effect. When combination takes place the valency electron is attracted more strongly to the molecule of the compound than it was to the electropositive member when uncombined. One could get a measure of the affinities of different elements for zinc, by observing the shortest wave-length necessary to cause ionisation in various zinc compounds. The experimental difficulty is that the critical wave-lengths will usually be beyond the region that can be conveniently used in experiments.

(ix.) The inside of the apparatus surrounding the illuminated plate was covered with the same layer of soot throughout the experiments. As carbon is of marked electronegative properties it is probable that the fall of potential across the surface layer, which may be present, is not more than a fraction of a volt. To correct for this, the values of V_0 should all be altered by this small amount. This correction should be given by an experiment in which the inside of the case as well as the illuminated plate is covered with the same distilled metal.

9. *Variations in k and* V_0 *with Atomic Volume.*—POHL and PRINGSHEIM found from their investigations on the alkali metals that the photo-electric effect may be divided into two parts—the "normal" effect and the "selective" effect. In the normal effect the emission of photo-electrons is determined solely by the amount of light absorbed, and the ratio of the photo-electric current to the energy in the light increases continuously with decreasing wave-length. The emission of photo-electrons in the selective effect only occurs when a component of the electric force in the light beam is in the plane of incidence. The ratio of the photo-electric current to the energy in the incident light rises to a very well-marked maximum for a certain wave-length which varies from metal to metal. This maximum becomes less defined and moves towards the ultra-violet as the element becomes more electronegative. A selective effect has been observed for Rb, Li, Na, K and Ba, and the maxima correspond to wave-lengths within the region λ 5000 to λ 2000. The question arises as to whether the velocities of the electrons produced in the two effects are identical or not. If the two effects originated in different systems we should not expect a coincidence. Even if they are fundamentally the same, it is not self-evident that the velocity of the electrons produced near the maximum should obey the same law as the velocities at two points well away from the maximum. The selective effect is generally regarded as a resonance phenomenon, and therefore the emission velocities near the maximum of the effect might possibly possess unusually high values. No selective effect has been

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* HUGHES, 'Proc. Camb. Phil. Soc.,' XVI., p. 378, 1911.

† The shortest wave-length is given in the paper as λ 2300. It should be corrected to λ 1849, which was discovered later.

observed for the elements investigated in this research. LINDEMANN[*] has given a formula which connects certain constants of the elements with the maximum of the selective effect. Except in the case of Li, the agreement with experiment is fairly good. The formula is

$$\lambda_{\text{max.}} = 65{\cdot}3\,(a/n)^{1/2}$$

where a is the atomic volume and n the valency. The application of this formula to the elements used in this research is given in Table V. It is recognised that the process of extrapolation to elements of valency greater than 2, has no experimental justification.

TABLE V.

Element.	Atomic weight.	Atomic volume.	Valency.	$\lambda_{\text{max.}}$	k.	V_0.
Ca	40·1	25·4	2	λ 2330	$3{\cdot}17 \times 10^{-15}$	2·57 volts
Mg	24·3	14·0	2	λ 1730	3·39	3·08
Cd	112·4	13·0	2	λ 1670	3·66	3·49
Zn	65·4	9·2	2	λ 1400	3·79	3·77
Pb	207·1	18·1	4	λ 1390	3·55	3·42
Bi	208·0	21·2	5	λ 1340	3·63	3·37
Sb	120·2	18·1	5	λ 1240	3·69	3·60
As	75·0	13·1	5	λ 1060	≏3·7	≏4·5
Se	79·2	17·6	6	λ 1110		≏4·8
O_2	16·0	12·6	6	λ 940		≏8·0

The calculated value of the maximum of the selective effect in Ca is well within the range of wave-lengths used in this research, and that for Mg is not very far outside. Yet there was nothing abnormal in the emission velocities from Ca compared with those from other metals.

In looking for some connection with the selective effect, a remarkable relation between the values of k and V_0 and the atomic volume was noticed (Table V). In any set of elements of the same valency there is a regular increase in k and V_0 with decreasing atomic volume. As we pass from one valency to another, the relation is discontinuous, the discontinuity always being in the same direction. This may be expressed by saying that if each atomic volume were multiplied by a suitable fraction which becomes smaller with increasing valency, then the values of k and V_0 would change continuously with the product of the atomic volume and a factor depending upon the valency.

There is no clear connection between the changes in k and V_0 with changes in the atomic weight.

10. *Summary.*—(1) The maximum velocity of photo-electrons from the surfaces of a number of elements prepared by distillation *in vacuo* has been measured.

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[*] LINDEMANN, 'Verh. d. D. Phys. Ges.,' XIII., p. 482, 1911.

(2) It has been shown that the energy of the fastest electrons emitted when monochromatic light falls on the surfaces is proportional to the frequency of the light. The results are expressed in the form $V = kn - V_0$, where V is the velocity measured in volts and n the frequency. LADENBURG's law, that the velocity is proportional to the frequency, has been shown to be incorrect.

(3) The values of k and V_0 have been found directly for the elements Ca, Mg, Cd, Zn, Pb, Sb, Bi, and As, and the values of V_0 for Se and O_2 indirectly.

(4) The values of k and V_0 for elements of the same valency change regularly with the atomic volume.

(5) The product of V_0 into e, the charge on an electron, has been identified with the work required to separate an electron from the molecule.

(6) It has been shown that the velocity distribution curves usually obtained in photo-electric experiments do not by any means represent the actual distribution of velocities of the electrons.

(7) The maximum emission velocity of photo-electrons from a continually forming mercury surface is identical with the velocity from a surface of mercury prepared by distillation.

The spectrograph used in this research was obtained by means of a Government Grant through the Royal Society.

In conclusion, I wish to express my best thanks to Prof. Sir. J. J. THOMSON for his interest and encouragement during the course of this investigation.

[*Note added July* 11, 1912.—The preceding paper will be rendered more complete by a short reference to two papers which appeared after it was written, and which bear upon some of the points discussed therein. In Table V. the maximum of the selective effect for Mg is given as λ 1730 by LINDEMANN's formula. POHL and PRINGSHEIM ('Verh. d. D. Phys. Ges.,' p. 546, 1912) have obtained the interesting result that a freshly distilled surface of Mg does not show any selective effect, but that, in less than an hour after distillation, a well-marked selective effect appears with its maximum at λ 2500. It was mentioned in connection with Table V. of this paper that the emission velocities for Mg are quite regular, although this metal is different from the other elements (except perhaps Ca) in that it has a selective effect with its maximum within the range of wave-lengths used in this investigation. The emission velocities appear, therefore, to be unaffected by the presence of a selective effect.

From a consideration of the spectrum of the source of light used by LENARD in his recent experiments on the ionisation of air by ultra-violet light, LYMAN ('Phys. Zeits.,' XIII., p. 583, 1912) concludes that the ionisation of air by light does not take place unless the light contains wave-lengths less than about λ 1300. This confirms the experimental result which I obtained in an earlier research, and which I have used in the present paper to determine the ionising potential of oxygen.]

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BY

J. J. MANLEY, HON. M.A. OXON,
DAUBENY CURATOR, MAGDALEN COLLEGE, OXFORD.

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VIII. *On the Apparent Change in Weight during Chemical Reaction.*

By J. J. Manley, *Hon. M.A. Oxon., Daubeny Curator, Magdalen College, Oxford.*

Communicated by Prof. J. H. Poynting, *F.R.S.*

Received May 29,—Read June 27, 1912.

Contents.

(1) *Introductory.*—During the year 1890 the late Prof. Landolt inaugurated his prolonged researches upon the apparent alteration in the total mass of chemically reacting substances. From the time of its inception until it was brought to a conclusion in 1907, the experimental work was freely varied both as regards the conditions and the nature of the chemical reactions involved. The methods and precautions adopted, together with the final results obtained, are to be found embodied and set forth in detail in Landolt's important memoir, "Über die Erhaltung der Masse bei Chemischen Umsetzungen."*

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* 'Königl. Akademie der Wissenschaften,' Berlin, 1910.

Published separately, September 12, 1912.

Before proceeding to deal with my own investigations in this field of research, it may not be inappropriate first very briefly to recall the chief features of LANDOLT'S work and conclusions.

From LANDOLT'S memoir we find that in all some 15 different chemical reactions were used; these were, for very obvious reasons, brought about within hermetically-sealed vessels. Convenient methods were adopted for ensuring a very slow mixing of the reacting bodies, the period allowed for this purpose varying from two to four days, and therefore the heat evolved during the chemical transformation was so dissipated that no very perceptible rise in the temperature of the vessels and their contents occurred. By following this plan it was hoped that all measurable temporary changes in the volumes of the reaction vessels would be avoided.

In connection with the weighings, devices were introduced for securing as nearly as possible a truly symmetrical disposition of the combined masses of the suspended vessels, their contents and carriers, about the vertical lines passing through the terminal knife-edges of the balance. The relative weights of the reaction vessel and its compensating counterpoise were determined according to the method advocated by GAUSS. The oscillations of the balance beam were observed with the aid of a telescope placed at a distance of 3 metres from the balance; and from the same distance (3 metres), by means of suitable apparatus, the balance was both loaded and the positions of the contents of the pans interchanged. LANDOLT effected most of his final weighings at a temperature approximating 19° C.; this temperature was, for convenience, selected as a standard one, and if at the time of weighing the temperature deviated from the standard value, then from a knowledge of the temperature coefficient of the balance it was possible to calculate the value which the observed resting-point of the beam would possess at 19° C.

It appears that the balance prior to the majority of the weighings was duly fatigued, but whether the necessary fatigue was designedly imposed or was merely the outcome of accidental convenience it is difficult to say.

The fully corrected final values derived from the whole of LANDOLT'S most trustworthy observations are tabulated on pp. 153–4 of his memoir. From those values we find the minimum apparent change in mass during any one chemical reaction to be $\pm \cdot 001$ mgr., and the two maxima $+ \cdot 021$ mgr. and $- \cdot 038$ mgr. respectively. Of the 48 final values, 23 show an apparent *increase* in weight and the remaining 25 an apparent *decrease*. The mean positive difference deduced from all the tabulated results we find to be $= \cdot 009$ mgr., and the mean negative difference $= \cdot 015$ mgr.

Combining the whole 48 corrected values, we obtain as a final result an apparent decrease in weight $= \cdot 006$ mgr.

Now LANDOLT estimated his possible experimental error to be approximately $= \pm \cdot 03$ mgr.; in his memoir he also expresses the opinion that $\pm \cdot 03$ mgr. represents the present attainable degree of accuracy in weighing; it will therefore be observed that both the probable error and the limit of accuracy in weighing, as estimated by LANDOLT, are just five times as large as the final value for the apparent decrease in weight during chemical reaction. The only legitimate conclusion that could be drawn was that which LANDOLT himself drew, namely, that if there occurs any real change in the total mass of reacting substances, then in the cases investigated any such change is less than ±1 in 10,000,000 parts. This then was LANDOLT'S final verdict after much tedious and highly refined work conducted with patience, skill and resourcefulness, during the lengthy period of 17 years.

For the sake of brevity and to avoid repetition, certain other very important points connected with LANDOLT'S investigations are considered in later portions of this paper; their influence upon the final result is also discussed.

In concluding these introductory remarks, we may observe that a number of experiments bearing upon the apparent want of strict constancy of mass have been conducted by HEYDWEILER.[*] The reactions chosen were carried out along the lines set down by LANDOLT; but HEYDWEILER'S estimated possible experimental error was larger than LANDOLT'S, being = ±·04 mgr.; therefore for the purpose which we have in view further comment is unnecessary.

In an earlier communication to the Royal Society, the present author suggested that the differences in weight recorded by LANDOLT were in all probability due, at least in part, to the presence of slight and unsuspected disturbing factors within the balance beam itself. In the belief that this was the correct view, in June, 1910, one of LANDOLT'S experiments was repeated under circumstances still more favourable than those which obtained during the German chemist's investigations As the conditions, precautions and refinements which are absolutely indispensable when weighings of the highest order of accuracy are to be undertaken have been described and discussed in two former communications, the author would beg to refer any reader seeking information upon those points to his two other papers.[†]

We now proceed to describe—

(a) The manner in which the various experiments were conducted;

(b) Some additional refinements which were introduced for securing a still higher degree of accuracy in the weighing of counterpoised glass vessels; and

(c) The final results obtained by the several methods and their bearing upon LANDOLT'S work and conclusions.

(2) *The Balance.*—The balance used in this research was one which has already been fully described.[‡] We may, however, repeat that the chief features of the instrument are as follows:—The beam is cantilever in type; its length is 14 cm., and the maximum load for which the balance was built = 200 gr. The beam is cut out from solid, hard-rolled phosphor-bronze plate; the terminal knife-edge blocks are

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[*] A. HEYDWEILER, 'Ann. d. Physik.' (4), vol. V., 1901, p. 394.

[†] 'Phil. Trans.,' A, vol. 210, pp. 387–415; 'Roy. Soc. Proc.,' A, vol. 86, 1912, pp. 591–600.

[‡] 'Phil. Trans.,' A, vol. 210, p. 407.

secured in positions which fall within the outer struts of the beam. The practically perfect rigidity of such a beam is proved by the fact that the sensibility of the instrument remains, so far as can be demonstrated by actual experiment, quite constant for all loads varying from 0–200 gr. The knife-edge blocks and the planes they engage are of agate ; beam, pans and stirrups are highly gilt. The beam is enclosed by one of the author's protecting inner cases which effectively excludes all disturbances which would otherwise be produced within the beam during the time the ordinary case is open for the loading and unloading of the pans, &c. By means of a platinum wire bolometer placed within the beam case, we were at any time able to test the air temperature in the immediate neighbourhood of the extremities of the beam ; the bolometer was capable of detecting temperature differences so small as 1/10,000° C. The actual temperatures of both the interior and exterior of the beam case were noted by means of delicate mercury-in-glass thermometers ; with these instruments we were able to read to 1/100° C. The sensibility, S, of the balance, was set moderately high ; it was equal to 45 scale divisions per 1 mgr. and was kept unchanged throughout.

(3) *The Reacting Substances.*—In commencing this investigation some little difficulty was felt in selecting a reaction likely to be the most suitable and convenient for the object in view. Of the 15 chemical reactions chosen by the original investigator, a well defined apparent decrease in the total mass of the reacting substances was usually obtained by means of ferrous sulphate and silver sulphate ; and this was particularly the case during the earlier experiments. In two other series of experiments, silver nitrate was substituted for silver sulphate, the second body being, as before, ferrous sulphate. For the one series the final result was + ·003 mgr., and for the other − ·003 mgr. ; the mean final value was therefore = 0. Our choice ultimately fell upon the latter reaction, which in LANDOLT'S hands had, from the standpoint of the present-day theory of the strict conservancy of the total masses of reacting bodies, led to the most satisfactory conclusions.

LANDOLT states the reaction which takes place between silver nitrate and ferrous sulphate in the form of the equation

$$6AgNO_3+6FeSO_4 = 6Ag+2Fe_2(SO_4)_3+Fe_2(NO_3)_6.$$

He, however, remarks, that the reaction is not complete. In the sequel it will be shown that this conclusion is correct. It will also be shown that had LANDOLT experimented more freely and extensively with silver nitrate and ferrous sulphate the degree of concordance observed by him would, in all probability, have been considerably modified.

(4) *The Reaction Vessels and their Preliminary Treatment.*—For the first series of experiments, the form chosen for the reaction vessels was that largely adopted by LANDOLT ; it is best described as an inverted U, the two limbs of which were cylindrical bulbs, each having a capacity of about 70 c.c. Two such vessels were

prepared and used together in every experiment. Each limb of a reaction vessel was charged, the one with a convenient quantity of concentrated silver nitrate solution, and the other with an equivalent amount of solution of pure re-crystallized ferrous sulphate. The charges were introduced, as in LANDOLT'S own experiments, through side tubes, t_1, t_2 (fig. 1). After the vessels had been charged they were weighed, and the weights of the two vessels and their contents were almost equalised by adding distilled water to the lighter one. Then the vessels were allowed to stand side by side for some hours, after which the side tubes were hermetically sealed by the blowpipe. The external volumes of the charged and sealed vessels were now separately measured by the hydrostatic method, and to the one having the smaller volume was added a sealed auxiliary bulb, the volume of which had been adjusted by trial, until it was as nearly as possible equal to the difference in the volumes of the two vessels. One of the side tubes of the vessel having the larger volume was then opened, and water introduced to compensate the weight of the auxiliary bulb of the other vessel; the tube was then re-sealed. The vessels were next immersed in fairly concentrated nitric acid for ten days; after being removed from the acid, they were continuously washed with water for some hours; and then finally wiped with a fine linen cloth and placed under a glass cover until required for use. Proceeding in the manner described, we obtained two charged reaction vessels having as nearly as possible a common volume and therefore an almost equal air displacement; and as their weights differed but slightly, the vessels when suspended from the arms of the balance almost exactly counterpoised each other.

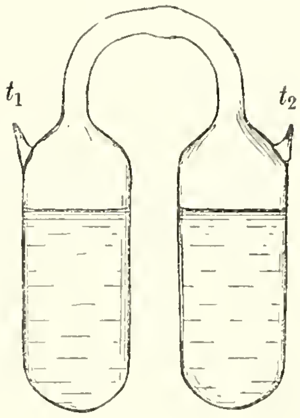

Fig. 1.

(5) *Of the Manner in which Weighings were Conducted. Series I.*—At the outset it was desired to discover the degree of approximation that might be attained when LANDOLT'S determinations were compared with my own; the first series of experiments were therefore planned and conducted on the same general lines as those laid down by LANDOLT, but with the addition of the distinctly more favourable conditions which accrue from the use of a protected balance beam. Here it may also be stated that throughout this research all weighings were carried out in a darkened room, the one window of which faces N.E. The ivory scale of the balance was, at the time of weighing, brightly illuminated by a convergent beam of yellow light; for this purpose a large lens was placed in front of a 6-litre flask filled with a dilute solution of potassium chromate solution in which a carbon filament lamp was placed centrally.

On July 11, 1910, the prepared and charged vessels which have been described in the preceding section were momentarily immersed in distilled water and then wiped with old fine linen, care being taken to avoid contact between the vessels and the hand; they were then suspended from the balance by means of attached platinum wire loops. As vessel A was a little heavier than vessel B, the necessary weights were added to B to establish equilibrium ; the beam was then duly fatigued, and the differential bolometer placed within the beam case read ; if the reading = 0, then, with the aid of a reading-telescope, a first set of observations of the oscillating pointer was taken, and the temperature of the air surrounding the beam noted ; after this, the bolometer was again read ; if the difference between the first and second bolometer readings did not exceed 1/5,000° C., then, and then only, was the set of observations retained for calculating the resting-point, R.P., of the beam.

July 18, 1910.

TABLE I.

Vessel A in left pan.					Vessel A in right pan.				
Obser-vations.	Pointer readings.	Obser-vations.	Pointer readings.	R.Ps.	Obser-vations.	Pointer readings.	Obser-vations.	Pointer readings.	R.Ps.
No. 1	164	No. 2	68	115·5	No. 1	152	No. 2	28	89·3
,, 3	162	,, 4	71	116·0	,, 3	149	,, 4	31	·5
,, 5	160	,, 6	72	115·5	,, 5	147	,, 6	33	·3
,, 7	158	,, 8	74	·5	,, 7	144	,, 8	37	·5
,, 9	156	,, 10	76	·5	,, 9	140	,, 10	39	·0
,, 11	154	,, 12	78	·5	,, 11	138	,, 12	42	·8
,, 13	152				,, 13	137			
			Mean =	115·6				Mean =	89·4
Temperature of beam case { before observation = 17°·40 C. after ,, = 17°·40 ,,					Temperature of beam case { before observation = 18°·42 C. after ,, = 18°·44 ,,				
Mean R.P. reduced for 18° C. = 114·2. (1).					Mean R.P. reduced for 18° C. = 90·4. (2).				
Other reduced R.Ps. similarly obtained during the same day were { = 115·1. (3). = 114·7. (5).					Other reduced R.Ps. similarly obtained during the same day were { = 90·8. (4). = 90·5. (6).				

Taking the sensibility of the balance = 45, we find from (1) and (2) the difference in the weights of the two vessels to be

$$\frac{114 \cdot 2 - 90 \cdot 4}{2 \times 45} = 0 \cdot 264 \text{ mgr.}$$

Using convenient lifters, the positions of the vessels A and B were now interchanged and the beam again fatigued ; observing the precautions and same method of procedure as before, new data were obtained for calculating the R.P. In general, the data secured both before and after reversing the positions of the two vessels enabled us to make six independent calculations of the R.P. The average value deduced from each set of six R.Ps. was then, by means of the temperature coefficient of the balance, reduced for a standard temperature of 18° C. We now possessed all the information necessary for a first determination of the difference in the weights of vessels A and B.

Leaving the positions of the vessels unchanged and the beam free to swing, we, somewhat later, effected, by the methods of reversal and vibration described above, a second determination of the apparent difference in the weights of A and B. Following this plan, we usually obtained during the course of a day from 2 to 3 complete and perfectly independent comparisons of the relative masses of A and B. From these completed determinations, a mean difference value for the whole day was deduced. With the object of removing any possible ambiguity, the actual data together with the final results secured during one day are set out in Table I. on p. 232.

Similarly, by using every possible combination of the two sets of reduced R.Ps., we obtain the differences tabulated below :—

TABLE II.

	mgr.	mgr. Differences from the final mean value.
From experiments (1) and (2), A =	B+0·264	−·004
„ „ (1) „ (4) „ =	„ ·260	−·008
„ „ (1) „ (6) „ =	„ ·263	−·005
„ „ (3) „ (2) „ =	„ ·274	+·004
„ „ (3) „ (4) „ =	„ ·270	+·002
„ „ (3) „ (6) „ =	„ ·273	+·005
„ „ (5) „ (2) „ =	„ ·270	+·002
„ „ (5) „ (4) „ =	„ ·266	−·002
„ „ (5) „ (6) „ =	„ ·269	+·001
Final mean differences found on July 18 =	·268	± ·004

This table shows the maximum variations from the final mean value for the day to be approximately = ± ·007 mgr.; and as the vessel and its contents weighed 127 gr. we observe that in this case, which is one of the most concordant of the whole series, the mean value was liable to a fluctuation the order of which was about 1 in 17,000,000 parts.

Proceeding according to the plan just explained and indicated in Tables I. and II., we obtained the 9 daily final mean differences in the weights of A and B set forth in Table III.; the maximum variations to which the several mean values were subject, and also the corresponding degrees of accuracy attained are likewise stated. There were in all 169 weighings of A against B before reversal, and 173 after.

At 10.30 a.m. on July 25, the contents of A were mixed; 7 hours later the first of the new series of weighings was commenced and continued at intervals during the succeeding 5 days, after which the observations ceased. The daily final mean values for the difference in the weights of A and B were the following :—

	July 25,	26,	27,	28,	29,	30.	
Differences in milligrammes =	0·37,	·28,	·22,	·35,	·37,	·36.	Mean = ·325.

TABLE III.

Date.	Differences in the weights of A and B.	Maximum variations.	Approximate degree of accuracy.
	mgr.	mgr.	
July 14, 1910 . .	0·265	± ·033	±1 in 3·8 millions
„ 15 „ . .	·338	·005	„ 25·4 „
„ 16 „ . .	·285	·016	„ 8·0 „
„ 18 „ . .	·268	·007	„ 17·0 „
„ 19 „ . .	·223	·009	„ 14·0 „
„ 20 „ . .	·260	·020	„ 6·4 „
„ 21 „ . .	·360	·038	„ 3·3 „
„ 22 „ . .	·350	·035	„ 3·6 „
„ 23 „ . .	·280	·042	„ 3·0 „
Mean . . .	·292	± ·023	±1 in 9·4 millions

We may here mention that the maximum variations in the daily mean values, and also the degrees of accuracy indicated, were of the same order as those shown in Table III.

The final result of all the experiments of Series I. may now be stated thus :—

Before mixing the contents of A, the difference A−B = +0·292 mgr.
After „ „ „ „ „ A−B = + ·325 „
Apparent change in mass = + ·033 „

It is curious that the apparent change in mass here shown is almost exactly equal to the limit given by LANDOLT for accurate weighing.

Series II.—After the observations and experiments which have been dealt with in the immediately preceding section had been completed, various circumstances arose which for a time prevented me from continuing this research; but in April, 1911, opportunity was again afforded for resuming the work.

Adopting, with slight modifications, the method of procedure followed in Series I., the weight of A in terms of B was again determined, the number of independent values obtained being 36. The final mean value deduced from the whole of the observations for the difference in the weights of the two vessels and their contents was

$$A-B = +0{\cdot}026 \text{ mgr.}$$

In this set, the maximum and minimum values found for the difference A−B were respectively +·042 mgr. and +·005 mgr. Of the 36 determinations, 20 exhibited an average variation from the mean value = +·007 mgr.; for the remaining 16 determinations the average variation was = −·008 mgr.; for any one determination the average deviation from the final mean value may therefore be taken as approximately = ±·008 mgr.

After mixing the contents of B, 16 independent determinations of the difference, A – B, were made; from these was calculated the final mean difference

$$A-B = +{\cdot}022 \text{ mgr.}$$

During this set of measurements the observed maximum and minimum values for the difference A – B were respectively equal to +·049 mgr. and +·003 mgr. Of the 16 determinations, 9 showed an average deviation from the mean value = +·009 mgr.; for the remaining 7, the average deviation was = –·011 mgr.; the final mean variation may therefore be taken as = ±·010 mgr.

Concisely stated, the final conclusion reached by means of Series II. is,

Before mixing the contents of B, the difference A – B = +·026 mgr.
After ,, ,, ,, ,, ,, A – B = +·022 ,,
Apparent change in mass = –·004 ,,

The apparent change here observed is of the order of about 1 in 32,000,000 parts. We now proceed to review, very briefly, the results yielded by the two series of experiments, and to indicate the probable causes and sources of the observed variations.

(6) *Of the Possible Errors associated with the Experiments of Series I. and II.*—In itself, and from a certain point of view, the final result secured by means of the experiments of Series II. was both excellent and gratifying. We may not, however, ignore the important fact, that this result is not in harmony with the final result obtained from Series I. As the two sets of measurements were effected under precisely similar conditions, the two final values are, so far as can be known, equally reliable. If we combine the two final values, then the apparent change in mass is equal to

$$\tfrac{1}{2}({\cdot}033 - {\cdot}004) = {\cdot}015 \text{ mgr.}$$

Or, the apparent change in the whole weighed mass is equal to 1 in 8·5 million parts; this degree of accuracy was frequently attained by LANDOLT and by him sometimes surpassed.

In our opinion it was now definitely established that the observed apparent changes in mass arise, not from any appreciable inherent or unallowed-for defects in the balance itself, but that the fluctuations were the natural outcome of certain unsuspected variables associated with the glass reaction vessels and their contents. It is believed that at least three such variables have been unwittingly allowed to creep, not only into my own experiments, but also into the majority of those of other observers. These three variables may be generated by—

(α) Very small yet sufficiently distinct, irregular and unequal convection currents in the air near the balance pans.

(β) Slight differences in the total external areas of the two vessels.

(γ) A want of strict equality in the temperature of the contents of the two vessels.*

We now proceed to a more detailed consideration of each of the above-named variables; we shall also attempt to show how the errors incidental to each may be either overcome or eliminated.

(6) α. *Of certain Irregularities produced by Air Streams.*—From the law of uniform decay, we know that the path of a vibrating pendulum will shorten by nearly equal steps during each successive vibration; and therefore in a series of observations of the extreme positions of an oscillating balance pointer, we expect to find the same law operative; in practice, however, we frequently get not *uniform* but well marked *irregular* decay.

On a former occasion† I was able to show that the temperature of the air within an ordinary balance case is seldom or never either constant or uniform. Any differences in temperature, however small, tend to set up a more or less complicated and ever-changing system of convection currents; and these currents produce certain effects upon any object that is being weighed. If the volume of the object be considerable, then by using the most refined methods available for weighing, the existence of the air streams should be rendered evident by corresponding irregularities in the successive differences in a series of pointer readings. That such irregularities are not only theoretical possibilities, but also insistent realities, may be seen by referring to the columns headed "pointer readings" in Table I., p. 232. In the first of those columns of "pointer readings" the successive differences have a common value, namely 2; it is suggested that the equality of the differences is due (*a*) to the absence of appreciable air streams, or (*b*) to the presence of two practically equal air streams acting in opposition, and therefore mutually compensating each other's effects. In the third and fourth columns of "pointer readings" (Table I.) we observe that successive differences, instead of possessing a common value, range in value from 1 to 4. Any or all of these variations might well be brought about by—

(1) A single air stream acting upon one pan only;
(2) Two or more air streams acting in unison upon both pans;
(3) Differential effects produced by opposition air streams.

Probably, however, they were sometimes due to one cause and sometimes to another—for it is difficult to see how an ever-changing temperature, such as the one the existence of which I was able to prove upon a former occasion, could possibly give rise to perfectly steady and uni-directional air streams.

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* There is also a possibility that during sudden changes in the temperature of the room, the balance shelf may undergo a minute but perceptible warping and thus temporarily tilt the balance case and so introduce a fourth variable. As this point has been dealt with in the 'Roy. Soc. Proc.,' A, vol. 86, p. 598, we do not further allude to it here.

† 'Phil. Trans.,' A, vol. 210, p. 405.

Granting, then, the existence of air streams which vary both in direction and intensity as proven, the question which now confronted us was: How can these air streams be best suppressed, or their effects neutralised? As it appeared impossible to institute any simple or convenient scheme for neutralising the disturbances, an attempt was made to eliminate their cause.

As a result of earlier experiments, it was known that a delicate bolometer placed within an ordinary balance case almost invariably reveals the existence of continuous fluctuations in the temperature of the contained air. In general, the fluctuations assume the form of minute and somewhat irregular oscillations about some mean temperature. Such disturbances occurring in the vicinity of the beam may be reduced to a vanishing point by the simple expedient of enclosing the whole beam with a small additional inner case. With these facts before us, it was concluded that the difficulties arising from the presence of air streams might be successfully met by completely enclosing the pans and stirrups by means of shells having a very high conductivity for heat. Theoretically, the following very distinct advantages are gained by the use of such shells, more particularly if the exterior surfaces are polished and the interior coated with carbon :—

(1) The effective volume of the disturbed air is very greatly reduced ;

(2) A shell having a high conductivity for heat may, when placed within a balance case, be regarded as possessing throughout a strictly uniform temperature; in consequence of this, combined with the fact that the inner or carbon skin has the power of rapidly absorbing and radiating heat energy, the contained air will also acquire the same uniform temperature ;

(3) Radiant energy falling upon the outer polished surface of the shell will be almost entirely reflected; the insignificant fraction that may enter will be incapable of producing any appreciable disturbing effects in the air enclosed by the shell.

All these advantages were effectually secured in the following way :—

Four half cylinders of stout sheet copper were prepared, the diameters of two being made a trifle less than the diameters of the other two. Using two half-cylinders, one of each size, a complete closed cylinder could at any time be formed by so placing the two portions that the vertical edges of the wider half slightly overlapped and just gripped the two corresponding edges of the narrower one. The height of the compound cylinders was as nearly as possible equal to the vertical distance between the upper surface of the base of the ordinary balance case, and the lower surface of the aluminium base-plate of the auxiliary beam case above. Before being used their inner surfaces were coated with Indian ink and their outer surfaces rough polished with fine sand-paper. The device was now tested. First, the reaction vessels were re-wiped and again suspended from the arms of the balance; then the two pans, together with their contents, were enclosed by means of the copper cylinders. Taking all the usual precautions numerous determinations of the R.P. were now made; in any one series the observed rate of decay in the amplitude of the vibrations was, with very few exceptions, almost perfectly uniform, and even in the exceptional cases, the deviations from uniformity were so small as to become negligible. The conclusion was therefore drawn that this device amply fulfils the functions for which it was designed.

The success which attended the introduction of the enveloping cylinders is primarily attributed to the fact that the fluctuations in the temperature of the air within an ordinary balance case are so extremely small; so minute are they that all ordinary attempts to discover their existence must necessarily end in failure. We desire to emphasise the importance of this fact: for we believe that in the presence of abnormally large fluctuations, measures even more stringent than those adopted here might be required for maintaining perfect uniformity in the temperature of the air within the cylinders. It is only by preventing *all* fluctuations in the temperature of the air immediately surrounding the pans and stirrups that we can hope to completely suppress disturbing air streams. We do not, of course, assert that the disturbing effects of air streams were *completely* neutralised, but we are convinced that their magnitude was so far reduced that, for all present practical purposes, the assumption of a zero value was permissible.

(6) β_1. *Of certain Errors producible by Differences in the Areas of two Reaction Vessels.*—In the immediately preceding section is given a method whereby small air streams flowing in the vicinity of the balance pans may be suppressed; and in the same section it is also stated that under the new conditions a very concordant set of values for the reduced R.P. may generally be obtained from *any one series* of pointer readings. It was, however, found that the mean R.P., deduced from one series of observations, frequently deviated very slightly from the mean R.P. value calculated from another series; slightly differing values were obtained not only from day to day, but sometimes also from hour to hour during the same day. After many tentative experiments, the conviction was borne in upon us that the deviations were, in all probability, due to corresponding variations in the amount of moisture condensed upon the surfaces of the reaction vessels.

LANDOLT and others have laid great stress upon the fact that the *volumes* of the two vessels used in any given experiment were adjusted by trial until they were not appreciably different; any difference that might exist between the two was removed by adding to the one possessing the smaller volume a suitable length of sealed glass *tubing*. Now, if nothing more than a cursory thought is bestowed upon the matter, it may easily be unconsciously assumed that as the two vessels are almost, though not quite, equal in volume and very similar in form, their superficial areas are, for all practical purposes, identical. An analysis of the actual facts may lead, as will be seen, to a very different conclusion. We would draw attention to several very important and interesting points. Let us consider the following three cases and the possible attendant errors :—

(1) The two vessels have identical forms but *decidedly* different volumes ;
(2) The two vessels are identical in form but possess *slightly* different volumes ;
(3) The two vessels are precisely equal in volume, but whilst the form of the one is truly *spherical* that of the other is slightly *ellipsoidal.*

Case 1.—In one of my own experiments (*vide infra*) the difference in the volumes of the two vessels was found to be = 8 c.c. It was decided to equalise the volumes by adding to the vessel possessing the smaller volume a spherical glass bulb. Accordingly a bulb was formed and its diameter repeatedly altered until it was found to be 2·47 instead of the exact value 2·48 cm. demanded by theory. Neglecting the attached thin stem and hook, we find the external area of an 8 c.c. sphere to be = 19·2 sq. cm. The volumes of the two reaction vessels were respectively 145·2 c.c. and 137·2 c.c. ; and assuming the vessels are truly spherical in form, we find that the corresponding external areas are 133·6 sq. cm. and 128·7 sq. cm. On adding the volume-compensating sphere to the smaller vessel, the respective and opposed external areas of the two become 133·6 sq. cm. and 128·7+19·2 = 147·9 sq. cm. The difference in the areas is therefore = 14·3 sq. cm. Had LANDOLT's plan been followed the air displacement of the two vessels would have been equalised by using a cylinder of the required volume prepared from a glass tube. Let the cylinder having V = 8 c.c. be made from tubing (*a*) 2 cm., and (*b*) 1 cm. in diameter. In the former case the length of the cylinder will be 2·55 cm. and in the latter 10·20 cm. The external area of the shorter cylinder will be = 22·3 sq. cm., whilst that of the longer one will be = 33·6 sq. cm. The superficial areas of the two cylinders will therefore exceed that of a sphere of the same volume by approximately 3 sq. cm. and 14 sq. cm. respectively. Or, the ratios of the opposed areas of the two reaction vessels will be changed from 147·9/133·6 to the respective values of 151/133·6 and 162·3/133·6.

Case 2.—This case also may best be illustrated by means of the actual data acquired in a particular experiment. For the sake of brevity we term the two reaction vessels X and Y. For X, V_1 = 145·15 c.c., and for Y, V_2 = 143·56 c.c. ; and therefore $V_1 - V_2$ = 1·59 c.c. The volume of the compensating sphere used was found to be 1·68 c.c. instead of the required exact value 1·59 c.c. ; its external area therefore equalled 6·8 sq. cm. Regarding X and Y as spheres we find their respective superficial areas to be 133·5 sq. cm. and 132·6 sq. cm. ; therefore the total external area of Y plus that of the volume-compensating sphere = 139·4 sq. cm. ; and the ultimate difference in the areas of X and Y is equal to 5·9 sq. cm.

If the volume compensator be formed from tubing having a diameter of 1 cm., we find that its external area will be = 8·3 sq. cm. ; the final ratio of the surfaces of X and Y exposed to the influence of the air will therefore = 140·9/133·5.

Case 3.—In this case it is assumed that the two reaction vessels have strictly equal volumes; also, that whilst the one is a true sphere, the form of the other is ellipsoidal. It follows, therefore, that although the volumes are identical the superficial areas of the two vessels will be somewhat different.

I desire to express my indebtedness to Mr. H. HILTON, formerly Fellow of Magdalen College, Oxford, for his kindness in determining for me the changes that occur in the superficial area of a prolate spheroid as the ratio of the major and minor axes is varied within the limits 1 : 1 and 1 : 0·667. Mr. HILTON'S results are here given in tabulated form:—

Ratio of axes of prolate spheroid of volume = 200 c.c.	1	0·95	0·90	0·80	0·75	0·667
Surface of spheroid in square centimetres	= 165·39	165·48	165·71	166·79	167·71	169·93

From the above data it follows that when the ratio of the axes is 1 : 0·765, the superficial area of the spheroid is greater than that of a sphere of the same volume by 2 sq. cm. Very similar changes are found for corresponding oblate spheroids.

(6) β_2. *Of the Weight of a Water Skin on the Surface of Jena Glass.*—Having satisfied ourselves that the superficial areas of two vessels of similar form and equalised volumes may differ considerably, the next obvious and important step in our enquiry was to determine, as accurately as possible, the weight of water vapour that might condense upon a glass surface. It is well known that glass is hygroscopic, and that different varieties of glass exhibit distinctly different hygroscopic properties. In all the final experiments described in this paper, vessels of Jena glass only were used; we therefore confine our attention to that particular glass and its comportment towards aqueous vapour.

By repeated trials we at last obtained a suitable and almost perfectly spherical bulb of Jena glass; the attached tube, which was short and of small diameter, was drawn out and bent round so as to form a small hook, the tip of which was sealed before the blowpipe. A small stool bridged one of the balance pans and upon it was placed a cylinder containing a little distilled water. The glass sphere was then, by means of a fine silver wire, suspended from the balance and placed within the cylinder and as near the water as circumstances permitted. Observing the usual precautions for refined weighing, the apparent weight of the sphere was repeatedly determined; when its weight was found to remain constant the water was removed from the cylinder and a similar volume of concentrated sulphuric acid introduced. After the lapse of some considerable time the apparent weight of the sphere was repeatedly re-determined. The barometer was read and reduced for temperature, and the temperature of the balance case noted at intervals; finally, the mean diameter of the glass sphere was measured and the corresponding external area calculated. We now possessed all the data necessary for estimating, with the aid of certain tables, the total weight of the invisible water skin (as it may be appropriately termed) that had formed upon the sphere during the time it was suspended in air saturated with aqueous vapour; presumably this skin had been removed when the final weighings over sulphuric acid were effected. The data, together with the final result, are set forth below:—

$$\text{Jena glass sphere}\left\{\begin{array}{l}\text{Diameter} = 3\cdot 0 \text{ cm.}\\ \text{External area} = 28\cdot 4 \text{ sq. cm.}\\ \text{Volume} = 14\cdot 1 \text{ c.c.} \quad (\text{Taken} = 14 \text{ c.c.})\\ (\text{Apparent weight in damp air}) - (\text{apparent weight in dry air}) = 0\cdot 118 \text{ mgr.}\end{array}\right.$$

Reduced barometer = 753 mm. = P.
Mean absolute temperature in balance case = 295°.
Pressure of water vapour at 295° A = 20 mm. of mercury = p.
Weight of I.L. of dry air at 753 mm. and 295° A . . . . . . = 1·185 gr.
,, ,, moist ,, ,, ,, $\frac{P - \cdot 38p}{760} \times \frac{273}{295} = 1\cdot 179$,,

Therefore 14 c.c. dry air at 753 mm. and 22° C. weigh ·016590 gr.
and 14 ,, moist ,, ,, ,, ,, ·016506 ,,

Loss of buoyancy for sphere = difference = ·000084 gr.

The increase in the apparent weight of the sphere is due to the joint effects of two causes acting in the same direction—

(1) a decrease in the density of the air owing to the presence of aqueous vapour; and
(2) the formation of a water skin upon the sphere.

The weight of the water skin will therefore be equal to 0·118 – ·084 = ·034 mgr. From this we find the weight of the water skin upon 1 sq. cm. to be equal to ·034/28·4 = ·0012 mgr.; and this we accept as the maximum value obtainable under the conditions of pressure and temperature that existed during the determination.* In practice, the maximum density for the water skin would very seldom be realised. In connection with some of the experiments carried out during the summer of the year 1910, a hygrometer was set up quite close to the balance case. The mean air temperature for some days was approximately equal to 19° C., and the mean reading for the wet bulb thermometer for the same period was approximately 16°·5 C.; the truth will therefore be closely approached if we assume the mean weight of the water skin per 1 sq. cm. of the glass to be equal to ·001 mgr. instead of ·0012 mgr. as found above. Accepting the smaller value, we find the respective weights of the water skins that

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* Ihmori, experimenting with boiled-out Jena glass, found that the water skin varied within the limits ·035 and ·068 mgr. per 100 sq. cm., or a mean approximately = ·0005 mgr. per 1 sq. cm. (Quoted in Landolt's memoir.)

may be formed upon the several volume-compensators discussed in Cases 1 and 2 (pp. 239 and 240) to be as follows :—

Case 1.—Spherical compensator. Water skin . . . . = ·014 mgr.
Short cylindrical compensator. Water skin. . = ·017 ,,
Long ,, ,, ,, ,, . . = ·029 ,,

Case 2.—Spherical compensator. Water skin . . . . = ·006 ,,
Cylindrical ,, ,, ,, ... = ·007 ,,

It is almost superfluous to point out that the density of the water skin will be subject to fluctuations; it is, in fact, a variable dependent upon three others; namely, the pressure, temperature, and hygrometric state of the adjacent air.

The difficulties and uncertainties associated with the variations in the weight of a water skin were, it is believed, successfully met and overcome by the simple device which we now describe.

(6) β_3. *Of the Methods used for the Removal of Water Skins.*—Some observers may be considerably surprised to learn that anyone should attempt to weigh accurately glass vessels without previously drying the air within the balance case in the usual manner. This departure from a time-honoured, orthodox, and, as we shall try to show, sometimes worse than useless custom, was, on our part, of deliberate design.

Let us consider the actual facts. As ordinarily practised, the air within a balance case is dried by means of such substances as solid calcium chloride, sticks of caustic potash or soda, phosphorus pentoxide, or by concentrated sulphuric acid contained in shallow vessels placed upon the bottom of the case. Any of the substances named will lap up the moisture in the lowest layers of air with great avidity; but as the density of air increases with the removal of moisture, and as an attempt is usually made to maintain the temperature of the balance both uniform and steady, it will be necessary to depend almost exclusively upon the inter-diffusion of the dry and damp air for completing the removal of the moisture. Remembering the law governing the rate of the diffusion of one gas into another, and that usually for our present purpose we may take the ratio of the densities of ordinary and of dried air as 1/1·005, it will be at once apparent that such a process is both lengthy and inconvenient.

Again, whenever the shutter of the balance case is lifted the greater portion of the dried air will be lost; this loss can only be replenished by the further expenditure of valuable time. The introduction of some form of stirrer for mixing the air during the initial process of drying would frequently be objectionable; for a stirrer in motion would create a suction in places and so dust, otherwise harmlessly reposing in out of the way crevices, would be drawn into the air and in part be subsequently deposited upon the balance pans and upon the objects placed upon them. But a still further objection to the use of the ordinary method of drying the air may be given.

In the course of some preliminary experiments with desiccating reagents, a distinctive odour frequently manifested itself when solid caustic soda was used; and it was suspected that the odour indicated the presence in the air of minute particles of the more or less hydrated reagent. Our suspicions were tested in the following way:—Two clean porcelain dishes, each 4½ inches in diameter, were taken; the one was charged with short sticks of caustic soda, and the other with a little "conductivity" water which was then tinted with methyl orange; the two dishes were placed side by side and covered with a large bell-jar. After the lapse of several hours the bell-jar was removed and held in a horizontal position; a Bünsen flame was then introduced; the flame was at once tinged faintly but perceptibly yellow, thus showing the presence of soda particles. It was next observed that the colour of the methyl orange was markedly yellow, thus indicating the presence of free alkali; we therefore proceeded to titrate the alkaline solution with N/100 HCl, and found that between 4 c.c. and 5 c.c. of the acid were required for the neutralisation of the absorbed alkali; from this it follows that the amount of caustic soda present in the water was equal to nearly 0·2 mgr.* Acid was then added until the colour of the indicator was decidedly pink and the dishes were again covered with the bell-jar. After some considerable time it was found that the excess of acid had been neutralised, the methyl orange having re-assumed a bright yellow tint. From these observations we conclude that the moisture in the air is so powerfully attracted by the drying reagent that a perceptible rebound from the absorbing surface follows. Although no experiments were made, it appears reasonable to conclude that similar phenomena would attend the use of other desiccating bodies.

In concluding this brief criticism of existing methods, we desire to remark upon some possible inaccuracies that may follow the use of sulphuric acid as a desiccating reagent.

On exposure to air concentrated acid quickly becomes diluted over its surface; as dilution proceeds the acid develops an appreciable vapour tension; it therefore follows that surfaces exposed in the vicinity of the acid will first lose their water skins and so become lighter; then, with prolonged exposure, they will acquire acid skins. I myself have frequently noted an increase in the weight of a porcelain crucible over-dried (if I may use the term) in this way.†

Seeing then that the usual method for drying the air can but lead in the direction of uncertain values it was abandoned for the following plan which proved both convenient and highly satisfactory.

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* This experiment has recently been repeated. The volume of N/100 acid required for neutralising the alkali absorbed by the water in the dish = 1·5 c.c., or 1/3 the amount required in the experiment described above.

† The following evidence tends to confirm the accuracy of the views expressed above. The upper portions of the interiors of 18 Scheibler desiccators, which had been in constant use for 8 weeks (some being used much more frequently than others), were examined by wiping them with wet blue litmus paper; in 12 cases a distinct acid reaction was obtained.

A large glass jar, J (fig. 2), was fitted so as to form a blower, the exit tube of a water pump being made to enter through a side tubulure near the bottom; the desired air pressure, p, was provided by suitably proportioning the length of stem of the funnel F. By duly regulating the working of the pump the jar was kept full of air; any air entering in excess of that actually drawn off through the tap t escaped with the water through the funnel. The bulb of the funnel should be large, and it must communicate freely with the external air, otherwise the attached waste pipe comports itself as a water pump and so greatly interferes with the uniform delivery of air through t. On stopping the supply of water, that which still remains in the jar automatically syphons off through the pump and its air tube; consequently the apparatus is always ready for immediate use. On leaving the jar by way of the tap t, the air is by means of two other taps, situated beyond the first, divided into two equal streams, each of which is then driven through a Drecshel wash-bottle charged with concentrated sulphuric acid; the acid serves a two-fold purpose: it removes the greater portion of the contained moisture and also indicates the rate at which the air is passing. As the partially dried air emerges from the wash-bottles, each stream enters its own set of 3 purifying tubes; the first half of each set is packed with small fragments of soda-lime and the second half with similar pieces of calcium chloride; finally, the air is allowed to filter through plugs of glass wool and is then conducted by glass tubing through one side of the balance case to the interior of the copper cylinders which surround the pans and stirrups. The glass air-tubes were passed through niches cut in the upper edges of the cylinders, their free ends being bent so that the air streams were delivered centrally and downwards.

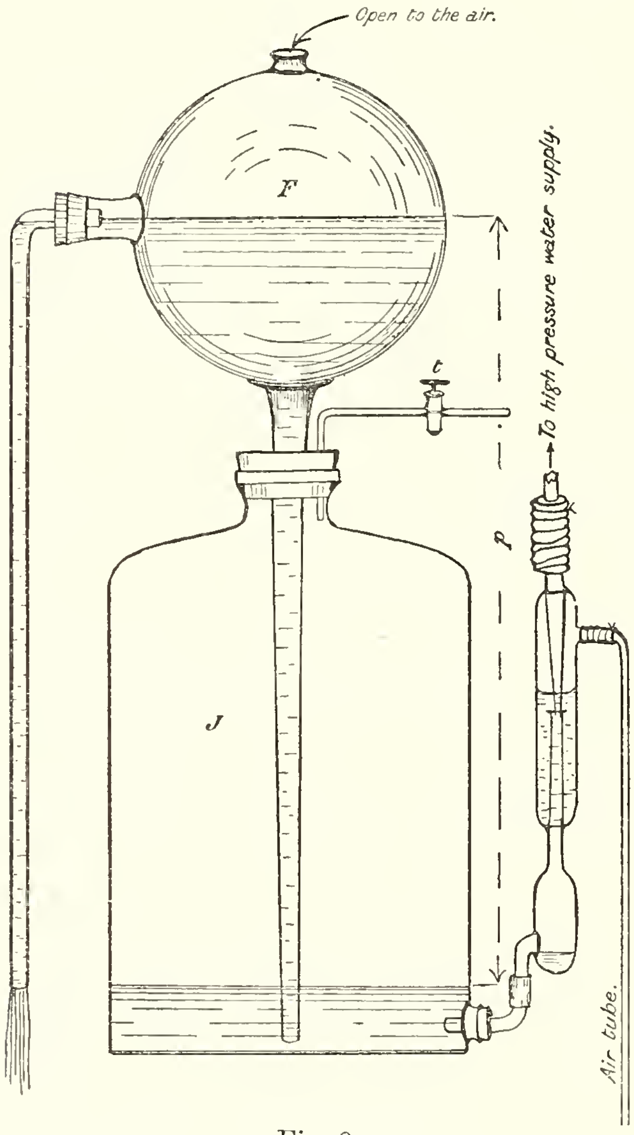

Fig. 2.

The apparatus just described enabled us to subject any objects, the masses of which we desired to subsequently compare, to a very perfect washing with air freed from carbon dioxide, moisture and dust; in fact, we were now, for the first time, in a position to weigh an object under well-defined and easily re-producible conditions. The efficacy of the newly devised method was now put to the test; for this purpose another pair of reaction vessels was made and charged as in the earlier experiments, and their volumes equalised as before. After the usual preliminary cleaning and wiping, the vessels were suspended from the balance, the necessary small weight added to one of the pans and the beam fatigued. During the first series of determinations which were then undertaken, the weighings were conducted in the presence of the ordinary air; but the second and third series of weighings were effected in the presence of dried and purified air only. In using the purified air, the streams were allowed to flow continuously until just before the actual weighing was commenced when they were temporarily arrested by closing the tap *t*. The first and third series of determinations each extended over a period of 7·5 hours; the second series occupied a period of 5·5 hours. The final results obtained are given below:—

TABLE IV.

Date.	Experiments.	Air used.	R.Ps. reduced for 22° C.				Number of determinations.
			Mean.	Maximum.	Minimum.	Maximum difference.	
August 21, 1911	Series 1	Ordinary	106·1	108·3	105·1	3·2	15 sets of 3
" 22 "	" 2	Purified	104·8	105·3	104·1	1·2	11 " 3
" 23 "	" 3	"	104·7	105·3	104·2	1·1	7 " 3

In connection with the above table two points may be noted. (*a*) In Series 1, the mean value for the reduced R.P. is 1·3 greater than the corresponding value deduced from Series 2 and 3; it is believed that this difference is due to a probable want of equality in the areas of the two vessels. Our data showed that the reaction vessel, to which a small volume compensator had been attached, suffered the loss of weight indicated by the change in the R.P.; this is, as we have already shown, exactly what we should expect; for, generally speaking, we find that the volume compensator causes the area of the compensated vessel to exceed the area of its companion. (*b*) Notwithstanding the very considerable additional refinements that had now been introduced, there still remained some residual disturbing factor, the magnitude of which was approximately represented by the extreme variations in the R.P., observable in Series 2 and 3. Doubtless a portion of the small variation was due to unavoidable experimental error; but at least another portion was probably due to a cause which we shall now proceed to discuss in the next section.

(6) γ. *Of Errors Arising from Slight Variations in the Temperature of the Contents of a Vessel.*—Coming now to a brief consideration of the influence exercised by the third variable (γ, p. 236), we note that some workers have been somewhat perplexed and exercised in their minds as to what material constitutes the most appropriate substance for wiping glass vessels that are to be weighed; some advocate the use of silk, others are in favour of the use of old and fine linen, others again

recommend a preliminary immersion of the vessel in distilled water. Various observers have found that the apparent weight of a vessel which has been wiped with silk is somewhat changed if re-wiped with linen, and *vice versâ*. Certain experiments which we have made with the view of elucidating the cause of the admitted and observed differences, suggest that the apparent change in weight is intimately bound up both with the *manner* in which the vessel is finally prepared for weighing and with the *nature* of the substance used for wiping. A typical case which is simpler than but equivalent to one of my own experiments will make this clear. The selected case is that of a glass sphere having a capacity of 150 c.c. and filled with water. The operation of wiping and the attendant rise in the temperature of the vessel and its contents will, in general, effect—

(1) Slight variations in the weight of the water skin;
(2) A very small alteration in the air-displacing power of the vessel; and
(3) A decrease in the buoyant properties of the surrounding air.

Passing over the first-named variable which we have already fully discussed, and ignoring yet another associated with possible minute changes in the weight of an air skin as distinguished from one of water, we observe that a glass sphere having a volume $V = 150$ c.c. at some temperature $t°$ C., and a cubic coefficient of expansion $= \cdot 00003$, will at $t+1°$ C. assume the approximate volume of 150·005 c.c.; ·005 c.c. of air weighs something like 1/170 mgr. The great majority of workers would, by following the methods usually adopted for accurate weighing, quite fail to detect so small a change with any degree of certainty; and therefore, for our present purpose, the variation may be treated as an insignificant factor which calls for no further comment.

In considering the effects which may be produced by the last of three variables named above, we would first note that when the buoyancy of the air is to be allowed for, a thermometer is placed in some convenient position within the balance case and read at the time the object is weighed; the density of the air at the observed temperature is then taken into account and the proper correction applied. For very many cases this way of treating the problem in hand is doubtless sufficiently accurate and calls for little or no criticism. Yet it must be admitted that a close examination of the actual facts will show that such a plan must not infrequently lead to the adoption of an inaccurate correcting value for the buoyancy. To obtain a rigorously true correcting value, the temperature of the air should be taken, not as is often done *anywhere* within the balance case, but at a point *infinitely near* the object weighed; for, unless the temperature of the air which is in close contact with the object upon the balance pan be accurately known, it will be impossible to assign to the correcting factor a precise value. The following remarks will, it is hoped, render evident the nature of the error that may be introduced by pursuing the usual instead of the ideal method.

Let the temperature of a sphere having V = 150 c.c. be 0°·1 C. greater than the mean temperature of the air within the balance case; we shall commit no serious error if we assume that the enveloping shell of air which is in close contact with and therefore readily warmed by the walls of the vessel is likewise 0°·1 C. greater than the mean temperature of the general body of air; for theory shows that such a shell of warmer air, though thin, will be appreciable and fairly well defined. Taking the weights of 1 c.c. of dry air under $p = 760$ mm., and at the respective temperatures of 15°·0 C. and 15°·1 C. as ω_1 and ω_2 mgr., we find the difference $\omega_1 - \omega_2 = \cdot 0005$ mgr.; the corresponding difference for 150 c.c. (the volume of the sphere) is therefore = ·075 mgr. Under the conditions which existed during our final experiments it was estimated that the smallest change in weight that could be detected with certainty equalled ·002 mgr.; and therefore ·075 mgr. would, comparatively speaking, produce a very marked effect upon the R.P. value.

In order to discover how far the temperature might be affected during the process of wiping, we introduced into a reaction flask, containing 150 c.c. of water, a thermometer graduated in $\frac{1}{10}$° C.; holding the flask by the upper end of the neck the contents were shaken and the temperature noted. A doubled silk or linen handkerchief was then employed in the usual manner and the flask wiped for the space of half a minute preparatory, as it were, to weighing, and the temperature again noted; this experiment was repeated a number of times both with the silk and the linen; in each case the results were surprisingly concordant. With silk the mean rise in the temperature was 0°·15 C. and with linen 0°·25 C. These experiments, therefore, show the correctness of the more or less prevailing idea that for the purpose of wiping glass vessels silk is superior to linen, the superiority being with reference to the resultant temperature changes and, according to our measurements, in the ratio of 25/15.

If we assume an otherwise strictly constant temperature within the balance case and apply the Stefan-Boltzman law of cooling, it becomes evident that a very considerable period must elapse before it will be possible to weigh correctly the slightly warmed vessel and its contents. If the above line of argument followed for the assumed difference of 0°·1 C. be extended so as to include the results obtained in the experiments upon the effects produced during wiping, it is found that the apparent increase in the weight of the vessel due to this cause alone is respectively 0·113 and 0·188 mgr.; in practice, however, other effects such as those arising from the action of convection currents would modify and lessen these values. So far as I am aware, little or no attention has hitherto been given to the possible effects following *very slight* differences in the temperature of a vessel and the general body of air surrounding it; for our present purpose the influence exercised by even minute differences in the temperature of the air and that of the vessel may become highly important and must not be neglected.

Having reviewed and indicated the sources and approximate magnitudes of at least some of the errors associated with the operations of refined weighing, we now proceed to give as brief an account as may be of the results obtained during the final experiments connected with this present research.

(7) *Of the Final Experiments Conducted with Silver Nitrate and Ferrous Sulphate Solutions.*—During the earlier part of this research use was made, as already stated, of inverted **U**-shaped vessels; but according to our experience such vessels are not so free from sundry inconveniences as we could wish for. It was therefore decided to substitute for those vessels others of a more or less globular form; and in order that the surfaces, volumes, and figures of the two vessels might be as nearly as possible identical, recently purchased Kjeldahl flasks of Jena glass were chosen. The two flasks were then repeatedly softened in a blowpipe flame and re-blown until by trial it was found that they were in all essential respects very similar; it is believed that the repeated softening in the flame also ensured, as no other treatment could have done, a very close similarity in the nature of the surfaces of the flasks.

With the object of separating the two reacting bodies, another flask of convenient volume was blown within each of the two Jena glass vessels. The silver nitrate solutions were introduced into the small inner flasks, and the equivalent weights of ferrous sulphate solutions into the outer and larger vessels; the necks of the outer vessels were then softened, thickened, and drawn out in the form of capillary tubes; these when cold were re-heated and bent hookwise and their tips sealed in the flame. The volumes of the vessels were next measured hydrostatically, and to the one possessing the smaller volume was added the necessary spherical compensator having $V = 1{\cdot}59$ c.c. The sealed tip of the lightest vessel was now removed and distilled water introduced until the weights of the two vessels, together with their contents, were almost exactly equal; the tip was then re-sealed. After subjecting the vessels to the usual preliminary and extended cleaning with (*a*) nitric acid, (*b*) potash, and (*c*) water, and finally wiping, the weighings were commenced and conducted under the newer conditions which have been outlined and discussed in the immediately preceding sections.

In planning the final experiments it was decided that the operations of weighing should be simplified as far as might be consistent with the conditions demanded for the high degree of accuracy to which we hoped to attain; the method of double or reversed weighing was therefore, in our opinion, with advantage discarded, for in this present enquiry a knowledge of the absolute weights of the reacting bodies is inconsequent. The question which we were endeavouring to answer was an apparently remarkably simple one, namely, Does the total mass of two or more interacting bodies undergo any appreciable change during chemical reaction? Now LANDOLT had already shown that if such changes take place they must be so small that there would result but a very slight displacement in the R.P. of a balance adjusted to a high degree of sensibility; in fact, so slight was any possible displacement likely to be that for the final comparison it would be quite unnecessary even to change the position of the rider upon the beam.

From the results obtained during the wiping of a charged flask (*vide supra*), it was inferred that the less frequently we repeated the operation of wiping the reaction vessels, the greater would be the reliability of final results drawn from a whole series of experiments. Again, the oftener the balance case is opened the greater will be the risk incurred from falling dust, varying temperature, and moisture effects ; and with oft-repeated reversals we incur the further danger due to possible minute alterations in weight brought about by the friction between the hooks of the reaction vessels and those of the balance stirrups.

Further, we were convinced that the elaborate precautions taken by LANDOLT for centering the masses under comparison upon the balance pan were unnecessary. Modern precision balances are so constructed that masses placed in their pans or suspended from the hooks above are automatically centred ; but in order to remove, as far as our own balance was concerned, any doubt that might arise on this point, a number of experiments carried out with the aid of the inverted U-tubes conclusively showed that the contained liquid might be either equally or otherwise divided between the two limbs of the vessel without producing any perceptible change in the apparent weight of the whole.

After the two Jena glass reaction vessels, henceforth termed X and Y, had been similarly wiped, they were suspended from the hooks of the balance stirrups and equipoised with the aid of a small weight and the rider ; the balance pans and their contents were next completely enclosed by the copper cylinders (p. 237), and the tubes delivering dry and purified air, placed *in situ*. The shutter of the balance case having been closed the beam was released and fatigued for a prolonged period ; the actual weighing was then commenced and continued at intervals during successive days. For every determination of the relative weights, five pointer readings were taken for deducing the R.P. and the temperature of the balance beam noted. By means of the temperature coefficient of the balance, the various R.Ps. were then reduced for a standard temperature of 16° C. The streams of purified air were always arrested during the time of the actual weighing, but allowed to flow freely at all other times.

From September 28 to October 2, preliminary weighings only were undertaken ; for it follows from the theoretical considerations which have already been given that it would be quite useless to attempt thus early to discover the true relative weights of the two vessels and their contents. The results obtained during the preliminary weighings served chiefly to indicate the cessation of temperature fluctuations within the contents of the vessels which had, of necessity, been so freely handled. As may be seen from Table V., p. 250, in which the summarised results are set forth, the fluctuations as represented by the variations in the R.P. gradually die away and ultimately become quite small.

From the above evidence it was concluded that the vessels and their contents had, on October 2, assumed an almost truly normal state ; but it was thought to be safer to wait yet another day before beginning a final comparison of the weights of the two.

TABLE V.

Date.	Number of determinations.	Reduced R.P. values.				
		Maximum.	Minimum.	Differences.	Variation in weight.	Mean.
					mgr.	
September 28, 1911	21	108·7	105·0	3·7	·082	106·8
„ 30 „	12	111·5	109·8	1·7	·032	110·7
October 2 „	6	107·0	106·6	·4	·009	106·8

On the morning of October 3, the vessels were in succession removed from the balance and held by a suitably designed lifter whilst they were very lightly and quickly re-dusted with silk; the operation was so effected that there was practically no risk of producing an appreciable rise in the temperature of their contents. Before the vessels were re-introduced the balance pans were also re-dusted and the whole apparatus arranged as before. The weighings were commenced an hour after the beam had been released and repeated at moderately short intervals throughout the day. Three independent determinations of the R.P. were made upon each occasion, and each of these was calculated as in the preliminary experiments from 5 observations of the extreme positions of the pointer; the mean value of the 3 determinations was accepted as the true one, and this was then reduced as before for the standard temperature of 16° C.

Proceeding in this manner we obtained in the course of 9 hours 20 groups of 3 R.P. values; from these again were calculated 20 mean values, from which a final mean value for the relative weights of X and Y, before mixing the contents of either, was deduced. An actual example will serve to illustrate the method of procedure adopted—

Example.

Group.	Time.	R.Ps.				Temperature.	R.P. at 16° C.
No. 1	11.10 a.m.	119·6	119·4	119·3	119·4	10·8	106·9

The chief points of interest associated with the 20 groups of determinations may be conveniently set forth as follows:—

The Final Mean value deduced for the R.P. = 107·0. Of the 20 mean values obtained during the day the maximum value equalled 107·3 and the minimum value 106·5; 10 of the 20 mean values were greater than the final mean and 7 were smaller; the remaining 3 values were equal to the final mean. The mean + difference was (still in terms of the R.P.) = 0·15, and the mean − difference = 0·16. We therefore obtain a close approximation to the truth by taking as a final mean R.P. = 107·0 ± 0·15. With a sensibility, S, of the balance = 45, we find that the variation ±0·15 in the R.P. = 15/450 = $\pm\cdot 00\dot{3}$ mgr. As the total mass in either pan was approximately equal to 127 gr., the variation $\pm\cdot 00\dot{3}$ is equivalent to 1 in 42·3 millions.

(8) *After mixing the Contents of* X.—On the following day (October 4) two additional groups of 3 R.P. determinations were obtained; their mean values at 16° C. were respectively equal to 107·0 and 107·1; the accuracy of the value of the R.P. given above was thus confirmed.

The contents of X were now rapidly mixed and the vessel replaced. Observing the usual precautions, the relative weights of X and Y were frequently determined during an ensuing period of 6 hours. The first comparison showed that the value of the R.P. had increased from 107 to 122·4; but when the weighings were brought to a conclusion for the day the value had fallen to 107·8; it was observed that the decline was fairly uniform throughout the 6-hour period. The comparisons were continued on October 5 and 6 and very fully repeated on October 10. Briefly the results were as follows:—

Table VI.

Date.	R.P. values at 16° C.				Number of determinations.
	Maximum.	Minimum.	Differences.	Means.	
October 4, 1911 . .	122·4	107·8	14·6	115·8	14
„ 5 „ . .	110·7	106·1	4·6	108·3	14
„ 6 „ . .	111·1	95·6	15·5	104·9	8
„ 10 „ . .	109·2	107·2	2·0	108·2	60

The final result obtained from the series of determinations on October 10 shows that the R.P. value had increased from 107·0 before mixing the contents of X, to 108·2 after mixing; the difference 1·2 is equivalent to an apparent *increase* in the weight of X of ·027 mgr.

(9) *After mixing the Contents of* Y.—As the variations in the apparent weight of X and its contents showed immediately after mixing some degree of uniformity, it was decided so to conduct the weighings, after mixing the contents of Y, that it would be possible to determine in this case the actual rate with which the decrease in the apparent weight proceeded. Accordingly, the solutions in Y were quickly mixed, both X and Y were then wiped and replaced in the balance, and the usual preparations completed for weighing. The first weighing was made 20 minutes after the reacting bodies had been mixed; other weighings followed at known intervals, which though at first brief, became more extended as the experiment progressed. In this way there

were obtained between the hours of 10 a.m. and 8.30 p.m. 19 independent R.P. values. The weighings were continued during the three succeeding days. The results obtained during the four days over which this experiment extended are given in a very condensed form in the following table :—

TABLE VII.

Date.	R.Ps. reduced for 16° C.				Number of determinations.
	Maximum.	Minimum.	Differences.	Means.	
October 11, 1911 . .	110·0	91·6	18·4	102·8	19
„ 12 „ . .	109·7	108·4	1·3	108·9	45
„ 13 „ . .	109·8	109·1	·7	109·6	18
„ 14 „ . .	112·2	109·6	2·6	111·1	12

The results obtained during October 11–14 inclusive are represented graphically and in a more detailed manner by Curve No. 2 (fig. 3). Curve No. 1 exhibits the small variations observed in the relative weights of X and Y before the contents of either were mixed, and at the same time indicates not only the degree of accuracy attained under the improved conditions introduced for weighing glass vessels, but also serves the useful purpose of a standard with which the other curves may be compared. The several curves are formed by plotting the differences in the apparent weights of X and Y against the times when those differences were measured.

Curve No. 2 presents two interesting features, the most arresting of these being the well defined undulations in the first portion. The slope of the axis of the undulations, though at first steep, becomes with lapse of time, less pronounced ; finally the undulations die away and the further apparent changes in weight are from that time onward best represented as an approximately straight line curve having a direction which tends to become horizontal. The mean path of the whole graph suggested to our minds a very strong resemblance to a cooling curve ; we were thus led to suspect the existence of some simple relationship between the decreasing temperature of the recently mixed contents of X and the changes in the apparent weight of the same. We therefore decided to measure the rate of cooling for X and its contents under conditions similar to those which obtained during the weighings. With this object in view, another vessel, similar in all essential respects to X, was charged with solutions of silver nitrate and ferrous sulphate, the quantities used being the same as those employed in our LANDOLT experiment. A thermometer graduated to 0°·1 C. was introduced and read ; the two solutions were then mixed, and the thermometer again read ; the increase in the temperature equalled 4°·8 C. and this was therefore the range of temperature for which the rate of cooling had to be determined. In carrying out the cooling experiment, the vessel, loosely corked and fitted with a thermometer placed centrally within, was first warmed and the temperature of its contents raised about 6° C. above that of the surrounding air ; it was next placed upon a light three-point support of fire clay and surrounded with one of the copper cylinders from the balance case ; this done, the top of the cylinder was covered with a tin-foil lid through which the stem of the thermometer projected ; finally, one of the tubes leading from the air-purifying apparatus was passed downwards and just through the tin-foil lid, and the whole covered with a large glass dome. The time required for the vessel and its contents to cool from 21° C. to 16°·2 C. was then determined, a chronometer being for this purpose read for each fall of 0°·5 C. until the temperature had sunk to 16°·5 C. ; as the rate of cooling had then become very slow, chronometer readings were recorded for three succeeding temperature steps each of 0°·1 C.

For this experiment we purposely chose a day when the weather was dull and the air fairly still ; under those conditions the temperature of our balance room is remarkably constant ; in this present instance the variations kept within the limits 15°·2 C. and 15°·4 C. during the 6 hours the experiment lasted. The results derived from this experiment were now set forth in the form of a curve (No. 3) of dimensions corresponding to those chosen for Curve No. 2 ; we were thus enabled to institute a direct comparison between the two.

Superposing the cooling and decrease in weight curves, it is found that the former very approximately coincides with the axis of the undulations of the latter ; this very approximate coincidence appears to persist and improve until finally the two curves merge into one and so become indistinguishably the same. The portion $\alpha\beta$ of the change in weight curve was obtained by extrapolating, and the point marked γ indicates the result obtained during our final weighing in this portion of our experiment.

The results we have just given and briefly discussed afford strong confirmatory evidence of the correctness of the theory already advanced, and which indicates that for a body of some considerable volume the apparent mass, as determined within a very restricted air space free from convection currents, must appreciably increase when the temperature of the body is raised, and decrease when the temperature is allowed to fall.

With regard to the undulations which appear in the first portion of the Curve No. 2, it must be confessed that we are not yet in possession of sufficient data to be able to definitely assign a cause from which they may arise ; we may, however, state that the results of several experiments led to the conclusion that the undulations will be inappreciable unless the temperature of the charged vessel which is being weighed exceeds that of the air by 1° C. or more. The more or less harmonic form of the undulations suggest two possibilities : (1) for a given temperature difference. periodic oscillations may be set up in the air shell which encloses the warm vessel, (2) the transference of the heat energy from the interior to the bounding surface of the cooling liquid proceeds not in one perfectly and steadily decreasing flow, as might at first be expected, but in the form of a surging stream. It is hoped that further experimental evidence will reveal that which is now obscure.

We now briefly refer to the results set forth in Tables VI. and VII. Comparing the corresponding data of the two tables, very distinct differences are at once apparent; but that which claims our immediate attention is the want of agreement between the two final results; the first of these indicates an apparent *increase* in weight = ·027 mgr., and the second an apparent *decrease* = ·067 mgr. As these apparent changes in weight constitute, relatively speaking, large discrepancies of a wholly contradictory character, we began to suspect that the marked irregularities were due to the presence of some hitherto unlooked for variable; but before deciding upon any other course, additional comparisons of X and Y were effected at intervals for some days longer; the large fluctuations in the relative weights showed that it would be useless to further prolong experiments in this direction. Curve No. 4 (fig. 3) represents some of the irregular results obtained from the additional weighings.

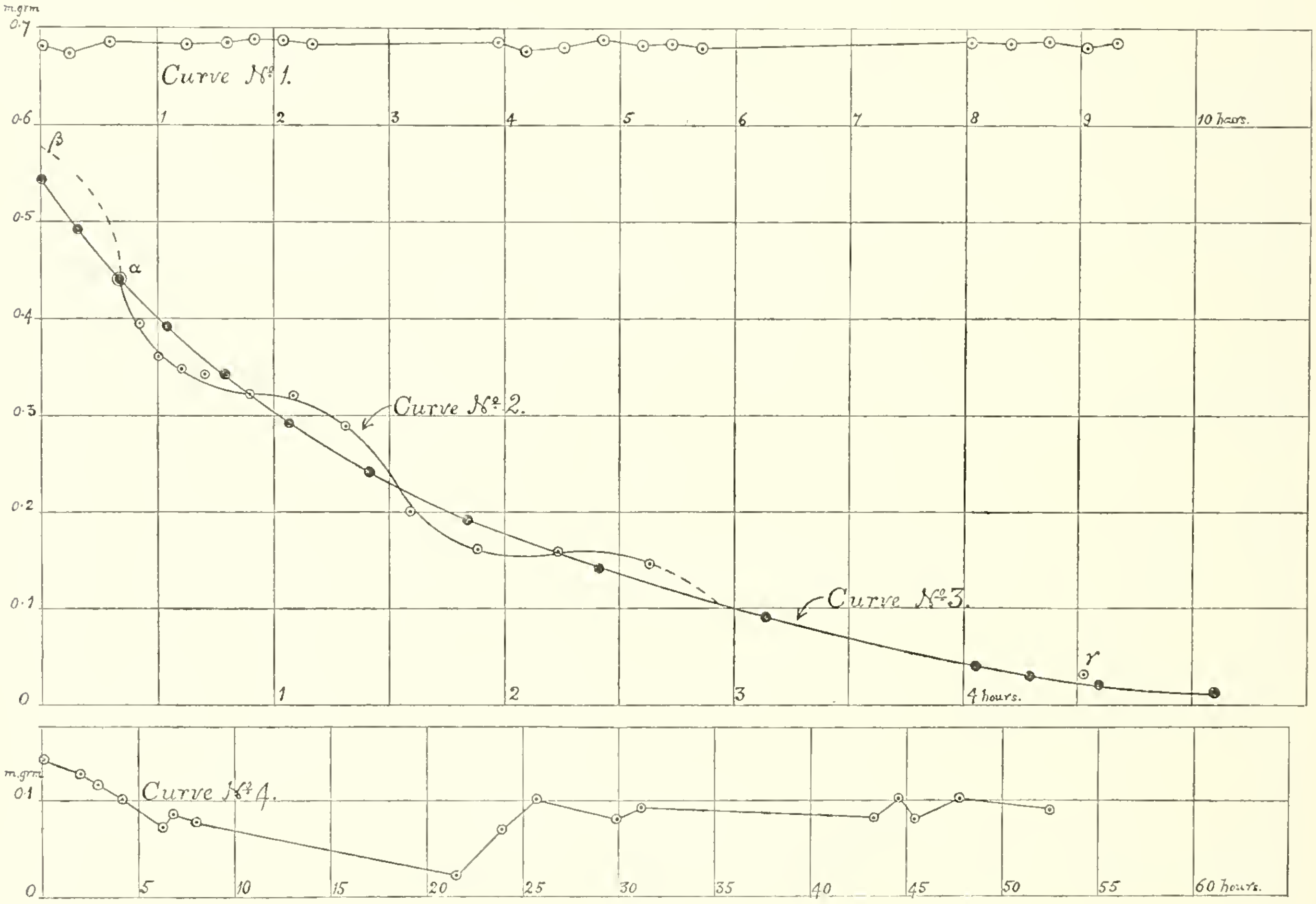

Fig. 3.

At this period of the investigation we obtained a clue so valuable that we were enabled to perceive the probable cause of the frequent changes in the relative weights of X, Y and their contents. During an earlier experiment, not previously mentioned, whilst the contained solutions were being mixed a fine crack was developed across the lower portion of a sealed reaction vessel; this crack rendered the vessel useless for the purpose for which it was designed. Following a habit we have of retaining for the time being anything connected with our work, the vessel was placed inside a beaker and set aside. At the end of about eight weeks it was discovered that the whole of the liquid had left the vessel and passed out into the beaker; seeing that the vessel was still intact, it was obvious that a considerable pressure had been generated within; in no other conceivable way was it possible to account for the ejection of the liquid.

An experiment was now devised to enable us to measure the growth in the pressure which follows the mixing of the two solutions. A flask was prepared and charged after the manner already described, but the capillary tube was made as uniform as possible and longer, and then bent so as to assume the form shown in fig. 4. A spot at the base of the capillary tube was softened before the blowpipe, and a short fine capillary tube, t, drawn out and left open; it was now possible to introduce a convenient quantity of mercury into the **U**-shaped limb; this done, the vessel was placed for some hours in a thermostat, maintained at a mean temperature of 29°·5 C., and then hermetically sealed by fusing the tips of the capillary tubes t and t_1; the atmospheric pressure at the time of sealing was observed and recorded. Next, the solutions were mixed, the vessel replaced in the thermostat, and the sealed mercury manometer, m, read from time to time. During the first day the manometer remained unaffected, but at the expiration of the second day its indications showed that the pressure within had commenced to fall; the diminution in the pressure became more and more marked until the sixth day during which the change reached a maximum; from this time onward the pressure began to slowly return towards its original value, the increase during the four succeeding days being equal to 20 mm. of mercury.

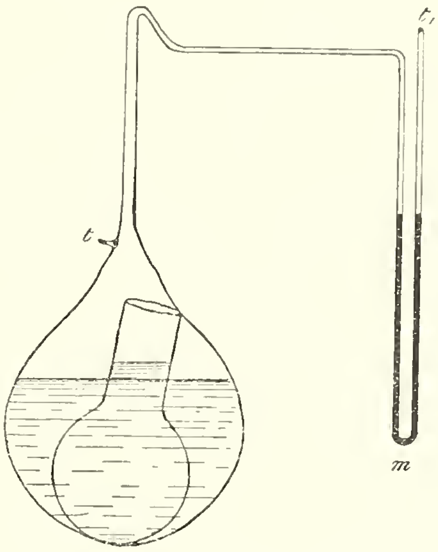

Fig. 4.

We next tried the effect of light upon the mixture, and in order to carry out this experiment the flask was removed from the thermostat, allowed to cool, and then placed together with a 25 candle-power "tantalum" lamp inside a bright tin box, the top of which was then covered with tin-foil. Switching on the lamp for short intervals only, the pressure was now observed to increase so rapidly that it was deemed wise to terminate the experiment at the end of an hour. The flask was then replaced in the thermostat and the new pressure measured; this pressure remained unaltered during the succeeding day, but 24 hours later it had still further increased. The experiment, which had by this time been proceeding for a fortnight, was now brought to a conclusion by opening the tip of the manometer under mercury; when this was done, a considerable quantity of gas escaped from the reaction flask; the bulk of this was caught in a tube previously filled with mercury. An analysis showed that the gas consisted of nitrogen and nitric oxide, their volumes being approximately in the ratio of 1 : 2.

The determination of the cubic coefficient of expansion of the flask for pressure was next undertaken, in order that we might be in a position to calculate the changes in the apparent weight of the flask resulting from the related variations in the buoyancy of the air.

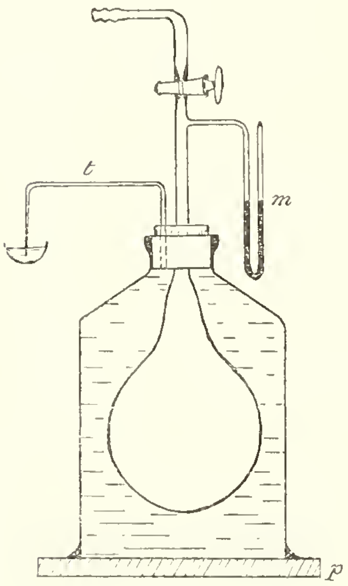

Fig. 5.

The pressure coefficient of expansion was measured with the aid of the apparatus represented in fig. 5. The flask, previously emptied and dried, was introduced into a small bell-jar and its neck passed up through a cork securely fixed in the mouth of the jar; the wide open end of the jar was then closed by means of a stout iron plate, *p*, which was attached with cement. The jar, together with the tube *t*, were next completely filled with air-free water, and, except when in use, the fine capillary jet in which the tube *t* terminates was kept immersed in water. In measuring the pressure coefficient, the water was removed from under the jet and a small weighed capsule substituted for it; air was then forced into the reaction vessel until the internal pressure was equal to 3 atmospheres, as indicated by the sealed mercury manometer *m*; as the pressure distended the flask, water was ejected through *t* into the capsule, which was then removed and again weighed. With slight modifications the contraction coefficient of the vessel was also determined. Both determinations were carried out several times and the results obtained were very concordant. It was thus found that an additional pressure of 1 atmosphere increased the volume of the reaction vessel by an amount equal to ·02 c.c. The weight of ·02 c.c. of air may be taken = ·024 mgr., and this is therefore the change produced in the buoyancy effects of the air upon the flask by a pressure = 760 mm. of mercury. We now give in Table VIII. which follows a summary of the results obtained during this branch of our inquiry.

The contents of Table VIII. are almost sufficiently self explanatory. It may be seen that on mixing the two reacting bodies, two hitherto absent variables the one dependent upon the other, were unknowingly introduced; there were prolonged, unsuspected and complicated chemical changes producing an irregular temperature and consequent loss in the buoyant properties of the air enveloping the reaction vessel; and as a necessary result of the chemical changes, a quantity of gas with its attendant pressure was generated within the vessel which, becoming distended, displaced additional air and was thus rendered more buoyant. The observed fluctuations in the

TABLE VIII.

At the time of sealing the bulb the barometric reading = 744 mm.

	Date.	Pressure within bulb.	Change in pressure.	Change in volume of bulb.	Equivalent change in weight.
	November 16, 1911 . .	744 mm.	± 0	± 0	± 0
After heating	,, 17 ,, . .	744 ,,	± 0	± 0	± 0
	,, 18 ,, . .	670 ,,	− 74 mm.	− ·0015 c.c.	+ ·002 mgr.
	,, 19 ,, . .	Not read.			
	,, 20 ,, . .	611 mm.	− 133 ,,	− ·0026 ,,	+ ·003 ,,
	,, 21 ,, . .	578 ,,	− 166 ,,	− ·0033 ,,	+ ·004 ,,
	,, 22 ,, . .	587 ,,	− 157 ,,	− ·0031 ,,	+ ·004 ,,
	,, 23 ,, . .	587 ,,	− 157 ,,	− ·0031 ,,	+ ·004 ,,
	,, 24 ,, . .	593 ,,	− 151 ,,	− ·0030 ,,	+ ·004 ,,
	,, 25 ,, . .	598 ,,	− 146 ,,	− ·0029 ,,	+ ·004 ,,
	,, 26 ,, . .	Not read.			
After exposure to light	,, 27 ,, . .	1594 mm.	+ 850 ,,	+ ·0167 ,,	− ·020 ,,
	,, 28 ,, . .	1594 ,,	+ 850 ,,	+ ·0167 ,,	− ·020 ,,
	,, 29 ,, . .	1674 ,,	+ 930 ,,	+ ·0183 ,,	− ·022 ,,

relative weights of the two vessels, X and Y, are therefore to be attributed to the sum of the two variables, one of which tends to increase, and the other to decrease the weight of either vessel. If the two variables have been, and still are, equally operative in both vessels, there will follow strictly equal opposition effects ; as the sum of these = 0, the balance remains unaffected, and the presence of the variables remains unsuspected. In all probability this is just what happened in LANDOLT'S experiments with silver nitrate and ferrous sulphate. There is, however, one other possibility. Further experiments have proved that for the secondary reactions occurring, the period of induction may be very considerable ; that is to say, the primary reaction may proceed to a point where a first chemical equilibrium may be established, and then no further appreciable changes follow before the whole experiment is completed. Viewed mathematically, we have but re-stated the case ; in so far as the actual weighing is concerned, the results are precisely the same.

The mixture left in the flask after concluding the experiments with the tantalum lamp, proved on examination to be very acid. The clear liquid obtained on filtering, contained in addition to acids, ferrous, ferric, and silver salts ; the undissolved portion which was somewhat yellow, contained metallic silver, silver nitrate and some salts of iron. We must now leave the chemical problem here presented to be more fully dealt with in some future communication ; but from the remarks made, it will be abundantly evident that the chemical equation set forth on p. 230 gives but a very incomplete representation of the actual facts ; that equation may indeed represent more or less correctly, the initial stage of the whole reaction, but it is quite clear that other and perhaps somewhat involved and little understood chemical changes are induced some time later, the period varying greatly with the conditions of light, heat, &c.

Seeing then that a close study of one apparently simple chemical reaction led to such totally unexpected conclusions, and remembering that the nature of some of the other reactions made use of by LANDOLT cannot, in all probability, be simpler than that of the reaction which we have investigated somewhat imperfectly here, it would naturally appear that a more perfect knowledge of the chemical changes which were made use of by LANDOLT, combined with the application of the methods we have advocated and practised for refined weighing, would enable us to explain at least some of those obscure points which arise in LANDOLT'S memoir. We now pass to the consideration of one final experiment and the results which were obtained by its aid.

(10) *Of some Results obtained with Barium Chloride and Sodium Sulphate.*—With the object of securing additional and confirmatory evidence in support of the correctness of the views which we had now formed, a final experiment was devised and carried out.

It will be universally admitted that the reaction which follows the mixing of barium chloride and sodium sulphate solutions is, for all practical purposes, instantaneous and complete. We are not, however, aware that either this or other similarly rapid and complete reactions have been deliberately and systematically made use of by preceding investigators; but the results we have obtained and described force us to the inevitable conclusion that the only reactions we may legitimately make use of for our present purposes are just those in which the chemical changes terminate within a reasonably brief period; further, the products of the reaction must be of such a nature that the pressure within the vessel is not appreciably altered.

For the purpose of carrying out the final experiment two re-blown Jena glass vessels, similar to those used in the preceding experiments, were prepared; but as it was not intended to duplicate the experiment, one vessel only was supplied with an inner flask; the other vessel was used simply as a counterpoise. The reaction vessel was charged with equivalent quantities of almost saturated solutions of highly purified barium chloride and sodium sulphate, the latter being placed in the small inner flask; the counterpoise was charged with the proper weight of water; the reaction vessel and its counterpoise were then sealed, their volumes and weights determined and afterwards equalised; finally the vessels were cleaned. All these necessary operations were performed in the manner described on pp. 231 and 248. The subsequent weighings were conducted under precisely the same conditions and with the same precautions as those introduced and observed during the final experiments with silver nitrate and ferrous sulphate. The results obtained during the course of this experiment are summarised and set forth in the following table:—

TABLE IX.

Date.	Number of determinations.	Reduced R.P. values.*					
		Mean values.	Number above mean.	Average difference from mean.	Number below mean.	Average difference from mean.	Number of zero differences.
		BEFORE REACTION.					
December 30, 1911	6 groups of 3	97·50	2 determinations	+0·30	4 determinations	−0·15	0
January 1, 1912	6 ,, 3	·74	2 ,,	+ ·20	3 ,,	− ·12	1
,, 3 ,, ...	6 ,, 3	·11	2 ,,	+ ·18	4 ,,	− ·09	0
,, 4 ,, ...	6 ,, 3	·55	4 ,,	+ ·10	2 ,,	− ·19	0
	Final means . .	$97 \cdot 48 = M_1$		+0·20		−0·14	
					±0·17		
		AFTER REACTION.					
January 12, 1912	9 groups of 3	97·39	3 determinations	+0·26	6 determinations	−0·36	0
,, 13 ,, ...	12 ,, 3	·62	3 ,,	+ ·44	9 ,,	− ·33	0
	Final means . .	$97 \cdot 51 = M_2$		+0·35		−0·35	
					±0·35		

Difference . . . . . $M_2 - M_1 = + \cdot 03 = \cdot 0007$ mgr.

---

* All these R.Ps. were corrected for changes in atmospheric pressure. The corrections were rendered necessary by the fact that the air displacements of the vessel and counterpoise were, through a small arithmetic error (discovered after the experiments had been concluded), not quite equalised. A variation in the barometric height = 10 mm. resulted in a change in the relative apparent weights = ·002 mgr.

From the above tabulated results it may be seen that there were 72 5-point determinations of the relative weights of the reaction vessel and its counterpoise before effecting the chemical reaction, and 63 similar determinations after. The maximum variations observed amongst the several daily mean values (Column 3) were 0·63 before the reaction and 0·23 after; these variations in the R.P. correspond respectively to ·014 and ·005 mgr. The mean values of all the daily average differences in the R.P. (Columns 5 and 7) before the reaction are +0·20 and −0·14 respectively, or a final mean variation ±0·17. After the reaction the corresponding values are respectively +0·35 and −0·35, or a final mean variation = ±0·35. Expressing the two final means in the form of weight variations, we have for the first ±·004 mgr. and for the second ±·008 mgr. The increase in the average variation here shown, though in itself small, is, we believe, definite, and we think that it is quite possible that as a result of the chemical reaction some at present unknown minute disturbing factor has been introduced; further research may bring this to light.

Taking the final mean variation in the relative weights = ±·006 mgr., it appears that the additional refinements and precautions which we have introduced and described have resulted in raising the attainable degree of accuracy in weighing from the lower limit of ±·03 mgr. given by LANDOLT to one having just 1/5th of that value.

The weight of the reaction vessel and its contents may in round numbers be taken = 109 gr.; if, therefore, the difference M_2-M_1 be taken = ·001 mgr., instead of the smaller difference ·0007 mgr. as found experimentally, the apparent increase in the total mass during the chemical reaction is of the order of 1 in 109,000,000 parts; but this, it may be observed, is 6 times smaller than the average variations exhibited throughout these final experiments.

Reviewing then the whole available evidence, we are led to conclude that this present research has tended but to confirm the truth of an almost universally accepted belief, that a given total mass is an unchanging and unchangeable quantity.

In conclusion, I desire to acknowledge my indebtedness to the Government Grant Committee of the Royal Society for the continued loan of certain apparatus which has considerably facilitated this research. My best thanks are due to Mr. R. T. GÜNTHER, Fellow of Magdalen College, and to Mr. N. V. SIDGWICK, Fellow of Lincoln College, Oxford, for the valuable assistance which both have rendered me. Lastly, I would express my appreciation of the kindness shown me by the Radcliffe Observer. In the absence of data afforded by Dr. RAMBAUT's continuous barograph records it would have been difficult to apply certain minute but necessary corrections to the final R.P. values of the barium chloride and sodium sulphate experiments.

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OPTICAL ROTATORY DISPERSION.

PART I.—THE NATURAL AND MAGNETIC ROTATORY DISPERSION IN QUARTZ OF LIGHT IN THE VISIBLE REGION OF THE SPECTRUM.

BY

DR. THOMAS MARTIN LOWRY.

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IX. *Optical Rotatory Dispersion.—Part I. The Natural and Magnetic Rotatory Dispersion in Quartz of Light in the Visible Region of the Spectrum.*

By Dr. Thomas Martin Lowry.

Communicated by Prof. H. E. Armstrong, *F.R.S.*

Received May 24,—Read June 27, 1912.

Contents.

1. *Introduction.*

The phenomena of rotatory dispersion are of special interest from two points of view. To the chemist they afford the most hopeful clue to the solution of the difficult and much discussed question as to why a particular substance possesses a given rotatory power. To the physicist, they contribute important data for the discussion of the mechanism involved in the propagation of light through matter, on the lines laid down by Maxwell, in 1869, and extended by the subsequent work of Sellmeier, Von Helmholtz, Larmor, Drude, and others. On the chemical side, progress depends mainly on the accumulation of data as to the rotatory dispersion of a large number of substances for a few selected wave-lengths; in particular also upon the development of simple and effective laboratory methods, permitting of the measurement of rotatory dispersion being made a part of the ordinary routine of every laboratory in which polarimetric studies are undertaken. Progress on the physical side demands that a few selected substances shall be examined with light of many

Published separately, October 28, 1912.

wave-lengths, extending over the whole of the available range of the spectrum, and that the measurements shall be made with the highest degree of accuracy.

The present investigation of rotatory dispersion, which has been in progress continuously since 1905, is concerned with the natural rotatory power of crystals and of optically active liquids, and also with the rotatory power induced in them by a magnetic field. It was undertaken primarily from the chemical standpoint with a view to obtaining information as to the variations of rotatory power with wave-length in organic liquids. But it was soon found that the two lines of investigation indicated in the preceding paragraph were inseparable, since the only satisfactory way of establishing standard laboratory methods for everyday use was to make measurements of rotatory dispersion with light of every available wave-length and to strive persistently to increase the degree of accuracy attained. Only in this way could adequate experience be gained as to what was possible in work of this kind. Thus, after making observations with light of some thirty wave-lengths, it was found that measurements of the highest degree of accuracy could be made with twenty-four lines in the spectra of the elements Li, Na, Tl, Zn, Cd, Hg, Cu, Ag; nine of these were used in the earliest series of laboratory-measurements, but the number was soon reduced to seven and finally to four (or even two) lines, which were found to give an adequate representation of the rotatory dispersion of the simpler organic compounds.

The measurements which are now described of the rotatory power of quartz for twenty-four wave-lengths in the visible region of the spectrum were undertaken originally in order to test the methods which were being devised for general laboratory use. But it was soon apparent that measurements might be made which would be much more accurate than those that had been recorded hitherto, even including the measurements of SORET and SARASIN which have been accepted as standards during the past thirty years. The observations were therefore continued and extended in order to provide material which could be used in testing with the greatest stringency the relationships between rotatory power and wave-length which have been put forward by DRUDE and others. Measurements of magnetic rotatory dispersion in quartz were also made, in order to test, under more stringent conditions than those which have generally been adopted, the validity of G. WIEDEMANN'S Law of the proportionality of natural and magnetic rotatory dispersions.

Experiments are in progress to extend the measurements of the natural rotatory power of quartz in such a way as to cover the whole of the spectrum transmitted by the mineral. Up to the present, measurements have been made from λ 17000 to λ 2327; it is hoped that, by the adoption of new methods, it may be possible ultimately to carry the experiments into the unexplored regions lying beyond these limits, but this final extension will be accomplished only after overcoming a number of new and serious difficulties.

Measurements have also been made of natural and magnetic rotatory dispersion in some fifty or sixty paraffinoid compounds, including a series of twenty-three optically-active alcohols prepared by Dr. R. H. PICKARD; these will be described in a separate communication as soon as two series of active alcohols now under examination have been completed and tested.

2. *General Review of Previous Observations and Methods.*

Although much work has been done on the optical rotatory power of organic compounds, it is remarkable that almost the whole of the observations have been made with light of one colour—the yellow doublet of sodium. Observations have been made occasionally with light of other wave-lengths, usually by physicists who have proceeded from the study of quartz or of sodium chlorate to analogous observations on the rotatory dispersion of some optically active liquid such as turpentine or ethylic tartrate. But the measurement of rotatory dispersion has never become a part of the normal work of the chemical laboratory. Chemists have been content to devote their energies to the elucidation of the effect of solvents, of temperature and of chemical constitution on the rotatory power of substances for sodium light, usually without paying attention to the influence of the nature of the light on the property in question.* This limitation is the more remarkable since many of the substances selected for examination are known to exhibit anomalous rotatory dispersion, and cannot, therefore, be expected to exhibit any simple relationships until attention is directed to the whole course of the rotatory dispersion-curve rather than to any one arbitrarily selected point.

Measurements of magnetic rotatory dispersion have been even more uncommon. PERKIN made a few scattered observations with lithium and thallium in addition to sodium light; a few measurements have also been made in order to determine the form of the dispersion-curve or to test the validity of WIEDEMANN'S Law of the proportionality between natural and magnetic rotatory dispersion, but practically the whole of the literature of magnetic rotatory power, like that on natural optical rotation, is expressed in terms of the effects produced on yellow sodium light.

The influence of wave-length on the optical rotatory power of crystals has been studied much more fully than in the case of liquids. Of some thirty substances which show this property, about one-third have been examined with light of three or more wave-lengths. In the case of quartz and of sodium chlorate, the observations have been extended by SORET, SARASIN, and GUYE ('Geneva Archives,' 1882 [III.], vol. 8, 5–59, 98–132, 201–228; 1889 [III.] vol. 22, 130) from the visible to the ultra-violet region of the spectrum. Observations of the optical rotatory power of quartz in the infra-red region have been made by E. CARVALLO ('Comptes Rendus,' 1892, vol. 114, 288) and by R. DONGIER ('Comptes Rendus,' 1897, vol. 125, 228). As questions of solvent, concentration and chemical constitution enter scarcely at all into the study of the optical rotatory power of crystals, this property has been investigated mainly from the standpoint of crystallography or of pure physics. In addition to the influence of the wave-length of the light, the effect of temperature has been the problem mainly studied. In particular, the optical rotation produced by quartz plates has been measured over the range of temperature from +840° C. (JOUBERT, 'Comptes Rendus,' 1878, vol. 87, 497) to −190° C. (MOLBY and GIBBS, 'Phys. Rev.,' 1910, vol. 30, 77–91; vol. 31, 291–310).

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* See, for instance, Prof. FRANKLAND'S review of the subject in his Presidential Address to the Chemical Society, March 28, 1912.

NOTE.—It does not appear to be generally known that chemists and physicists have adopted different conventions as regards the sign of an optical rotation, so that dextro-quartz and dextro-camphor actually rotate the plane of polarisation in opposite directions. In the case of dextro-quartz the rotation is clockwise to an observer looking along the path of the light; in the case of dextro-camphor the rotation is clock-wise as viewed from the eye-piece of the polarimeter.

The methods used in measuring rotatory dispersion differ from one another mainly in two respects:—

1. As regards the source of light, which may give (*a*) a continuous spectrum or (*b*) a line-spectrum, either monochromatic or multichromatic;
2. As regards the methods used in selecting a line or portion of the spectrum, which may depend (*a*) upon a spectroscope whereby the light is resolved either before or after it passes through the polarimeter or (*b*) upon the use of absorption-screens.

BROCH'S *Method*.—The earliest measurements of rotatory dispersion were made on quartz with the help of sunlight falling upon a vertical slit; after passing through a simple polarimeter (consisting of movable polariser, quartz plate and analyser) the light was resolved by means of a single glass prism, without a telescope or eye-piece; the polariser was rotated until a dark extinction-band was superposed on one after another of the Fraunhofer lines from B to G (BROCH, 'Ann. Chim. Phys.,' 1852, vol. 34, 119–121; from 'Repertorium der Physik,' 1846, vol. 7, 113). The same method was suggested in general terms a year previously by FIZEAU and FOUCAULT ('Comptes Rendus,' 1845, vol. 21, 1157). This method was improved by G. WIEDEMANN ('Pogg. Ann.,' 1851, vol. 82, 215–232), who added a telescope to the refracting prism, and with this apparatus made the first exact observations of the natural rotatory dispersion of liquids (turpentine and lemon oil for the Fraunhofer lines B to G) and of their magnetic rotatory dispersion (carbon disulphide and turpentine for the Fraunhofer lines C to G), and discovered the proportionality of the two rotatory powers over a series of wave-lengths (turpentine for the Fraunhofer lines C, D, E, B, F gave the ratios 4·07, 4·12, 4·10, 4·14, 4·12). A. ARNDTSEN used a cross-wire in the telescope to locate the positions of the Fraunhofer lines and measured the rotatory dispersion of sugar, tartaric acid,[*] malic acid and camphor. J. STEFAN ('Wien. Ber.,' 1864 [II.], vol. 50, 88–124) developed this method of working into its final form by using, in series with a simple polarimeter, a complete spectroscope, with a prism of crown-glass, flint-glass, water or quartz, or a grating, to refract the light; he used an artificial source of light,[†] measured the positions of the extinction-bands on the circle of the goniometer (polariser and analyser fixed) and, after establishing a linear relationship between the rotatory power of the quartz and the refraction of the prism, calculated the rotatory power of the quartz for the seven Fraunhofer lines B to H. STEFAN showed that, whilst the rotatory dispersion could not be represented by BIOT'S formula $\alpha = k\lambda^{-2}$, a satisfactory concordance between theory and experiment could be obtained by using CAUCHY'S formula $\alpha = k_1 + k_2\lambda^{-2}$. STEFAN'S method[†] was used by V. VON LANG ('Wien. Ber.,' 1875 [II.], vol. 71, 707–714) in measuring the influence of temperature upon the optical rotatory power of quartz; he calibrated the spectroscope by means of lithium, sodium and thallium flames and brought the extinction-bands to these three positions by rotating the analysing Nicol prism. A complete spectroscope in series with a simple polarimeter was also used by SORET and SARASIN ('Geneva Archives,' 1882 [III.], vol. 8, 5–59, 98–132, 201–228) with solar light as illuminant and Fraunhofer lines as standards of wave-length in their measurements of optical rotation in quartz; the same arrangement was used by GUYE ('Geneva Archives,' 1889 [III.], vol. 22, 130) with artificial light in his measurements of optical rotation in sodium chlorate.

LIPPICH'S *Method*.—In order to read rotations which are too small in magnitude to give rise to narrow bands, LIPPICH ('Wien. Ber.,' 1885 [II.], vol. 91, 1070) passed the light through a spectroscope *before* it reached the polarimeter; the spectrum, instead of being received by an eye-piece, fell upon a second slit,

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[*] BIOT, who discovered the phenomenon of anomalous rotatory dispersion in tartaric acid ('Mem. Acad. Sci.,' 1838, vol. 15, 93; vol. 16, 229; 'Ann. Chim. Phys.,' 1844, (3), vol. 10, 5, 175, 307, 385; vol. 11, 82; 1850, vol. 28, 215, 351; vol. 29, 35, 341, 430), merely used blocks of the spectrum, in the red, yellow, green, &c., without attempting to locate accurately their positions in the spectrum.

[†] LANDOLT ('Optical Rotating Power,' 1902, p. 423) attributes to VON LANG the method described by STEFAN eleven years previously of using artificial light in place of sunlight.

which formed the source of light for the polarimeter. The difficulty of having to move the light-source, collimator and prism for every fresh colour is effectively overcome by using a constant-deviation prism (CHRISTIE, 'Roy. Soc. Proc.,' 1878, vol. 26, 8) mounted on a spectroscope in which both slits are fixed and the colour is varied by merely rotating the prism (see F. TWYMAN, 'Phil. Mag.,' 1907, vol. 13, 481). LIPPICH'S method of working has the great advantage that it can be applied to his half-shadow instruments with a double or triple field.

LANDOLT'S *Method*.—Another method in which a continuous spectrum is used as a source of light is that of LANDOLT ('Sitz. Akad.,' Berlin, 1894, 323; 'Ber. Deut. Chem. Ges.,' 1894, vol. 27, 2872), in which five filters are used to separate light in the red, yellow, green, light blue and dark blue portions of the spectrum, the optical mass-centres of the transmitted light at wave-lengths 6659, 5919, 5330, 4885, and 4482 being near to those of the Fraunhofer lines C, D, E, F, G at 6563, 5893, 5270, 4861, and 4308 respectively. This method, which avoids the use of a spectroscope, is the only one that has been adopted widely in chemical laboratories (WINTHER, 'Zeit. Physikal. Chem.,' 1907, vol. 60, 563; WALDEN, 'Zeit. Physikal. Chem.,' 1906, vol. 55, 1; TSCHUGAEFF, 'Zeit. Physikal. Chem.,' 1911, vol. 76, 469; GROSSMANN, 'Zeit. Physikal. Chem.,' 1910, vol. 75, 129).

PERKIN'S *Method*.—The use of a small direct-vision spectroscope in front of the eye-piece of the polarimeter was introduced by Sir WILLIAM PERKIN as a method of purifying the flame-spectrum of sodium. But it is capable of a much wider application as affording the simplest and one of the most efficient means of measuring rotatory dispersion in ordinary laboratory practice. PERKIN used it in reading the magnetic rotation of red lithium and of green thallium light, salts of these metals being added to a platinum boat, already containing a sodium salt, heated by a jet of oxygen in the centre of the flame of a Bunsen burner. Used in conjunction with the lithium and sodium flames and the enclosed mercury arc, PERKIN'S method satisfies all the requirements of a standard laboratory method for modern use.

In reviewing the methods described above, it is necessary to emphasise the fundamental requirement for accurate polarimetric work, namely, that *the field of the polarimeter must be uniformly lighted with monochromatic light.* Of the methods in which a continuous source of light is used, BROCH'S method cannot be used to measure optical rotations of small magnitude and (as will be shown in a later paper) it can be improved considerably even in the case of large rotations by using a polarimeter with a triple field and replacing the continuous spectrum by a crowded line spectrum, such as that of the iron arc; LANDOLT'S method, on the other hand, breaks down completely in the case of rotations exceeding a very few degrees, the large blocks of spectrum employed giving no extinction at all with rotations of larger magnitude; the LIPPICH method is also unsatisfactory, especially in the case of large rotations, on account of stray light; this point is discussed in a later paragraph (p. 266). Of all the methods described above, the only one that is available for the accurate measurement of rotations, both of large and of small magnitude, is that of PERKIN, in which a light-source containing two or three strong spectrum lines is resolved by means of a direct-vision prism placed in front of the eye-piece of the polarimeter.

3. *New Methods and Devices for Measuring Rotatory Dispersion.*

PERKIN'S method gives excellent results when applied to light comprising only a few spectrum lines. It is very economical of light and, after repeated trials of other methods, has been found to be the best method now available for reading:—

The red lithium line	6708·2
The green thallium line	5350·65
The violet mercury line	4358·58.

It can also be used very satisfactorily to read :—

The green mercury line	5460·97
The yellow sodium doublet	5890·19 5896·16
The yellow mercury doublet . . .	5769·16 5790·49.

The two doublets are only available for reading small rotations and must be resolved into separate lines if large rotations are to be observed.

The flame spectra of lithium, sodium and thallium, and the arc spectrum of mercury (LANDOLT, p. 433 ; DISCH, 'Ann. Phys.,' 1903 (IV.), vol. 12, 1155 ; SCHÖNROCK, 'Zeit. Vereins Deutsch. Zuck.-Ind.,' Tech. Part, 1903, vol. 53, 652), giving the six colours shown above, were the only line spectra that had been effectively made use of in polarimetry* at the time when the present investigation was commenced. In order to increase the number of available light-sources, recourse was had to the brilliant line-spectra of the metallic arcs, as described in Section 4 of the paper. With these new light-sources PERKIN'S method can no longer be used, the glare of adjacent lines being so great that it is impossible to take accurate readings of the line that is being brought to extinction. Under these conditions it is necessary to resolve the light spectroscopically before it enters the polarimeter. This was done by means of a constant-deviation spectroscope, the instrument being arranged so that an image of the slit fell upon the triple-field of a polarimeter in the position normally assigned to the eye-piece of the spectroscope ; a wide slit opening symmetrically was inserted immediately in front of the triple-field and could be used to cut off the light from lines immediately adjacent to the one under observation.

At an early stage in the work it was discovered that, whilst this arrangement was fairly satisfactory for lines in the middle of the spectrum, it was seriously defective for lines in the red and blue, on account of stray light from the green and yellow lines. Thus readings of magnetic rotation in carbon disulphide were depressed from 70°·90 to 69°·33 in the case of the violet line Hg 4359 and from 58°·95 to 58°·28 in the case of the blue line Cd 4678 by stray light of longer wave-length. The readings, 40°·19, of the green line Hg 5461 were not affected by stray light ; but the value for the yellow doublet Hg 5780 was raised from 35°·14 to 35°·19 and that for the red line Cd 6438 from 27°·52 to 27°·68 by stray light of shorter wave-length ; the errors are here much less than in the case of the blue and violet lines but are sufficiently serious to destroy the value of the measurements as exact observations.

This fault, which does not appear to have been recognised previously, is inherent in all devices of the Lippich type, in which the light is resolved spectroscopically

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* DISCH had also taken readings with the red hydrogen line 6563·04 and with the mercury line 4916·41, but had been obliged to use half-shadow angles up to 30°.

before it enters the polarimeter. It was overcome by PERKIN'S device of using a direct-vision prism in conjuction with the eye-piece to throw out the stray light. This prism forms an essential part of the apparatus and can only be dispensed with under exceptional circumstances some of which are discussed later in the paper. When the prism at the eye-piece was required to aid in the resolution of a close doublet or in the elimination of a satellite or to throw out stray light from a closely-adjacent line, direct-vision prisms were used which had been specially constructed with a centre-prism of glass of refractive index 1·92; three of these prisms were used for the red, green and blue portions of the spectrum respectively. A greatly-increased dispersion was secured with the help of two prisms, specially constructed from the same dense glass, of the Rutherford pattern (see fig. 1), in which the angle of the central prism is so great that light travelling parallel to the base would be totally reflected at an air-surface but is actually brought in and out of the prism at grazing incidence by prisms of light glass cemented to the dense prism. One of the Rutherford prisms transmitted the spectrum to about λ 4800; the violet lines were here lost by total reflection but were transmitted by a second prism constructed with a slightly smaller angle; the actual angles were :—

For red, yellow and green . . $\left\{\begin{array}{l}\text{dense prism } 104^\circ \\ \text{light prisms } 8^\circ \text{ each}\end{array}\right\}$;

For blue and violet . . . . $\left\{\begin{array}{l}\text{dense prism } 98^\circ \\ \text{light prisms } 10^\circ \text{ each}\end{array}\right\}$.

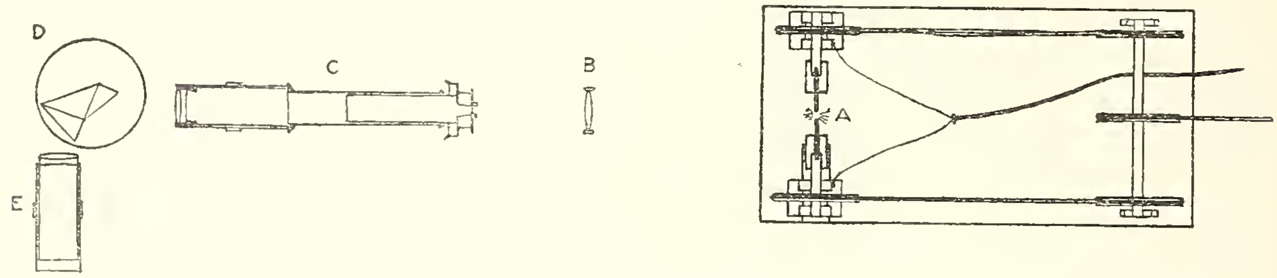
These prisms require more careful setting in front of the eye-piece than prisms of the ordinary direct-vision type and are more troublesome for the eye to find and to use; but their very high dispersion, combined with great economy of light, renders them of great value in cases where a system of specially high dispersive power is required.

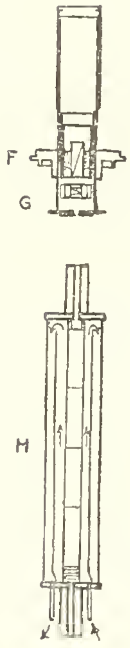
The primary purpose of the prism in front of the eye-piece of the polarimeter is to eliminate stray light rather than to resolve the lines of the spectrum; this resolution must be effected mainly by the constant-deviation spectroscope, in order that adjacent lines and satellites may be blocked out by the polarimeter slit and so prevented from producing a distracting glare of light in the neighbourhood of the line under observation. A high resolution is of value, both in separating the lines of a doublet, such as the yellow doublet of mercury or of sodium, and in increasing the width of the lines that can be used without overlapping, so that in many cases it is possible to cover the whole width of the aperture of the polarimeter with a block of pure monochromatic light. But high resolution is usually gained at the cost of a serious sacrifice of light, and it was only when using bright arc-spectrum lines in the central part of the visible spectrum that the most dispersive systems could be used with advantage.

Successive increases in the dispersive power of the spectroscope were obtained in the following way :—

1. The 11-inch lens of the "eye-piece" tube of the spectroscope was replaced by an

achromatic lens of 22-inch focus, whereby the linear dimensions of the image were doubled, a slit 1 mm. in width now giving an image 2 mm. in width.





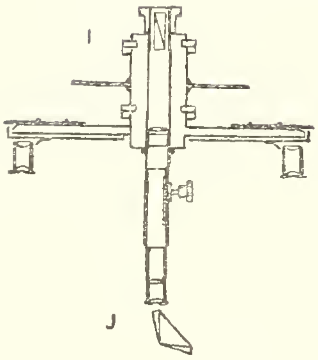


Fig. 1. General arrangement of apparatus for reading rotatory dispersion.

A. Rotating arc.

B. Condenser.

C. Collimator (11-inch focus).

D. Constant-deviation prism with grating replica on reflecting prism.

E. "Eye-piece tube" of constant-deviation spectroscope with lens of 22-inch focus.

F. Triple-field polariser.

G. Polarimeter slit.

H. Water-jacket with quartz cylinders.

I. Analyser.

J. Rutherford prism in front of eye-piece.

2. The light constant-deviation prism was replaced (*a*) by a dense prism of the same shape (*b*) by a pair of 30° prisms of the extra dense glass of refractive index 1·92 with a right-angle prism of light glass to act as reflector.

3. The right-angle prism was replaced by one bearing a Thorpe replica of a Rowland grating, placed so that the very bright first order diffraction spectrum on one side acted in co-operation with the two extra-dense 30° prisms to give the effect of a constant-deviation prism of exceptionally high dispersive power.

The resolution attained by these methods may be illustrated by giving the actual separation of the two mercury lines 5769·45 and 5790·49; these were used as test-lines during the early part of a series of experiments which had as their ultimate aim the effective resolution of the green silver doublet 5465·66 and 5471·73, and the yellow sodium doublet 5890·19 and 5896·16.

Actual Separation of Mercury Lines 5769 *and* 5790 *by Constant Deviation Spectroscope*:—

11-inch focus lens and light C.D. prism	0·1	mm.
22 ,, ,, ,, ,, ,, ,, ,,	0·2	,,
22 ,, ,, ,, ,, dense ,, ,,	0·3	,,
22 ,, ,, ,, ,, extra dense 30° prisms (1·92)	0·45	,,
22 ,, ,, ,, ,, grating replica	0·75	,,
22 ,, ,, ,, grating replica and extra dense 30° prisms	1·2	,,

Virtual Separation of Mercury Lines by Eye-piece Prisms:—

Ordinary D.V. prism	0·3	mm.
Extra dense (1·92) D.V. prism	0·4	,,
Rutherford prism	0·65	,,

The maximum separation was therefore $1·2+0·65 = 1·85$ mm.

The complete apparatus as used in resolving the green silver doublet is shown in fig. 1.

A photographic method of measuring rotatory dispersion, which is specially valuable in the ultra-violet region of the spectrum, will be described in a later paper; the methods used in the red and infra-red regions will also be described later.

4. *Light Sources.*

The principal light sources used in measuring the rotatory dispersion of quartz were:—

(1) The flame spectra of lithium and thallium;
(2) The mercury arc enclosed in glass and in silica;
(3) The spectrum of sodium in a carbon arc;
(4) The open arc spectra of silver, copper, cadmium, and zinc.

In almost every case it was necessary to produce a light of the greatest possible intensity: only in this way was it possible to make use of a dispersive system of sufficient power to guarantee the effective purification of the light. Even when light-sources of the highest intensity were used, it was often found to be desirable to work with a system of lower dispersive power (using narrower slits and a narrower line in the field of the polarimeter) in order to maintain sufficient brightness to render possible the use of a small half-shadow angle; this factor is specially important in the case of the open-arc spectra, which are difficult to maintain in a condition to produce steady illumination.

(1) *Lithium.* 6708·2.

The flame spectrum of lithium is of such low optical intensity that even under the most favourable conditions it could not be read with a half-shadow angle of less than 7°. In order to economise light, the red lithium line was read with a direct-vision prism in front of the eye-piece as the only dispersive system. As Perkin's arrangement of the lithium flame did not give sufficient light, the arrangement shown in fig. 2A was used, a long, narrow globule of lithium carbonate being supported on a bundle of platinum wire over a jet of oxygen led by a platinum tube through the grid of a "Mecker" burner.

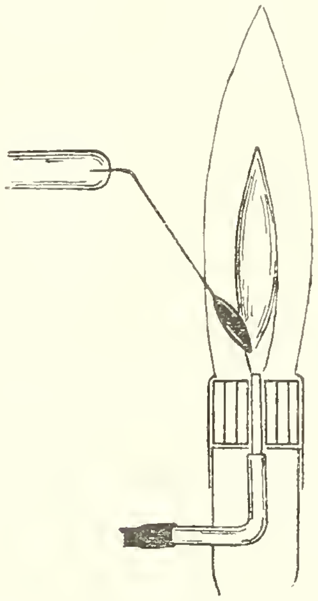


Fig. 2A. Lithium flame.

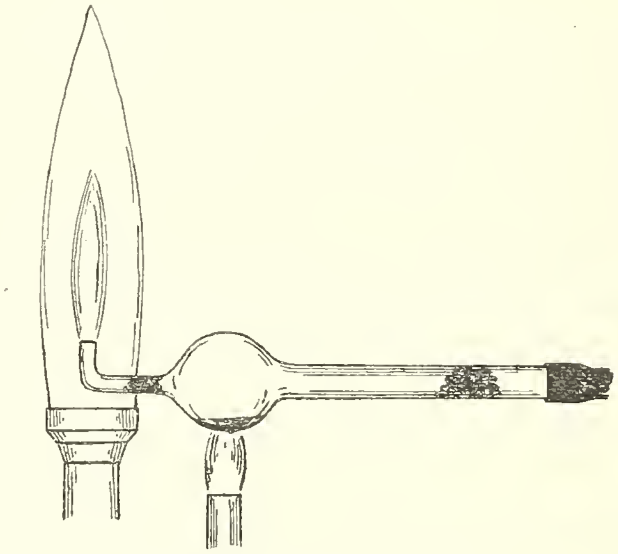


Fig. 2B. Thallium flame.

(2) *Thallium.* 5350·65.

Although the flame spectrum of thallium gives a very bright and pure monochromatic green light, its use was attended with very great difficulty on account of the extreme volatility of the chloride and the transient character of the light obtained by the ordinary methods of procedure. After many unsuccessful efforts, a steady light was finally obtained by the method shown in fig. 2B, the chloride being vaporised in a silica bulb and carried into the flame through a silica jet by a current of oxygen. With this arrangement, a very bright and steady illumination can be maintained during a period of several hours; the discovery of an equally efficient method for producing a steady lithium flame would be a very great convenience. The readings were taken with a dense direct-vision prism as the only dispersive system and a half-shadow angle of 5°.

(3) *Sodium.* 5896·16 and 5890·19.

The lines of the sodium doublet were by far the most difficult to read of the series now described. They could only be separated by using the highest available dispersion on the constant-deviation spectroscope, when the actual separation of the centres of the lines amounted to $\frac{1}{4}$ mm. Under these conditions the flame spectrum, even with the help of oxygen, was quite inadequate as a source of light. The actual readings were taken from a carbon arc with a thread of glass in the hollow core of the upper carbon. The main trouble was the reversal of the lines, which frequently appeared as a yellow band crossed by two very narrow black Fraunhofer lines. These reversed lines were admirably adapted for setting the spectroscope, the best possible adjustment being obtained when a black Fraunhofer line could be seen down the centre of the slit of the polarimeter, this slit being narrowed to about $\frac{1}{4}$ mm. in order to cut out the other line of the doublet; they were, however, quite useless for taking the actual readings. The device finally used to secure trustworthy observations consisted in levering open the jaws of the slit to see the character of the lines and releasing the jaws in order to take readings when the lines were seen to be narrow and luminous (without reversal). This condition could sometimes be maintained during several minutes but was never quite to be relied on; the reversal of the line could usually be detected even without opening the jaws of the slit, by the loss of sharpness of the extinction and a sudden change of perhaps 2° in the readings as the neighbouring line broadened and spread into the field of view; this effect was particularly troublesome in the case of the less refrangible line. The sodium lines were read without any prism on the eye-piece, as the half-shadow angle could be reduced from 10° to 5° by removing this prism; this exceptional course was justified (*a*) by the small amount of the stray light in the grating spectrum (*b*) by the fact that the stray light would be practically a continuous spectrum crossed by some scores of extinction bands and would not be likely to deflect the extinction more in one direction than in the other; the eye-piece would not in any case have been adequate to throw out stray light from the other sodium line.

A very promising method of producing a bright sodium spectrum *without reversal* consisted in adding sodium salts to a silver arc. But owing to the relative feebleness of the light and the extremely trying character of the work of taking readings, the attempt to utilise this method was finally abandoned.

(4) *Mercury.* 5790·49, 5769·45, 5460·97, 4358·58.

The mercury arcs used in these experiments included—

(*a*) *A Bastian lamp.* The arc is here formed in a zigzag glass tube 11 inches long and 3/16th inch diameter; this tube, which is normally in a horizontal plane, was tilted into a vertical plane for use with the polarimeter, one of the straight portions of the tube being focussed on the slit of the constant-deviation spectroscope. A long, straight arc of uniform luminosity, which can be focussed directly upon the slit, is an ideal source of light for work of this kind, as the uniform illumination of the triple field follows automatically without the careful adjustment that is necessary in the case of a spherical source of light. The Bastian lamp, taking a current of less than an ampere and capable of being connected directly to the ordinary lighting circuit, is the most convenient mercury lamp that has yet been devised and it is a matter for regret that it is no longer manufactured commercially.

(*b*) *An end-on mercury lamp* and

(*c*) *A vertical "Quartzlite" lamp*, both made of silica and taking a current of 3·5 amperes. These lamps were specially constructed for use with the polarimeter and have been described and figured in the 'Trans. Faraday Soc.,' 1912, vol. 7, 267.

(4) (A) *Mercury Green.* Hg 5460·97.

In reading rotations of large magnitude it is impossible to use sodium light as a standard, owing to the fact that the lines D_1 and D_2 are not extinguished together, the difference amounting in the experiments now described to 8° for the dextro-quartz and 11° for the lævo-quartz column. It was, therefore, necessary to adopt some other light for the purpose of making stringent tests on the quartz blocks before attempting measurements of rotatory dispersion. For this purpose the green mercury line was selected. The choice has been fully justified by practical experience during several subsequent years. Not only is the line one of the easiest to produce and read but it is the only line of the 24 which can be read as easily and as sharply to 0°·01 on a rotation of 12,000° as on one of 5°. Most of the measurements were made with the glass Bastian lamp as a source of light, a dense prism on the constant-deviation spectroscope and a dense direct-vision prism on the eye-piece. Although the line can be resolved on the *echelon* spectroscope, its spectral purity is incomparably greater than that of sodium (NUTTING, 'Bureau of Standards Bulletin,' 1906 [II.], 249), and it is undoubtedly the best line to use for standard measurements of natural and magnetic rotation, at least until the manufacture of enclosed cadmium arcs has been sufficiently perfected and simplified to render the green line Cd 5085·8240 available for general use. The green mercury line has the further advantage that it can be separated readily from the other lines of the spectrum by a direct-vision prism of low dispersive power and can, therefore, be used in everyday polarimetric work without an auxiliary spectroscope.

The yellow, green and violet mercury lines can also be separated by means of gelatine screens. This modification of LANDOLT's method is far more convenient than the original form in which absorbent solutions were used; it has the further advantage that it lends itself to accurate work, since the portions of the spectrum which are picked out are, except in the case of the yellow doublet, really monochromatic. But in spite of these merits this method of working has no advantage over the use of a direct-vision prism, which gives an even more efficient separation at about the same cost; the economy of light, as compared with the absorbent screens, more than compensates for the glare of the adjacent lines.*

(4) (B) *Mercury Yellow.* Hg 5790·49, Hg 5769·45.

The yellow doublet of the mercury spectrum can be resolved with the utmost ease by the apparatus described above, giving wide blocks of pure monochromatic light in the field of the polarimeter. Unfortunately, the vertical silica lamp, which was required to illuminate the field with the system of highest dispersive power, was found to yield appreciable quantities of continuous light in this part of the spectrum; the actual measurements were therefore made with the extra dense prisms (but no grating) on the spectroscope, and a Rutherford prism on the eye-piece, using a glass Bastian lamp and a half-shadow angle of 5°. For small rotations the two lines can be read as one, but there is no advantage in this, as so many purer light-sources are now available.

(4) (C) *Mercury Violet.* Hg 4358·58.

Owing to the weak visual intensity of the blue and violet portions of the spectrum, economy of light is of the utmost importance; thus, in spite of its extreme brightness, the violet mercury line must be read with a prism at the eye-piece as the only dispersive system. The line is accompanied by two more refrangible satellites 4348·0. and 4341·0; these are not usually seen in the polarimeter, but become important when using a silica lamp as a source of light for reading optical rotations of several thousand degrees.

The Rutherford prism, which had been constructed for these measurements, could not be used, as the violet line was covered by a strong glare of green stray light. The observations were therefore made with a dense direct-vision prism, the slit in front of the triple field being narrowed until the line was completely separated from the two satellites. In order to make the line *at extinction* of about the same intensity as the unextinguished satellites, it was necessary to increase the half-shadow angle to 7°, when an excellent series of readings was obtained.

(4) (D) *Optical Mass-centre of the Violet Mercury Line.*

On account of its extreme brightness and the ease with which it can be produced,

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[* *Note added August* 6, 1912.—In the case of the violet line, Dr. MEES has suggested to me that a screen of pure xylene red may be used with a direct-vision spectroscope to reduce the glare of the green. Although it would not, if used alone, give a pure monochromatic light, it absorbs much less of the violet light and is therefore much more suitable for the present purpose than a screen of density sufficient to absorb completely all the other lines of the mercury spectrum.]

the violet mercury line occupies the same dominant position for polarimetric work in the violet that the green line holds for work in the brighter portions of the spectrum. No other line in the blue or violet can be read with the same ease and accuracy, and no other line in this region is available for general laboratory use. For all ordinary purposes it is sufficient to separate the line from the light blue (4916·41) and violet (4078·03 and 4046·78) lines without attempting to resolve the satellites (4348·0 and 4341·0); this can be done with an ordinary direct-vision prism on the eye-piece, and no further elaboration is necessary or desirable for readings of less than 1000°. With this simple arrangement and a vertical silica mercury lamp, readings can be taken with a half-shadow angle of 4° and with an accuracy but little inferior to that obtained in reading the green. These readings are of very great importance in measuring dispersion, as it is only on this line that the smaller differences of dispersive power can be perceived; the variations at the red end of the spectrum are much smaller and much more difficult to detect with certainty. In a later paper it will be shown that the measurement of the ratio $\alpha_{4359}/\alpha_{5461}$ affords the best method at present available for characterising the rotatory dispersion of a substance.

In order to ascertain the effect on the readings of including or excluding the two satellites, the following experiments were made. After having established the ratio of the violet and green rotations to be 1·62700 for long columns of quartz, a further series of measurements was taken with a short rod 25·902 mm. in length, the slit of the polarimeter being opened widely so that there was no separation of the satellites from the chief line. The readings were as follows:—

	Rotation.	Ratio.
Mercury green	661°·47	1·00000
Mercury violet (current 3 amperes)	1076°·33	1·62717
,, ,, ,, 4 ,,	1076°·45	1·62729
,, ,, ,, 5 ,,	1076°·52	1·62747

These observations show that with a current of 3 amperes, the error produced by including the satellites amounts only to 1 part in 10,000 and would be inappreciable in readings of less than two right angles. In all ordinary polarimetric work involving readings of a few degrees only, the larger currents, giving an error of 1 part in 5,000 at 4 amperes and an error of 1 part in 3,000 at 5 amperes, may be used without hesitation, if desired.

(5) *Silver.* 5471·72, 5465·66, 5209·25.

Of all the open metallic arcs, the silver arc is that which is most readily adapted to polarimetric work. The chief features of the spectrum are the dark green line 5209·25 and the bright green doublet, 5471·72 and 5465·66, the more refrangible component of which approaches very closely to the green mercury line 5460·97. The dark and bright green lines could easily have been separated by a single direct-vision prism, but in practice all the open-arc spectra were resolved by means of the constant deviation spectroscope, the slit of which was adjacent to a small draught-hood in which the arc was placed.

The rotating arc shown in fig. 1 was a modification of that described by BALY ('Spectroscopy,' 1912, p. 391). Silver rods $1\frac{1}{4}$-inch long and $\frac{1}{4}$-inch in diameter were screwed into copper cylinders 1-inch long and $\frac{5}{8}$-inch diameter, which served to cool as well as hold the rods. The copper cylinders in their turn were screwed on to $\frac{3}{8}$-inch iron spindles which were rotated in opposite directions by means of pulley-wheels driven by belts from a small power shaft at the back of the machine, this shaft being run from a fan-motor in series with an adjustable resistance. One of the spindles was mounted on a pedestal provided with a slide, so that it could be moved inwards as the electrodes were burned away. In order to maintain a steady arc, free from serious flickering, it was necessary to exercise some care in centering the silver electrodes and also to run the machine at the highest convenient speed. A current of 5 amperes was usually employed but there is little doubt that in the case of the silver arc a heavier current up to 10 amperes might have been used.

(5) (A) *Silver Dark Green.* Ag 5209·25.

This line was read with the extra dense prisms on the constant deviation spectroscope but no grating and with a Rutherford prism in front of the eye-piece. The half-shadow angle was very small, about 3°, and the readings were amongst the easiest of those taken with the rotating arc.

(5) (B) *Silver Light Green.* Ag 5471·72 and Ag 5465·66.

This doublet, separated only by 6·06 units as compared with 5·97 units for the sodium doublet, was read quite easily with the system of highest dispersion, including the extra dense 30° prisms, grating, and Rutherford prism. The intensity of the light was so great that even in the case of the less refrangible weaker component, a half-shadow angle of only 5° could be used; the readings were among the most concordant of the whole series.

(6) *Cadmium.* 6438·4722, 5085·8240, 4799·9107, 4678·37.

Although an enclosed arc would undoubtedly be the ideal source of cadmium light, a very efficient substitute is afforded by an open arc with electrodes of a cadmium silver alloy (LOWRY, 'Phil. Mag.,' 1909, vol. 18, 320). This can be run very satisfactorily during about an hour with a current of 4 amperes, the current being adjusted so that the cadmium distils out from the end of one of the electrodes, occasionally in such a way as to leave a considerable cavity in the interior of the rod. Before starting up again it is necessary to file away the tip of the electrode in order to bring to the surface a fresh supply of cadmium.

(6) (A) *Cadmium Red.* Cd 6438·4722.

On account of the presence of continuous red light, this line is not easy to read when working with rotations of 3,000° to 4,000°; a specially narrow slit was used in conjunction with a Rutherford eye-piece and extra dense 30° prisms (without the grating) on the constant-deviation spectroscope. The half-shadow angle was 4°.

(6) (B) *Cadmium Green.* Cd 5085·8240.

This magnificent line, if more easily produced, would be the most suitable for use in place of the green mercury line as principal standard in polarimetric and refractometric work. It was read with the same dispersing system as the preceding line but with a half-shadow angle of only 3°.

(6) (C) *Cadmium Light Blue.* Cd 4799·9107.

This line was read with the same dispersive system but with the half-shadow angle increased to 5° or 6°.

(6) (D) *Cadmium Dark Blue.* Cd 4678·37.

This line is difficult to read on account of its smaller intensity and diminished visual efficiency; the presence of the silver line Ag 4668·70 presents a further difficulty in the case of large rotations, as it acts as a somewhat close satellite. The line was read with considerable difficulty, using the ordinary dense constant-deviation prism on the spectroscope, a dense direct-vision prism on the eye-piece and a half-shadow angle of 8°.

(7) *Zinc.* 6363·7, 4810·71, 4722·26, 4680·38.

The methods used to read the zinc lines were similar to those followed in the case of cadmium. Two alloys were used, a silver-zinc alloy and a brass specially prepared from pure zinc and electrolytic copper; the latter alloy was the easier to burn; it gave the best results with a small current of about 3 amperes.

(7) (A) *Zinc Red.* Zn 6363·7.

This line was more difficult to read than the corresponding cadmium line on account of the greater amount of continuous light in the spectrum—an unimportant factor with readings of ordinary magnitude but of vital importance when reading large rotations. It was finally read with the ordinary dense constant-deviation prism, Rutherford prism, specially narrow slit and a half-shadow angle of 7°.

(7) (B) *Zinc Blue.* Zn 4810·71, Zn 4722·26, Zn 4680·38.

These lines were read under the same conditions as the blue cadmium lines. The third zinc blue line presents practically the same difficulties as the second cadmium blue line, from which it is separated by only two Ångstrom units; it was read with brass electrodes, thus eliminating the silver line, and a half-shadow angle of 6°. The extreme difficulty of reading these lines serves to emphasise the extraordinary value of the violet mercury line, which is 320 units further on in the violet region and yet can be read with greater ease than even the least refrangible of the bright blue zinc and cadmium lines.

(8) *Copper.* 5782·30, 5700·39, 5218·45, 5153·33, 5105·75.

Unlike the alloys used to produce the spectra of cadmium and zinc, the copper arc can be used with heavy currents up to about 10 amperes, although the highest current used in the present experiments did not exceed 5 or 6 amperes. The spectrum is much more complex than those of the preceding metals and some care is needed to ensure spectral purity. Values are now given for the two yellow and three green lines but occasional readings have been made with four of the blue lines (4705, 4651, 4587·19, 4378·40), and by using a heavy current there is little doubt that some at least of these could be added to the list of 24 wave-lengths tabulated below.

(8) (A) *Copper Yellow.* Cu 5782·30, Cu 5700·39.

The yellow copper lines are of good spectral purity and are easy to read, specially so in the case of the less refrangible line. They were read with the extra dense 30° prisms on the spectroscope (without a grating), a Rutherford prism at the eye-piece and a half-shadow angle of only 4°.

(8) (B) *Copper Green.* Cu 5218·45, Cu 5153·33, Cu 5105·75.

The two more refrangible lines were read without difficulty under the same conditions as the yellow lines. In spite of the presence of two satellites, 5158·53 and 5144·35, the central line proved to be the best of the three copper greens; it may be noted that these satellites are of weak intensity and lie one on either side, so that even if they were not completely eliminated by the dispersive system they would probably have very little influence on the optical mass-centre of the line. The least refrangible line has a strong satellite at 5220·25; when using the system of highest dispersion it could be seen distinctly, although separated by only 1·80 Ångstrom units; but as it could not be eliminated by the methods then available, a direct-vision prism was substituted for the Rutherford prism and the readings were taken with line and satellite superposed; this is the only case in the whole series in which a line with a visible satellite was used as if it were a single line.

5. *Quartz.*

With the exception of sodium and thallium, complete series of readings of all the lines referred to in the preceding section had been taken as long ago as the spring of 1908. The delay of four years in the completion of the work may be traced almost entirely to the extreme difficulty of securing quartz of sufficiently high quality to withstand the more and more stringent tests that were found to be necessary in the course of the work. Much time and many thousands of readings might have been saved if these new tests had been discovered before the work of measuring the rotatory dispersion of the specimens was commenced.

The commonest type of flaw in quartz is that due to the "twinning" of the dextro- and lævo-rotatory varieties. When the intermingling is close the quartz becomes "feathery," and presents the striated appearance seen in an ascending current of hot air; when viewed through a Nicol prism, with light partially polarised by reflection from a glass surface, the striæ are coloured and can be seen without difficulty. It is scarcely necessary to add that this fault, and other obvious flaws, were carefully avoided in selecting plates for the investigation.

Plates 25 mm. in thickness were first cut from blocks of dextro- and lævo-quartz, and from each plate four cylinders 15 mm. in diameter were cut. On taking readings of the optical rotatory power of these cylinders with green mercury light, the whole of the four lævo-cylinders were rejected, some because striæ revealed by the monochromatic illumination rendered it impossible to take satisfactory readings, others because the readings of the cylinders (all cut from the same plate and accurately equal in length) not only differed from cylinder to cylinder, but also when the same cylinder was rotated about its own axis. The best of the four lævo-cylinders gave the readings:—

L_3	613°·17	613°·17	613°·30	613°·58.	Mean 613°·30.

Of the four dextro-cylinders, one gave readings ranging over 4° and the other three gave:—

R_1	613·14	613·16	613·08	613·03.	Mean 613·10.
R_2	613·02	613·38	613·28	613·02.	,, 613·17.
R_4	613·09	613·11	613·08	613·16.	,, 613·11.

As a result of these tests, the first and last of the dextro-cylinders, which differed only by 0°·01, were selected as satisfactory, the two other cylinders for which figures are given were rejected as doubtful, the remaining four were thrown out as obviously faulty.

Additional plates of dextro- and lævo-quartz were then cut to about the same thickness and cylinders cut and tested in the same way by reading each in four positions. The figures were:—

R_{10}	636·80	636·79	636·87	636·79.	Mean 636·81.
R_{20}	637·16	636·97	636·80	636·16.	,, 637·02.
R_{30}	636·81	636·76	636·75	636·76.	,, 636·77.
R_{40}	636·79	636·75	636·76	636·76.	,, 636·77.
L_{10}	640·27½	640·24	640·27	640·33.	,, 640·28.
L_{20}	640·27	640·25	640·29	640·31.	,, 640·29.
L_{30}	640·43	640·21	640·23	640·27.	,, 640·29.
L_{40}	640·24	640·21	640·22	640·26.	,, 640·23.
L_{50}	640·34	640·26	640·21	640·24.	,, 640·26.
L_{60}	Bad extinctions.				
L_{70}	640·19	640·21	640·19	640·14.	,, 640·18.
L_{80}	640·21	640·22	640·23	640·31.	,, 640·24.

After rejecting R_{20} and L_{60}, these cylinders with R_1 and R_4 were used for several complete series of measurements with light of all the available wave-lengths. As the whole of these readings, covering a period of nearly three years, were subsequently rejected, they need not be referred to in detail, except in the case of the mercury green readings which are of importance as bearing on the tests by which the validity of the values finally given was established.

After a number of preliminary experiments, the two groups of cylinders, each cemented into a rod, were found to give the following values (*a*) by setting to the position of minimum rotation (*b*) by setting with the help of a reflecting eye-piece :—

7 *L Cylinders*	(*a*) 4481°·78 (*b*) 4481·79	Rotation per millimetre 25°·5350.
5 *R Cylinders*	3136·51.	,, ,, ,, 25·5342.

After re-cementing, somewhat lower values were obtained :—

7 *L Cylinders*	4481·61.	Rotation per millimetre 25·5340.
5 *R Cylinders*	3136·41.	,, ,, ,, 25·5336.

In trying to determine the effects of the satellites upon the reading of the violet mercury line, the mechanical arrangement of the polariser was modified so that the half-shadow angle could be thrown either to the left or to the right. This was found to have a marked effect on the readings, which was subsequently recognised as occurring even in the case of the very pure mercury green line which gave :—

7 *L Cylinders* . . .	H.S. + H.S. −	4481·61 4481·53	4481°·57 = 25°·5338 per mm.
5 *R Cylinders* . . .	H.S. + H.S. −	3136·41 3136·53	3136·47 = 25·5338 per mm.

The method of reading with both positive and negative half-shadow angles had thus brought the values of the dextro- and lævo-cylinders into complete agreement and appeared to have provided the last device needed to ensure accurate readings. With the experience gained during the two preceding years, yet another series of readings was undertaken, therefore, in which every line was read with both a positive and a negative half-shadow angle. These readings, which were practically complete when the quartz was discarded, are referred to later as proving that faulty quartz gives incorrect figures for rotatory dispersion even when allowance has been made for errors in the absolute values.

At the close of this series, the cement was found to have been separated a little in some of the joints ; it was therefore all cleaned off and the cylinders were put together in optical contact, giving a greatly improved parallelism to the end faces of the column. After this alteration the cylinders were retested by setting each group in eight or more different positions and reading with both positive and negative half-shadow angles. The results were remarkable :—

7L	H.S. +	4481·78	1·37	1·58	1·53	1·50	1·41	1·54	1·57
	H.S. –	4481·88	2·34	2·07	1·89	1·76	2·01	1·98	1·99
Mean . . .		4481·83	1·85	1·83	1·71	1·63	1·71	1·76	1·78
Difference.		0·10	0·97	0·49	0·36	0·26	0·60	0·44	0·42

Mean of all readings = 4481·76.

5R	H.S. +	3136·07	6·27	6·24	6·57	6·32	6·21	6·37	6·55	6·60	6·67	6·66	6·49
	H.S. –	3137·00	6·85	6·55	6·49	6·72	6·74	6·53	6·53	6·53	6·51	6·50	6·71
Mean . . .		3136·53	6·56	6·40	6·53	6·52	6·47	6·45	6·54	6·56	6·59	6·57	6·60
Difference.		+0·93	+0·58	+0·31	–0·08	+0·40	+0·53	+0·16	–0·02	–0·07	–0·16	–0·16	+0·22

Mean of all readings = 3136·53.

It was evident that the difference between the values for the two half-shadow angles might be very serious, amounting to as much as 0°·97 in the lævo- and 0°·93 in the dextro-cylinders, but that positions might be picked out in which the discrepancy was very small; further, the average value for each position was seen to be almost independent of the variations produced by reversing the half-shadow angle. It was hoped that by placing the quartz columns in suitable positions satisfactory results might still be obtained, though the differences between the average values for the cemented cylinders and for the cylinders in optical contact could not lightly be set aside.

In seeking for the origin of the anomaly, the conclusion was reached that it might be accounted for by the presence of patches of material which failed to give a proper extinction, *e.g.*, because they produced elliptical or circular polarisation. Such a bright patch, if occurring in the centre of the field, would require to be compensated by bringing the analysing Nicol more nearly perpendicular to the main polarising Nicol; this would mean moving the analyser to the left or to the right according as the polarising Nicol had been turned to the left or to the right relatively to the smaller fixed Nicols used to produce the "half-shadow" effect; the presence of a non-extinguishing patch would therefore raise or lower the observed rotation and by approximately equal amounts according as the half-shadow angle was positive or negative, whilst the average rotation would be substantially the same as if the patch were absent.

As it seemed possible that a non-extinguishing film or patch might have been produced by the optical contact, the cylinders were separated and examined in groups and finally in units but still showed the same phenomena. Finally, the existence of actual flaws was detected in at least 10 of the 12 cylinders by viewing the quartz with monochromatic green mercury light, with a zero half-shadow angle, the eye-piece being drawn right out of the telescope of the polarimeter, so that it was possible for the first time to focus upon the interior of the quartz specimens, instead of looking through them to the Nicols of the triple field. Black and green bands, resembling interference fringes, were then seen, some of the specimens showing two series of bands running in directions inclined to one another.

As showing the extreme difficulty of procuring satisfactory material it may be mentioned that a pair of plates of dextro- and lævo-quartz to take the place of the defective cylinders was procured from a Continental firm under a guarantee that the specimens should be absolutely free from flaw when tested in the most stringent way; although each plate had an area of 25 sq. cm., the utmost that could possibly have been done with them would have been to drill out a single cylinder from one plate and possibly four or five of smaller diameter from the other, the whole of the rest of the material being shown to be grossly defective when viewed in the way described above.

Finally, Messrs. A. Hilger and Co. were able to provide a plate of dextro-quartz, 51 mm. in thickness after grinding and polishing, which showed some feathery patches and also groups of acicular crystals running through the block; but by careful examination, it was possible to pick out four 15 mm. circles which showed no flaw of any description. Two of these, unfortunately, were splintered in drilling and had to be reduced to about 40 mm. in length. Each of the four cylinders satisfied the following tests:—

(1) No flaw or irregularity could be seen on viewing the crystal between crossed Nicols with monochromatic green light.

(2) No differences could be detected between the optical rotations with positive and negative half-shadow angles; of fifty pairs of readings, taken without special precautions, only two pairs showed a difference greater than 0·05° and these were not confirmed on repetition.

(3) No differences greater than 0°·05 were found when the cylinders were rotated about their axes, each cylinder being set with the reflecting eye-piece and tested in six different positions.

(4) No differences could be detected in the rotatory powers of the four cylinders beyond those which might be ascribed to variations of temperature due to imperfect jacketing. The actual values at *about* 20° were:—

R_1 . . 25·5366, R_2 . . 25·5369, R_3 . . 25·5368, R_4 . . 25°·5365 per mm.

In order to increase the length of the quartz column, which had been reduced some 20 mm. by breakages, a bridge-piece, R_5, separating two of the cylinders in the block, was tested and cut. Examined in three positions, with positive and negative half-shadow angles, it showed an extreme variation of only 0°·03. But the rotation per millimetre was higher, at 25°·5378, a relative difference that was confirmed after regrinding; the piece (which had a clear aperture of only about 8 mm. instead of 15 mm.) was not used, therefore, in the final series of observations.

As the dextro-quartz, although withstanding all the new tests that had been devised during four years of continuous work, had been cut from the immediate neighbourhood of material that was obviously faulty, it was felt that some uncertainty might still attach to the absolute value of the observations made with it. Great importance, therefore, was attached to the discovery in Messrs. Hilger's stock of a large block of lævo-quartz in the form of a plate 58 mm. in thickness; this was badly cracked in places but showed no trace whatever of any optical flaw in a mass which must have weighed at least 6 pounds. The block was so large that the central part was reserved for a 30° Cornu prism 5 inches in height, only the outer portions being used in the present investigation. These outer portions were submitted to a further careful examination without revealing any flaw, after which nine 15 mm. cylinders were drilled out, one being broken in drilling and reground to two lengths of 22·2 and 25·9 mm. respectively. The eight complete cylinders were then tested by every available method and found to be optically perfect in every respect; the rotations at *about* 20° C. were :—

L_1 . . 25·5365 L_2 . . 25·5372 L_3 length not measured L_4 . . 25°·5362 per mm.
L_5 . . 25·5365 L_6 . . 25·5368 L_8 . . 25·5372 L_9 . . 25°·5372 per mm.

The separate values recorded above were found to be influenced by the air-temperature and, therefore, are only approximate. This objection does not apply to the group measurements which gave :

R_{12345} . . $l = 233·5716$ $\alpha = 5964°·51$ $\alpha/l =$ **25°·5361** per mm.
L_{1456} . . . $l = 231·4212$ $\alpha = 5909°·78$ $\alpha/l =$ **25°·5369** per mm.

During the drilling of the cylinders many of the surfaces were scratched by the emery and subsequently re-polished to unequal lengths. The optical contacts were found to be so weak and unsatisfactory that the cylinders were cemented together in groups and reground to exact parallelism and equal lengths.

The final figures after regrinding were as follows :—

	l_{20}.	α_{20}.	α_{20}/l_{20}.
R_1	38·4634	982·20	25·5360
R_2	41·6118	1062·60	25·5360
R_3	50·6814	1294·22	25·5364
R_4	50·6811	1294·22	25·5364
R_5	50·6809	1294·26	25·5373
L_1	56·5920	1445·21	25·5373$_5$
L_2	56·5915	1445·20½	25·5375
L_3	56·5910	1445·19	25·5374$_5$
L_4	56·5915	1445·20	25·5374
L_5	56·5914	1445·19½	25·5373$_5$
L_6	56·5921	1445·19½	25·5370$_5$
L_8	56·5911	1445·18½	25·5373
L_9	56·5918	1445·21	25·5376

The group figures were

R_{12345}	232·1194	5927·46	25·5363
R_{1234}	181·4382	4633·21	25·5360
L_{1256}	226·3670	5780·76	25·5371
L_{3489}	226·3654	5780·76	25·5373

The tests of the separate cylinders were exceedingly satisfactory. Thus, the extreme difference in 40 pairs of readings for positive and negative half-shadow angles in the case of the eight lævo-cylinders, was only 0°·04; the extreme range of variation in the average values for the eight cylinders was only 0°·02; the extreme variation in length after regrinding amounted only to 0·0011 mm. and the extreme variation of rotatory power per millimetre to 0°·0006 per mm.

The final values for the optical rotation of the quartz were

	Lævo.	Dextro.
Before regrinding	25·5369	25·5361
After ,, ...	25·5371	25·5363
,, ,, ...	25·5373	25·5360
	25·5371	25·5361

In view of the much more favourable conditions prevailing in the measurements of the lævo-cylinders, it was decided that these must be made the basis of the values finally taken, the dextro-cylinders being used mainly to balance the lævo-cylinders in measurements of rotatory dispersion. The value adopted for the rotatory power of quartz at 20° C. for Hg 5461 is therefore

25·5371 degrees per millimetre.

The sixth figure has been used and is of importance in connection with the column of relative values given in a subsequent table for twenty-four wave-lengths in the visible region of the spectrum; but it is impossible to regard it as having any absolute value until other equally good crystals of quartz have been found and tested and examined in the same way. When, however, it is noticed that the value 25°·5338 per mm. given by the faulty specimens used in the earlier part of the work differs only by 0°·003 per mm. from the value finally adopted and that the dextro-cylinders (selected with some difficulty from the only sound portions of a faulty block) gave a value 25°·5361 per mm., only 0°·001 below the final figure, there can be little doubt that the fifth figure in the value 25°·5371 per mm., given by the optically-perfect lævo-quartz crystal, may be regarded as correct.

6. *Experimental Methods.*

1. The *polarimeter*, a triple-field instrument of the Lippich pattern, made by the Cambridge Scientific Instrument Company, was graduated to read by means of a vernier to 0°·002; but in practice readings were usually taken only to 0°·01, without using the vernier. Whilst it may be possible under some conditions to read a polarimeter to the third decimal of a degree, it is only very rarely that such readings have any absolute value; in the present investigation the policy was deliberately adopted of making the readings so large that any impurities in the light or faults in the material should obtrude themselves to such an extent as to make the reading of the rotations impossible; relative values based upon minute readings of smaller rotations would have been of much less value, since most of the sources of error would have been overlooked. The aperture of the triple field was 6 mm., the main polarising and analysing Nicols being 10 × 10 × 30 mm.

2. The *spectroscopes* and *prisms* were by Hilger and need not be described in detail. The slits were arranged to open symmetrically; the slit of the spectroscope could be opened to a width of 3 mm. giving an image 6 mm. in width; the slit of the polarimeter could be opened to the full width (6 mm.) of the aperture in front of the triple field. The constant-deviation spectroscope was provided with a drum which could be calibrated in wave-lengths, so as to illuminate the polarimeter with light of any desired colour selected from a continuous spectrum; but it is impossible to recommend the use of such a method, as the wave-length of the light actually delivered to the slit of the polarimeter was found to be seriously affected when the half-shadow angle was altered. This displacement had not been anticipated when using flat-ended Nicols prisms but is a necessary consequence of the method followed in constructing them; it was discovered when using narrow lines to illuminate a narrow slit, by noticing that the line was displaced and partially obliterated on changing the sign of the half-shadow angle. This observation was regarded as a further justification of the policy of using monochromatic or multichromatic, instead of continuous, sources of light; the only effect of the displacement was then a slight narrowing of the line, which could be overcome by readjusting the drum of the spectroscope; with a continuous spectrum, the wave-length of the light would be altered and the readings would be rendered uncertain from a cause that would not easily have been detected or traced.

3. The *setting* of the quartz was effected with the help of a reflecting eye-piece. The pointer of the eye-piece was brought to coincide with the centre of the image of the slit of the spectroscope; the telescope was then racked in till focussed for infinity and the bright image of the pointer, reflected from the surface of the quartz, was brought point to point with the dark image of the pointer itself. The setting was effected in a very simple way: the water-jacket containing the quartz cylinders rested in a rectangular trough; by placing thin cards on one side or other of the trough, the quartz could be tilted in two planes at right angles to one another; the cards were

placed at one end or the other of the water-jacket, according as the quartz required to be tilted forward or backward. By means of the reflecting eye-piece, it would have been easy to set the quartz within a fraction of the thickness of a card but this was not required, as it was necessary to insert or remove some half-dozen cards before the readings were altered by more than 0°·01. The appearance of the reflected image was the best test of the optical contact of the cylinders ; if these came apart (as always happened if water was spilled into the jacket) a series of widely separated images was seen ; but if the optical contact held, the grinding was so perfect that it was barely possible to recognise the double character of the image reflected from the ends of the column of quartz, the error in parallelism being probably only a fraction of a minute of arc.

4. The *axis* of the quartz, which in the earlier plates had been located in the ordinary way by means of the interference rings, was set much more carefully in the later plates, using the very sensitive method described by J. WALKER ('Phil. Mag.,' 1909, vol. 18, 195). The error in setting the axis normal to the surfaces was estimated not to exceed 5 minutes of arc. As the cylinders could be tilted more than this without increasing the readings, there was no reason to suppose that the setting was not sufficiently accurate, even when taking readings to 0°·0001 per mm. This conclusion is all the more reasonable in view of the fact that readings concordant within about 0°·001 per mm. have been obtained by a number of different workers for the optical rotations of sodium light in thin plates of quartz, set to axis by the rougher methods generally in use.

5. The *temperature* was maintained at 20° C. by means of a generous flow of water at constant temperature. The spiral gas-regulator used in the thermostat was of the pattern designed in 1905 ('Trans. Chem. Soc.,' 1905, vol. 87, 1030–1034) and was capable of maintaining the temperature of the well-stirred bath, over long periods, within 0°·01 of the desired temperature. The water was drawn out of the bath and through the jackets by means of an Albany pump of $\frac{1}{2}$-inch bore, the arrangements being in other respects very similar to those described and figured in an earlier paper ('Trans. Faraday Soc.,' 1907, vol. 3, 119). As the pump works best with an ample flow of water, the water jackets were always arranged in parallel, thus avoiding the obvious drawbacks of a series arrangement. Thermometers were provided for reading the temperature of the return-flow, which usually differed from that of the bath by something of the order of 0°·01 for each degree of difference of temperature between the water bath and the atmosphere. All the jackets were double, the inner flow of water being shielded by an outer flow at practically the same temperature ; with the exception of about 2 feet of rubber tubing, all the cooling surface was on the return flow and it is reasonable to suppose that 90 per cent. of the drop of temperature took place there. Thus, although the readings of the polarimeter changed by about 0°·01 for each 0°·01 C., the regulation of temperature was probably quite sufficiently accurate for the purpose.

6. The *water-jackets* (fig. 3) were designed originally for use with organic liquids. But, unlike these liquids, quartz is an excellent conductor of heat and takes up a steady temperature within about 3 minutes, whereas liquids require at least this number of hours. But in spite of this excellent conduction, it is necessary to use great care to protect the ends of the quartz from atmospheric heating or cooling. This was discovered when cylinders which gave rotations of 1476°·14 and 1479°·99 before measuring their lengths, were found to give 1476°·21 and 1483°·03 after measurement; these differences were traced to the somewhat large changes of atmospheric temperature which had taken place in the interval. In these preliminary tests the cylinders were merely laid in a jacketed tube of 15 mm. diameter freely open at the ends and the variation was exceptionally large. In the final experiments all risk of temperature errors was eliminated (*a*) by using long columns of quartz so that the cooling of the ends was relatively much less important (*b*) by adding to each jacket a pair of heavy metal cylinders in good thermal contact with the jacket and having an aperture of only 10 instead of 15 mm. (*c*) by keeping the temperature of the room within about 2° of that of the bath. Arrangements were also provided whereby four cover-slips could be interposed between the ends of the quartz and the outside air; but these were not considered necessary and were discarded after the values for mercury green had been read.

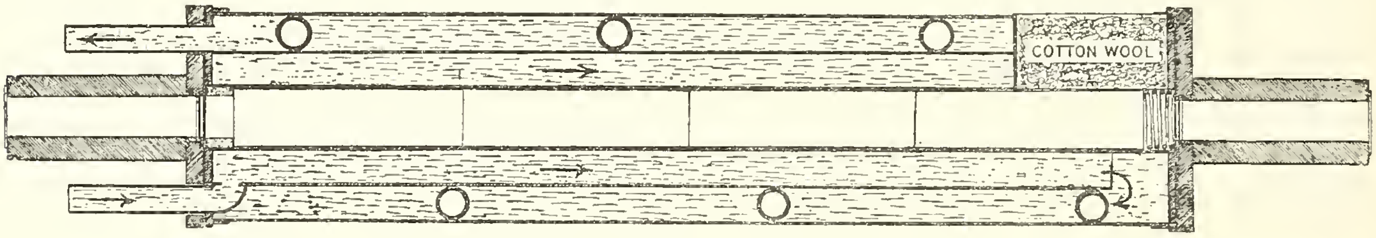

Fig. 3. Water-jacket for quartz cylinders.

The jacket is double, a spiral of compo-tubing being used to direct the water in the outer section. The quartz is held between a cylinder of cork on the left and a strong spiral spring on the right. Four cover-slips are shown, one at each end of the two brass extension pieces, protecting the quartz from cooling by the outer air. A slot at the top of the jacket was closed by cotton wool.

7. The *lengths* of the quartz cylinders were measured at the National Physical Laboratory to 0·0001 mm., with an estimated error of about 0·0003 mm. The conditions of working were such that greater reliance could be placed on measurements made with the separate cylinders and at atmospheric temperatures rather than on long columns jacketed to some fixed temperature. The accuracy of the length-measurements was of the same order as that of the measurements of optical rotation. The extreme variation between the individual cylinders of lævo-quartz corresponded with a difference of 0·0012 mm. in length or 0°·03 in rotatory power. The difference between the two groups of four cylinders could be represented by an error of 0·0016 mm. or 0°·04 and the difference before and after regrinding by the same figures; these differences are of the order of 0°·0002 per mm. and correspond with a possible error in the mean of about 0°·0001 per mm.

8. The *readings* were taken in accordance with the principle utilised by VON LANG (' Wien. Ber.,' 1876, vol. 74, 209–214) and by SORET and SARASIN (' Geneva Archives,' 1882, p. 54), according to which the measurements are most trustworthy when made by contrasting dextro- and lævo-quartz, rather than by reading either crystal separately against a zero taken in the ordinary way. This principle was regarded as specially important in the present investigation, because the glare of satellites, &c., was entirely without effect when reading a zero at which all the lines were extinguished together, whereas it became almost the dominant factor when reading long columns of quartz. For this reason it was felt that better results would follow from reading a lævo-column of 226·3670 mm. against the dextro-column of 181·4382 mm., than by attempting to read the whole of the available 500·8 mm. of lævo-quartz, either against a column of quartz of less than one-half this length, or against a zero. Valuable check-readings could be obtained by reading the two columns of quartz against one another with both a positive and a negative half-shadow angle. The readings of the dextro- and lævo-quartz, read separately against a zero, are, however, of value in considering the relative accuracy of the different experiments, since their concordance could not be seen until all the measurements had been taken and the results reduced to unit length.

7. *Tabulated Observations. Form of the Dispersion Curve.*

Table I. shows for a series of 24 lines :—

A. The wave-lengths in Ångstrom units;

B. The actual rotations produced by the dextro- and lævo-columns of quartz, read against a zero, with both positive and negative half-shadow angles;

C. The ratio of the readings for each wave-length relatively to those for mercury green in the case of—

(*a*) dextro-quartz, average of + and − half-shadow angles;
(*b*) lævo-quartz, „ „ „ „ „ ;
(*c*) dextro against lævo, half-shadow angle + ;
(*d*) „ „ „ „ „ − ;

D. The mean values of these dispersion-ratios and the average deviation (ranging from 1 to 13 parts per million) of the four ratios from the mean;

E. The rotation in degrees per millimetre taking for mercury green the value 25·5371 discussed and adopted in § 5;

F. The rotations in degrees per millimetre calculated for each of the 24 wave-lengths from the formula

$$\alpha = \frac{11·6064}{\lambda^2-\lambda_1^2} + \frac{13·42}{\lambda^2-\lambda_2^2} - \frac{4·3685}{\lambda^2},$$

where

$$\lambda_1^2 = 0·010627,\ \lambda_2^2 = 78·22,\ \lambda = \text{wave-length in microns.}$$

G. The differences between the calculated and observed rotations in degrees per millimetre.

TABLE I.—Rotatory Dispersion of Quartz in the Visible Region of the Spectrum.

	A.	B.	C.	D.	E.	F.	G.
	Wave-length.	Observed rotations.	Dispersion ratios.	Mean ratios (with average error × 10^6.)	Rotation in degrees per millimetre.		
		° °			Observed.	Calculated.	Difference.
Lithium red	6708·2	D+2999·95 L+3743·38 D−3000·12 L−3743·16	D ·647508 + ·647527 L ·647539 − ·647523	·647525 ± 9	16·5359	16·5356	+0·0003
Cadmium red . . .	6438·47	D+3269·82 L+4079·67 D−3269·91 L−4079·68	D ·705746 + ·705734 L ·705733 − ·705743	·705739 ± 5½	18·0225	18·0243	−0·0018
Zinc red	6363·7	D+3352·49 L+4183·03 D−3352·59 L−4182·93	D ·723589 + ·723598 L ·723604 − ·723597	·723597 ± 4	18·4786	18·4728	+0·0058
Sodium yellow, D_1 .	5896·16	D+3937·02 L+4912·28 D−3936·98 L−4912·25	D ·849735 + ·849753 L ·849760 − ·849745	·849735 ± 8	21·7001	21·7001	±0·0000
Sodium yellow, D_2 .	5890·19	D+3945·80 L+4923·05 D−3945·72 L−4923·25	D ·851628 + ·851630 L ·851644 − ·851642	·851636 ± 7	21·7483	21·7467	+0·0016
Mercury yellow . .	5790·49	D+4090·41 L+5103·62 D−4090·38 L−5103·57	D ·882843 + ·882855 L ·882859 − ·882848	·882852 ± 6	22·5455	22·5472	−0·0017
Copper yellow . . .	5782·30	D+4103·18 L+5119·45 D−4103·22 L−5119·43	D ·885607 + ·885602 L ·885600 − ·885604	·885603 ± 2	22·6157	22·6150	+0·0007
Mercury yellow . .	5769·45	D+4122·13 L+5143·13 D−4122·04 L−5143·13	D ·889683 + ·889696 L ·889698 − ·889687	·889691 ± 6	22·7201	22·7218	−0·0017
Copper yellow . . .	5700·39	D+4229·16 L+5276·65 D−4229·15 L−5276·70	D ·912792 + ·912795 L ·912801 − ·912798	·912797 ± 3	23·3101	23·3097	+0·0004
Silver green	5471·72	D+4614·09 L+5756·92 D−4614·12 L−5756·88	D ·995877 + ·995875 L ·995874 − ·995874	·995875 ± 1	25·4318	25·4293	+0·0025

Silver green. . . .	5465·66	D + 4624·92 D − 4624·88	L + 5770·34 L − 5770·30	D ·998206 L ·998194	+ ·998203 − ·998197	·998200 ± 4½	25·4911	25·4895	+0·0016
Mercury green . . .	5460·97	D + 4633·20 D − 4633·21	L + 5780·78 L − 5780·74	D 1·000000 L 1·000000	+1·000000 −1·000000	1·000000	25·5371	25·5362	+0·0009
Thallium green. . .	5350·65	D + 4939·10 D − 4939·5	L + 6037·55 L − 6037·68	D 1·044433 L 1·044433	+1·044430 −1·044437	1·044433 ± 2	26·6718	26·6720	−0·0002
Copper green . . .	5218·45	D + 5104·58 D − 5104·68	L + 6369·03 L − 6368·74	D 1·101748 L 1·101741	+1·101752 −1·101734	1·101744 ± 6	28·1353	28·1371	−0·0018
Silver green. . . .	5209·25	D + 5124·40 D − 5124·45	L + 6393·70 L − 6393·65	D 1·106021 L 1·106027	+1·106024 −1·106024	1·106024 ± 1½	28·2447	28·2434	+0·0013
Copper green . . .	5153·33	D + 5244·02 D − 5244·01	L + 6562·85 L − 6562·79	D 1·131833 L 1·131827	+1·131833 −1·131827	1·131830 ± 3	28·9036	28·9039	−0·0003
Copper green . . .	5105·75	D + 5349·54 D − 5349·48	L + 6674·48 L − 6674·42	D 1·154601 L 1·154597	+1·154605 −1·154593	1·154599 ± 4	29·4851	29·4848	+0·0003
Cadmium green . .	5085·82	D + 5394·03 D − 5394·06	L + 6730·15 L − 6730·05	D 1·164215 L 1·164224	+1·164223 −1·164217	1·164220 ± 4	29·7308	29·7332	−0·0024
Zinc blue	4810·71	D + 6080·74 D − 6080·78	L + 7586·82 L − 7586·65	D 1·312429 L 1·312412	+1·312428 −1·312413	1·312420 ± 8	33·5154	33·5165	−0·0011
Cadmium blue . . .	4799·91	D + 6109·85 D − 6109·87	L + 7623·31 L − 7623·03	D 1·318710 L 1·318715	+1·318724 −1·318700	1·318712 ± 7	33·6761	33·6798	−0·0037
Zinc blue	4722·26	D + 6329·81 D − 6329·62	L + 7987·33 L − 7897·29	D 1·366162 L 1·366134	+1·366159 −1·366134	1·366148 ± 13	34·8875	34·8898	−0·0023
Zinc blue	4680·38	D + 6453·72 D − 6453·63	L + 8052·30 L − 8052·03	D 1·392916 L 1·392926	+1·392940 −1·392903	1·392921 ± 12	35·5712	35·5701	+0·0011
Cadmium blue . . .	4678·37	D + 6459·88 D − 6459·74	L + 8059·43 L − 8059·63	D 1·394241 L 1·394199	+1·394215 −1·394220	1·394219 ± 12	35·6043	35·6034	+0·0009
Mercury violet. . .	4358·58	D + 7538·28 D − 7538·19	L + 9405·19 L − 9405·24	D 1·627001 L 1·626987	+1·626994 −1·626990	1·626992 ± 4½	41·5487	41·5481	+0·0006

The tabulation of the average errors gives a very fair idea of the degree of accuracy attained in the actual reading of the lines. As these errors average about 5 parts per million and do not exceed 13 parts per million, even in the case of the blue lines, it may be presumed that the first five decimals in the ratios can be relied on throughout the table, the probable error in nearly all the lines amounting only to a few units in the sixth decimal. These figures are multiplied by 25·5371 to give the rotations in degrees per millimetre; but when tabulated to four places of decimals the errors in the last significant figure are reduced to a quarter of their previous values; the average error of reading is thus 0°·0001 per mm. or less in 12 of the 24 lines; in the case of eight more lines it is 0°·0002 per mm. or less and in three lines only it reaches its highest value at 0°·0003 per mm.; the fourth decimal is, therefore, subject on the average to an error of reading of only a little over one unit.

The errors discussed in the preceding paragraph refer merely to the discrepancies introduced into the dispersion-ratios by changing from dextro- to lævo-quartz or from a positive to a negative half-shadow angle. They do not take any account of errors due to imperfect purification of the light or to incorrect figures for the wave-length (or optical mass centre) of the lines, which may in some cases be appreciable, *e.g.*, in the case of the two green copper lines, which are known to include satellites. Even the ordinary wave-length determinations may contribute appreciable errors, since an error of 0·01 Ångstrom unit would introduce an error of three units in the sixth decimal of the dispersion-ratios.

Some idea of the maximum amount of these irregular errors can be obtained from the values of the rotations calculated from a formula. Any attempt to discuss fully the equation to the dispersion-curve would be premature until work now in progress, on the rotatory dispersion in quartz, in the ultra-violet and in the infra-red regions of the spectrum, has been carried to completion; but a preliminary survey, for which I am greatly indebted to Mr. T. W. DICKSON, of the City and Guilds College, South Kensington, has shown—

(1) That the simple equation

$$\alpha = \frac{k_1}{\lambda^2-\lambda_1^2} + \frac{k'}{\lambda^2},$$

which DRUDE ('Theory of Optics,' p. 414) regarded as sufficient for calculating the rotatory dispersion of quartz to two places of decimals, is quite inadequate to represent the values now given to four places of decimals;

(2) But the equation

$$\alpha = \frac{k_1}{\lambda^2-\lambda_1^2} + \frac{k_2}{\lambda^2-\lambda_2^2} + \frac{k}{\lambda^2},$$

where $\lambda_1^2 = 0·010627$, $\lambda_2^2 = 78·22$ gives values which, in the case of 22 out of 24 wave-lengths, differ on the average from the observed figures by only a single unit in the third decimal place, *i.e.*, by 1 part in 25,000. This agreement is somewhat remarkable in an equation containing only three arbitrary constants.

The equation given above also shows a remarkably close agreement with a preliminary series of observations in the infra-red. It is, therefore, evident that the infra-red absorption is an essential factor in determining the optical rotation in quartz, both in the infra-red and in the visible region of the spectrum, and that DRUDE was in error in supposing "that the kinds of ions whose natural rotations lie in the infra-red are inactive" (*loc. cit.*, p. 413).

The equation does not agree so well with preliminary measurements in the ultra-violet region and cannot be made to do so without sacrificing the concordance obtained in the values for the visible region of the spectrum. It is considered probable that further experience may demand either (1) some modification in the value $\lambda_1^2 = 0{\cdot}010627$ at present accepted for the wave-length of the ultra-violet absorption, or (2) substitution for the term $\frac{k}{\lambda^2}$ of a term of the ordinary form $\frac{k_3}{\lambda^2 - \lambda_3{}^3}$. The exact nature of the modification needed to bring the values for the ultra-violet region into agreement with the observed figures will be discussed only when the experimental work in this region has been completed.

For the present the calculated values serve mainly to place a limit upon the maximum error from all sources that can be ascribed to the measurements now recorded. The readings for the red zinc line appear to be quite abnormal, as they differ from the calculated value by 0°·006 per mm. and cannot be brought into agreement by any modification of the constants without spoiling the concordance of the rest of the figures. Deviations amounting to nearly 0°·004 per mm. are observed in the case of the blue cadmium line; but these form part of a group of negative differences and must be attributed, at least to some extent, to imperfections in the formula, which (as has already been suggested) requires the addition of a fourth arbitrary constant to bring it into complete accord with the experimental figures. The necessity for a fourth term is shown by the fact that whilst the concordance between the observed and calculated values is very good at the ends and in the middle of the series, the differences being

Li 6708, +0·0003; Hg 5461, +0·0009; Hg 4359, +0·0006;

there is a predominance of positive differences in the first twelve and of negative differences in the last twelve values.

Thus, if all the values be included, the average differences are

Wave-length 6708 to 5461	+0·0007
Wave-length 5351 to 4359	−0·0007;

if the reading which shows the largest difference in each group be excluded, the average differences are

Wave-length 6708 to 5461	+0·00025
Wave-length 5351 to 4359	−0·00036.

These differences show clearly that the calculated curve is too flat from 5351 to 4359 and not quite flat enough from 6708 to 5461.

In estimating the actual errors of experiment, this limitation of the calculated curve must be taken into account, since this consideration serves to reduce the average error of the 24 readings from 0·0015 to less than 0·0008 and the average error of 22 out of 24 readings from 0·0011 to less than 0·0005; the average error of experiment is, therefore, probably not greater than 0°·0005 per mm. But even if no such allowance be made, it may be seen from the table that 10 out of 24 observed values differ by less than 0·001, 9 more by less than 0·002, 3 more by less than 0·003 and one each only by 0·004 and 0·006 from the calculated values.

8. *Comparison with Earlier Observations. Optical Mass-centre of Sodium Light.*

Comparison with previous observations is almost impossible, except in the case of sodium light, for which the figures are

	SORET and SARASIN.		LOWRY.	
	R Quartz "IV" (60 mm).	L Quartz "II" (30 mm).	R Quartz.	L Quartz.
D_1* . . .	21·696	21·684	21·6988	21·7004
D_2* . . .	21·724	21·727	21·7471	21·7485
Mean . .	21·710	21·706	21·7230	21·7245

In order to secure a wider basis for comparison and incidentally to determine the optical mass-centre of the light of the sodium doublet, readings were taken with a small piece of the lævo-quartz, 25·902 mm. in length. The rotations were

Mercury green	661°·47
Sodium yellow	562°·82

$$\left\{\begin{array}{lcl} \text{Ratio} \;.\;.\;.\;.\;.\;.\;. & = & 0{\cdot}85086 \\ \text{Ratio for } D_1 \;.\;.\;.\;. & = & 0{\cdot}84975 \\ \text{Ratio for } D_2 \;.\;.\;.\;. & = & 0{\cdot}85164 \end{array}\right\}$$

Whence, taking $D_1 = 5896{\cdot}155$, $D_2 = 5890{\cdot}186$, the optical mass-centre of the doublet is found to be 5892·64 and the ratio of the intensities of the two lines $D_1 : D_2 = 1 : 1{\cdot}42$. These figures agree fairly closely with the numbers 5892·5 and 1 : 1·6 calculated by LANDOLT from the data of LIPPICH and DIETRICH ('Optical Rotating Power,' p. 403).

Confirmation was also obtained of the observations of ZÖLLNER and of EBERT ('LANDOLT,' pp. 407–413) which showed that the optical mass-centre was shifted

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* Following LANDOLT ('Optical Rotating Power,' p. 403) the less refrangible line is distinguished as D_1.

towards the red on increasing the brightness of the lines. Thus sodium light, produced by placing a piece of sodium bicarbonate on the grid of a Mecker burner, gave the reading 562°·84, where light from a bead heated by an oxygen-jet in the flame of the burner (fig. 2A) gave 562°·80, the light being purified in each case by a D.V. prism on the eye-piece of the polarimeter; the mean of these two readings was used in the calculation of the optical mass-centre.

The observations of Zöllner ('Landolt,' p. 408) to the effect that the D_2 line widens symmetrically whilst D_1 widens more rapidly towards the red, are likewise in accord with the experience gained in the present experiments, where steady values for D_2 were obtained in the very first series of readings, whilst D_1, although only slightly weaker, gave very variable readings and was by far the most troublesome line of the whole series to read.

Whilst there is no great satisfaction, in view of the uncertainties as to its mass-centre, in giving figures for the sodium doublet, there is no other way of securing a comparison with the observations of other workers. The figures for light of wave-length 5892·64 are

$$\text{Lowry . . .}\ \left\{\begin{array}{ll}\text{R Quartz} & 21{\cdot}7270\\ \text{L}\quad ,, & 21{\cdot}7286\end{array}\right\}\ \text{Tabulated value } 21{\cdot}7283.$$

Comparison in the form given above with the observations of Soret and Sarasin is difficult, as their values for D_1 and D_2 differ by 0°·028 per mm. in one case and 0°·043 per mm. in the other and are obviously uncertain even in the second decimal; but Soret and Guye, working with Soret and Sarasin's Quartz "IV" found the value 21·7195, as compared with the values 21·7205 and 21·7132 which they quote from Soret and Sarasin; the mean value may be taken as 21·718. Landolt has calculated the values 21°·724 from the readings of Von Lang; 21°·723 from the readings of Soret and Guye; 21°·724 from readings given by Gumlich for plates from 5 to 10 mm. in thickness, the individual values ranging from 21°·717 to 21°·731: and 21°·722 from the readings of Schönrock for a plate only 5 mm. thick. The general average, 21°·723 is a little lower than the value given by the faulty specimens of quartz rejected in the course of the present investigation, for which the value 21·7255 may be taken and indicates that these were rather above than below the general average of quality of the specimens used in earlier investigations.

Some interest attaches to the dispersion-ratios of the defective cylinders of quartz which were rejected at the commencement of 1911. The best values for the extreme red and violet lines were

Li . . .	0·647589	instead of	0·647525	(+ 0·000064)
Hg . . .	1·626753	,, ,,	1·626992	(– 0·000239).

The differences for other lines were almost all positive towards the red and negative towards the violet. The behaviour of these specimens was in very close agreement with what would be expected in a substance obeying the same dispersion-law but possessing a rather lower dispersive power. The figures are of importance as showing that the defects reduced the dispersive power of the specimens, as well as the absolute values of the rotations. No such steady difference could be detected between the values for the specimens of dextro- and lævo-quartz finally selected. These gave the numbers

	Dextro.	Lævo.	
Li . . .	0·647508	0·647539	(– 0·000031)
Hg . . .	1·627001	1·626987	(+ 0·000014),

corresponding with errors of reading of about 0°·16 and 0°·07 respectively; the differences do not exceed the possible range of experimental error and (taking the lævo-cylinders as the standard) are also in the opposite direction to those recorded above for specimens that were known to be faulty.

9. *Tests of* WIEDEMANN'S *Law.*

The law of the proportionality of natural and magnetic rotatory powers over a range of wave-lengths was discovered by G. WIEDEMANN in 1851 ('Pogg. Ann.', vol. 82, 215) from experiments on turpentine, using a series of five Fraunhofer lines. It was tested after an interval of over half a century by DISCH ('Ann. d. Physik,' 1903 [IV.], vol. 12, 1153), whose results are given in a memoir which is of further interest as being the earliest in which the use of the Arons mercury lamp in polarimetric work is described. DISCH found a steady difference between the two dispersions as is shown by the following ratios:—

Wave-length		6563	5893	5780	5461	4916	4359	4050
Ethyl valerate	natural . . .	1·000	1·258	—	1·500	1·924	2·573	—
	magnetic . .	1·000	1·167	—	1·380	1·746	2·267	—
Quartz . . .	natural . . .	1·000	1·254	1·307	1·475	1·846	2·400	2·826
	magnetic . .	1·000	1·251	1·301	1·464	1·821	2·316	2·672

It is remarkable that DISCH should have concluded from these figures that "both the tables and the curves show that WIEDEMANN'S Law holds to a very close approximation: the quotient n/m is as good as constant, the ratios for the optical and magnetic rotations are nearly equal to one another and accordingly the two curves fall almost together." The deviations, which amount to 12 per cent. in one case and 5 per cent. in the other, were attributed by DISCH to a lack of optical homogeneity in the ester and to a lesser extent in the quartz.

As this matter was one of considerable importance, especially as regards the theory of magnetic rotation, experiments were made to test the law in the case of quartz as well as of a series of organic liquids whose optical and magnetic rotatory dispersions have been measured during the last six years. A description of the apparatus and methods used in these investigations will be given in a later paper dealing specifically with the rotatory dispersion of organic compounds. But the main results may be summarised in the words of a brief preliminary note, communicated to the Winnipeg meeting of the British Association in 1909, to the effect that "in the case of quartz there is an absolute agreement between the two dispersions, but every optically active liquid that has been examined shows a divergence between the two series of values, the optical dispersion being usually but not always higher than the magnetic dispersion."

Since the publication of this note, DARMOIS has described ('Ann. Chim. Phys.,' 1911 (VIII.), vol. 22, 247–281, 495–589) a series of measurements of the optical and magnetic rotatory dispersion of a number of compounds of the terpene series, some of the measurements being carried into the ultra-violet region. He concluded that "the law of proportionality was quite inexact, and that WIEDEMANN'S result was the result of a pure chance"; he further states that, since normal magnetic dispersion may accompany an anomalous optical dispersion, "WIEDEMANN'S Law has no longer any manner of significance."

This conclusion, differing so entirely from that of DISCH, although based upon observations of much the same character, is not in agreement with the conclusions that have been drawn from the present series of experiments. These were summed up in the note already referred to, in a reference to the general "identity of the optical and magnetic dispersion in crystals." The view that WIEDEMANN'S Law holds accurately for crystals but not for active liquids is at present based upon observations in the case of crystals of quartz only, but it is hoped at a later date to test it by analogous observations on sodium chlorate and other crystals.

In measuring the magnetic rotatory dispersion of quartz 4 pieces of lævo-quartz of length 100·29 mm. were set up with 4 pieces of dextro-quartz of length 98·83 mm., giving a total length of 199·12 mm. with only 1·46 mm. of lævo-quartz uncompensated. The following readings were obtained for the magnetic rotatory power at 20° C.:—

Water, 200·34 mm., gave 12°·61 for wave-length 5461.
Quartz, 199·12 mm., gave 16°·29 ,, ,, ,,

			Dispersion – Ratios.		
		Magnetic rotation.	Magnetic.	Optical.	Difference.
Li	6708	10°·53	0·646	0·648	+0·002
Na . . .	5893	13·86	0·851	0·851	±
Hg . . .	5461	16·29	1·000	1·000	±
Cd . . .	5086	19·01	1·167	1·164	−0·003
Cd . . .	4800	20·47	1·318	1·319	+0·001
Hg . . .	4359	26·50	1·627	1·627	±

The following values for 24 mm. thickness of silica discs, appear to indicate that the magnetic rotatory dispersion is a little higher in the vitreous than in the crystalline state:—

		Rotations.	Ratios.
Li	6708	1°·19	0·63
Hg	5461	1°·89	1·00
Hg	4359	3°·17	1·67

An equal length of quartz gave a rotation 1°·98 instead of 1°·89 for wave-length 5461. Later attempts to secure a rod of clear silica 100 mm. in length for accurate measurements of the magnetic rotatory dispersion, were not successful; although the material contained fewer bubbles than the discs prepared a few years before, the triple field of the polarimeter could not be seen through the rod, which gave instead a splendid demonstration of AIRY's spirals.

As contrasted with the exact accordance, throughout the range from 6708 to 4359, of the two series of dispersion-ratios for quartz, it may be noted that the nearest approach to equality in a series of 23 alcohols was found in the alcohol phenylmethyl-carbinol which gave for the ratio 4359/5461

Magnetic 1·739, Optical 1·736.

But the accidental nature of this concordance is clearly shown by the fact that the next homologue phenylethyl-carbinol gave the values

Magnetic 1·731, Optical 1·674.

10. *Summary.*

(1) A large crystal of optically perfect lævo-quartz has been found which produced a rotation of 25°·5371 per mm. in light of wave-length 5460·97. Cylinders, also apparently perfect, cut from a crystal of dextro-quartz, produced a rotation of 25°·5361 per mm. Cylinders cut from plates of dextro- and of lævo-quartz which gave the figure 25°·5338 per mm. were shown to be faulty by a new test, in which the specimen, mounted between Nicol prisms set to extinction, is examined with monochromatic green mercury light, with the help of a telescope focussed on the interior of the crystal. A very sensitive test of the optical purity of quartz consists in measuring its optical rotatory power for mercury green light with both a positive and a negative half-shadow angle.

(2) The rotatory dispersive power of quartz has been determined by measuring the rotation produced in light of 24 wave-lengths from Li 6708 to Hg 4359, using a column of lævo-quartz 226·3670 mm. in length and a column of dextro-quartz 181·4382 mm. in length. The average error of the readings amounts to about 6 parts per million; the average error from all sources in the absolute values is probably not more than 0°·001 per mm.

(3) By taking into account the infra-red absorption it has been possible to calculate the rotations in degrees per millimetre with an average error not exceeding 0·0015 degrees per millimetre.

(4) Wiedemann's Law of the proportionality of natural and magnetic rotations over a range of wave-lengths has been verified in the case of quartz but does not hold good in the case of optically active liquids.

A large part of the cost of the investigation has been defrayed by grants from the Research Fund of the Government Grant Committee of the Royal Society; the author is indebted to this Committee for generous consideration during a period of seven years. He is also indebted to Prof. Armstrong for the interest he has taken in the investigation during the whole of its course, to Prof. Sir William Tilden for help in securing the loan of a valuable polarimeter, to Mr. F. Twyman of Messrs. A. Hilger and Co. for many useful suggestions, to Mr. T. W. Dickson for a mathematical investigation of the experimental figures, and to Mr. W. P. Paddison and Mr. H. R. Courtman for help in the arduous work of reading the polarimeter under difficult and tedious conditions.

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THE EFFECT PRODUCED BY AN OBSTACLE ON A TRAIN OF ELECTRIC WAVES.

BY

H. M. MACDONALD, F.R.S.,
UNIVERSITY OF ABERDEEN.

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X. *The Effect produced by an Obstacle on a Train of Electric Waves.*

By Prof. H. M. MACDONALD, *F.R.S.*, *University of Aberdeen.*

Received June 21,—Read June 27, 1912.

INTEGRALS of the equations of propagation of electric disturbances in terms of the electric and magnetic forces tangential to any surface enclosing the sources of the disturbances have been already obtained.* It is proposed in what follows to apply these expressions to obtain the effect of an obstacle on a train of electric waves. The effect of the obstacle can be represented by a distribution of sources throughout the space occupied by the obstacle, and the determination of this distribution or, as appears from the investigation referred to above, the determination of the electric and magnetic forces tangential to the surface of the obstacle due to this distribution of sources, constitutes the solution of the problem. If X', Y', Z', α', β', γ' denote the components of the electric and magnetic forces respectively at the point ξ, η, ζ on the surface of the obstacle due to the distribution of sources inside it which represents its effect, X'_1, Y'_1, Z'_1, α'_1, β'_1, γ'_1 denote the values of these quantities when $t-r/V$ is substituted for t, where V is the velocity of propagation of the disturbances, and $r = \{(x-\xi)^2+(y-\eta)^2+(z-\zeta)^2\}^{1/2}$ is the distance of any point x, y, z from the point ξ, η, ζ, and l, m, n are the direction cosines of the normal to the surface at the point ξ, η, ζ drawn into the space external to the obstacle, the components of the magnetic force at any point outside the obstacle due to the obstacle are given by

$$\dot{\alpha} = \frac{1}{4\pi}\frac{\partial}{\partial t}\iint\left[\frac{\partial}{\partial y}\frac{\overline{\gamma}}{r} - \frac{\partial}{\partial z}\frac{\overline{\beta}}{r}\right]dS - \frac{1}{4\pi}\iint\left[\frac{\partial^2}{\partial x^2}\frac{\overline{X}}{r} + \frac{\partial^2}{\partial x\partial y}\frac{\overline{Y}}{r} + \frac{\partial^2}{\partial x\partial z}\frac{\overline{Z}}{r} - \frac{1}{V^2}\frac{\partial^2}{\partial t^2}\frac{\overline{X}}{r}\right]dS,$$

$$\dot{\beta} = \frac{1}{4\pi}\frac{\partial}{\partial t}\iint\left[\frac{\partial}{\partial z}\frac{\overline{\alpha}}{r} - \frac{\partial}{\partial x}\frac{\overline{\gamma}}{r}\right]dS - \frac{1}{4\pi}\iint\left[\frac{\partial^2}{\partial x\partial y}\frac{\overline{X}}{r} + \frac{\partial^2}{\partial y^2}\frac{\overline{Y}}{r} + \frac{\partial^2}{\partial y\partial z}\frac{\overline{Z}}{r} - \frac{1}{V^2}\frac{\partial^2}{\partial t^2}\frac{\overline{Y}}{r}\right]dS,$$

$$\dot{\gamma} = \frac{1}{4\pi}\frac{\partial}{\partial t}\iint\left[\frac{\partial}{\partial x}\frac{\overline{\beta}}{r} - \frac{\partial}{\partial y}\frac{\overline{\alpha}}{r}\right]dS - \frac{1}{4\pi}\iint\left[\frac{\partial^2}{\partial x\partial z}\frac{\overline{X}}{r} + \frac{\partial^2}{\partial y\partial z}\frac{\overline{Y}}{r} + \frac{\partial^2}{\partial z^2}\frac{\overline{Z}}{r} - \frac{1}{V^2}\frac{\partial^2}{\partial t^2}\frac{\overline{Z}}{r}\right]dS,$$

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* MACDONALD, "Electric Waves," 1902, pp. 16–17, 'Proc. Lond. Math. Soc.,' 1911.

Published separately, November 13, 1912.

and the components of the electric force at the point x, y, z are given by

$$\dot{\mathrm{X}} = \frac{\mathrm{V}^2}{4\pi}\iint\left[\frac{\partial^2}{\partial x^2}\frac{\bar{\alpha}}{r}+\frac{\partial^2}{\partial x\partial y}\frac{\bar{\beta}}{r}+\frac{\partial^2}{\partial x\partial z}\frac{\bar{\gamma}}{r}-\frac{1}{\mathrm{V}^2}\frac{\partial^2}{\partial t^2}\frac{\bar{\alpha}}{r}\right]d\mathrm{S}+\frac{1}{4\pi}\frac{\partial}{\partial t}\iint\left[\frac{\partial}{\partial y}\frac{\bar{\mathrm{Z}}}{r}-\frac{\partial}{\partial z}\frac{\bar{\mathrm{Y}}}{r}\right]d\mathrm{S},$$

$$\dot{\mathrm{Y}} = \frac{\mathrm{V}^2}{4\pi}\iint\left[\frac{\partial^2}{\partial x\partial y}\frac{\bar{\alpha}}{r}+\frac{\partial^2}{\partial y^2}\frac{\bar{\beta}}{r}+\frac{\partial^2}{\partial y\partial z}\frac{\bar{\gamma}}{r}-\frac{1}{\mathrm{V}^2}\frac{\partial^2}{\partial t^2}\frac{\bar{\beta}}{r}\right]d\mathrm{S}+\frac{1}{4\pi}\frac{\partial}{\partial t}\iint\left[\frac{\partial}{\partial z}\frac{\bar{\mathrm{X}}}{r}-\frac{\partial}{\partial x}\frac{\bar{\mathrm{Z}}}{r}\right]d\mathrm{S},$$

$$\dot{\mathrm{Z}} = \frac{\mathrm{V}^2}{4\pi}\iint\left[\frac{\partial^2}{\partial x\partial z}\frac{\bar{\alpha}}{r}+\frac{\partial^2}{\partial y\partial z}\frac{\bar{\beta}}{r}+\frac{\partial^2}{\partial z^2}\frac{\bar{\gamma}}{r}-\frac{1}{\mathrm{V}^2}\frac{\partial^2}{\partial t^2}\frac{\bar{\gamma}}{r}\right]d\mathrm{S}+\frac{1}{4\pi}\frac{\partial}{\partial t}\iint\left[\frac{\partial}{\partial x}\frac{\bar{\mathrm{Y}}}{r}-\frac{\partial}{\partial y}\frac{\bar{\mathrm{X}}}{r}\right]d\mathrm{S},$$

where

$$\bar{\alpha} = m\gamma'_1-n\beta'_1, \qquad \bar{\beta} = n\alpha'_1-l\gamma'_1, \qquad \bar{\gamma} = l\beta'_1-m\alpha'_1,$$

$$\bar{\mathrm{X}} = m\mathrm{Z}'_1-n\mathrm{Y}'_1, \qquad \bar{\mathrm{Y}} = n\mathrm{X}'_1-l\mathrm{Z}'_1, \qquad \bar{\mathrm{Z}} = l\mathrm{Y}'_1-m\mathrm{X}'_1,$$

and the integrations are taken over the surface of the obstacle. The quantities $\bar{\alpha}$, $\bar{\beta}$, $\bar{\gamma}$ are the components of the electric current distribution on the surface which would produce the tangential magnetic force on the surface due to the distribution of sources inside it, and the quantities $\bar{\mathrm{X}}$, $\bar{\mathrm{Y}}$, $\bar{\mathrm{Z}}$ are the components of the magnetic current distribution on the surface which would produce the tangential electric force on the surface due to the distribution of sources inside it. The waves incident on the surface can be represented as the effect of a distribution of Hertzian oscillators, and it will therefore be sufficient to consider the effect of a Hertzian oscillator situated at a point, O, outside the surface and emitting waves of a definite wave-length, $2\pi/\kappa$. Now, the conditions to be satisfied at the surface of the obstacle are linear relations involving the components of the electric and magnetic forces, and therefore the integrands in the above expressions for X, Y, Z, α, β, γ will each contain the factor $e^{-\iota\kappa(r+\Sigma\epsilon r')}$ where r is the distance of the point (x, y, z) from the point (ξ, η, ζ) on the surface, and the quantities r' are other distances. The remaining factors of the integrands will be non-oscillatory unless the surface has corrugations on it, for which the interval between successive corrugations is comparable with the wave-length $2\pi/\kappa$ of the oscillations. The principal parts of the expressions for X, Y, Z, α, β, γ are therefore contributed by the portion or portions of the surface in the neighbourhood of the point or points for which $r+\Sigma\epsilon r'$ is stationary. If the wave-length of the oscillations is small compared with both principal radii of curvature of the surface at a point at which $r+\Sigma\epsilon r'$ is stationary, the corresponding principal parts of X, Y, Z, α, β, γ are the same for a point, P, very near to this point Q on the surface as if the point Q were situated on a plane surface. Hence the principal parts of X, Y, Z, α, β, γ at points on the surface are related to the principal parts of the components of the electric and magnetic forces in the incident waves in the same way as if the surface were plane, but it should be observed that the incident waves to be taken into account may include waves due to the obstacle in addition to the waves due to the external oscillator. The electric and magnetic current distributions to be assumed on the surface of the obstacle are then the same at each point of the surface as if that point were on an infinite plane surface coinciding with the tangent plane to the surface of the obstacle at the point, and the principal parts of X, Y, Z, α, β, γ at any point x, y, z determined on this assumption are the leading terms in the asymptotic expressions for these quantities.

A Perfectly Conducting Obstacle.

When the obstacle is a perfect conductor the condition to be satisfied at the surface is that the electric force tangential to the surface vanishes; it follows from the above that the principal part of the effect of the obstacle is obtained by assuming an electric current distribution on the parts of the surface on which waves are incident which is double the electric current distribution that would produce the magnetic force tangential to the surface in the incident waves, a zero electric current distribution on the parts of the surface on which no waves are incident, and a zero magnetic current distribution on all parts of the surface.

Taking first the case where the perfectly conducting obstacle is a convex solid, the waves incident on any part of the surface are due to the oscillator outside it, and, if M is the electric current distribution at any point on the surface which would produce the magnetic force tangential to the surface in the incident waves, the electric current distribution to be assumed at this point is 2M, if the point is on the part of the surface of the obstacle next the oscillator, and zero if it is on the part of the surface remote from the oscillator.

Let the origin of the co-ordinates be at the point O, the axis of the oscillator being the axis of z. The components of the magnetic force $(\alpha', \beta', \gamma')$ at the point (ξ, η, ζ) due to the oscillator are given by

$$\alpha' = \frac{\kappa}{\mathrm{V}}\frac{\partial}{\partial\eta}\frac{e^{\iota\kappa(\mathrm{V}t-r_1)}}{r_1}, \qquad \beta' = -\frac{\kappa}{\mathrm{V}}\frac{\partial}{\partial\xi}\frac{e^{\iota\kappa(\mathrm{V}t-r_1)}}{r_1}, \qquad \gamma' = 0,$$

where

$$r_1^2 = \xi^2+\eta^2+\zeta^2.$$

If l, m, n are the direction cosines of the outward drawn normal to the surface at the point (ξ, η, ζ) on it, the components of the electric current distribution M which would produce the magnetic force tangential to the surface are

$$m\gamma'-n\beta', \qquad n\alpha'-l\gamma', \qquad l\beta'-m\alpha',$$

and the above hypothesis is equivalent to assuming an electric current distribution on the parts of the surface on which waves are incident whose components are

$$2\,(m\gamma'-n\beta'), \qquad 2\,(n\alpha'-l\gamma'), \qquad 2\,(l\beta'-m\alpha'),$$

a zero electric current distribution on the parts of the surface in the geometrical shadow, and a zero magnetic current distribution on all parts of the surface. The components of the magnetic force at the point (x, y, z) due to this distribution are by the above

$$\alpha = \frac{1}{4\pi}\iint\left[\frac{\partial}{\partial y}\frac{\bar{\gamma}}{r} - \frac{\partial}{\partial z}\frac{\bar{\beta}}{r}\right] d\mathrm{S},$$

$$\beta = \frac{1}{4\pi}\iint\left[\frac{\partial}{\partial z}\frac{\bar{\alpha}}{r} - \frac{\partial}{\partial x}\frac{\bar{\gamma}}{r}\right] d\mathrm{S},$$

$$\gamma = \frac{1}{4\pi}\iint\left[\frac{\partial}{\partial x}\frac{\bar{\beta}}{r} - \frac{\partial}{\partial y}\frac{\bar{\alpha}}{r}\right] d\mathrm{S},$$

where

$$\bar{\alpha} = 2\,(m\gamma'_1 - n\beta'_1), \qquad \bar{\beta} = 2\,(n\alpha'_1 - l\gamma'_1), \qquad \bar{\gamma} = 2\,(l\beta'_1 - m\alpha'_1),$$

$$r^2 = (x-\xi)^2 + (y-\eta)^2 + (z-\zeta)^2,$$

and the integration is taken over the portion of the surface on which waves from the oscillator are incident. Now

$$\alpha'_1 = \frac{\kappa\eta}{\mathrm{V}r_1}\frac{\partial}{\partial r_1}\frac{e^{\iota\kappa(\mathrm{V}t - r_1 - r)}}{r_1}, \qquad \beta'_1 = -\frac{\kappa\xi}{\mathrm{V}r_1}\frac{\partial}{\partial r_1}\frac{e^{\iota\kappa(\mathrm{V}t - r_1 - r)}}{r_1}, \qquad \gamma'_1 = 0,$$

whence

$$\bar{\alpha} = \frac{2\kappa}{\mathrm{V}}\frac{n\xi}{r_1}\frac{\partial}{\partial r_1}\frac{e^{\iota\kappa(\mathrm{V}t - r_1 - r)}}{r_1}, \qquad \bar{\beta} = \frac{2\kappa}{\mathrm{V}}\frac{n\eta}{r_1}\frac{\partial}{\partial r_1}\frac{e^{\iota\kappa(\mathrm{V}t - r_1 - r)}}{r_1}, \qquad \bar{\gamma} = -\frac{2\kappa}{\mathrm{V}}\frac{l\xi + m\eta}{r_1}\frac{\partial}{\partial r_1}\frac{e^{\iota\kappa(\mathrm{V}t - r_1 - r)}}{r_1},$$

and therefore

$$\alpha = -\frac{\kappa}{2\pi\mathrm{V}}\iint\left[\frac{y-\eta}{r}\frac{l\xi + m\eta}{r_1} + \frac{z-\zeta}{r}\frac{n\eta}{r_1}\right]\frac{\partial^2}{\partial r\,\partial r_1}\frac{e^{\iota\kappa(\mathrm{V}t - r_1 - r)}}{rr_1}\,d\mathrm{S},$$

$$\beta = \frac{\kappa}{2\pi\mathrm{V}}\iint\left[\frac{z-\zeta}{r}\frac{n\xi}{r_1} + \frac{x-\xi}{r}\frac{l\xi + m\eta}{r_1}\right]\frac{\partial^2}{\partial r\,\partial r_1}\frac{e^{\iota\kappa(\mathrm{V}t - r_1 - r)}}{rr_1}\,d\mathrm{S},$$

$$\gamma = \frac{\kappa}{2\pi\mathrm{V}}\iint\frac{n\,(x\eta - y\xi)}{rr_1}\frac{\partial^2}{\partial r\,\partial r_1}\frac{e^{\iota\kappa(\mathrm{V}t - r_1 - r)}}{rr_1}\,d\mathrm{S}.$$

The principal parts of these integrals are contributed by the elements near to the point for which the exponent of $e^{-\iota\kappa(r_1+r)}$ is stationary, that is, by the portion of the surface in the immediate neighbourhood of the point for which $r_1 + r$ is stationary. The conducting surface being convex towards the point O, at which the oscillator is, if the point P (x, y, z) is external to the tangent cone drawn from the point O to the conducting surface or internal to the tangent cone and on the same side of the conducting surface as the point O, the point for which $r_1 + r$ is stationary is the point of contact Q of a prolate spheroid which has the points O and P as foci and touches the conducting surface, and, if the point P is internal to the tangent cone from O to the conducting surface and on the side of the conducting surface remote from the point O, the point for which r_1+r is stationary is the point at which the straight line OP cuts the conducting surface nearest to the point O. The values of the principal parts of α, β, γ are therefore α_0, β_0, γ_0, where

$$\alpha_0 = \frac{\kappa^3 I}{2\pi V}\{(l\xi_0+m\eta_0+n\zeta_0)(y-\eta_0)+n(\eta_0 z-\zeta_0 y)\}\, e^{\iota\kappa Vt}/R^2R_1^{\,2},$$

$$\beta_0 = -\frac{\kappa^3 I}{2\pi V}\{(l\xi_0+m\eta_0+n\zeta_0)(x-\xi_0)+n(\xi_0 x-\zeta_0 x)\}\, e^{\iota\kappa Vt}/R^2R_1^{\,2},$$

$$\gamma_0 = -\frac{\kappa^3 I}{2\pi V}\, n(\eta_0 x-\xi_0 y)\, e^{\iota\kappa Vt}/R^2R_1^{\,2},$$

where (ξ_0, η_0, ζ_0) are the co-ordinates of the point Q for which r_1+r is stationary, l, m, n now denote the direction cosines of the outward drawn normal to the surface at the point Q, I is the principal value of the integral

$$\iint e^{-\iota\kappa(r_1+r)}\, dS,$$

and

$$R^2 = (x-\xi_0)^2+(y-\eta_0)^2+(z-\zeta_0)^2, \qquad R_1^{\,2} = \xi_0^{\,2}+\eta_0^{\,2}+\zeta_0^{\,2}.$$

To calculate the value of I, it is convenient to choose for axes of reference the normal to the surface at the point Q (ξ_0, η_0, ζ_0) as the axis of ζ, the tangent to the surface in the plane of incidence as the axis of ξ, and the perpendicular tangent as the axis of η. Let the equation of the surface referred to these axes be

$$2\zeta = A\xi^2+2H\xi\eta+B\eta^2+\ldots,$$

let $(x_1, 0, z_1)$ be the co-ordinates of the point O, and let (x_2, y_2, z_2) be the co-ordinates of the point P referred to these axes, then

$$r_1^{\,2} = (\xi-x_1)^2+\eta^2+(\zeta-z_1)^2, \qquad r^2 = (\xi-x_2)^2+(\eta-y_2)^2+(\zeta-z_2)^2,$$

and further

$$r_1\frac{\partial r_1}{\partial\xi} = (\xi-x_1)+(\zeta-z_1)(A\xi+H\eta+\ldots),$$

$$r\frac{\partial r}{\partial\xi} = (\xi-x_2)+(\zeta-z_2)(A\xi+H\eta+\ldots),$$

$$r_1\frac{\partial r_1}{\partial\eta} = \eta+(\zeta-z_1)(H\xi+B\eta+\ldots),$$

$$r\frac{\partial r}{\partial\eta} = \eta-y_2+(\zeta-z_2)(H\xi+B\eta+\ldots).$$

Now, r_1+r is stationary at the point Q for which

$$\xi = \eta = \zeta = 0,$$

therefore

$$\frac{x_1}{\mathrm{R}_1}+\frac{x_2}{\mathrm{R}} = 0, \qquad y_2 = 0\,;$$

whence

$$\frac{z_1^{\,2}}{\mathrm{R}_1^{\,2}} = \frac{z_2^{\,2}}{\mathrm{R}^2}, \qquad \text{that is} \qquad \frac{z_1}{\mathrm{R}_1} = \pm\frac{z_2}{\mathrm{R}}.$$

In this result the upper sign corresponds to the case where the point P is external to the tangent cone from the point O to the surface, or inside the tangent cone and on the same side of the surface as the point O; the lower sign corresponds to the case where the point **P** is inside the tangent cone and on the side of the surface remote from the point O, and in this case the point Q lies on the straight line OP. Considering first the case where OQP is a straight line, writing

$$x_1 = -\mathrm{R}_1 \sin\phi, \qquad z_1 = -\mathrm{R}_1\cos\phi,$$

it follows from the relations

$$z_1/\mathrm{R}_1+z_2/\mathrm{R} = 0, \qquad x_1/\mathrm{R}_1+x_2/\mathrm{R} = 0,$$

that

$$x_2 = \mathrm{R}\sin\phi, \qquad y_2 = 0, \qquad z_2 = \mathrm{R}\cos\phi\,;$$

hence

$$r_1^{\,2} = \mathrm{R}_1^{\,2}+2\xi\mathrm{R}_1\sin\phi+2\zeta\mathrm{R}_1\cos\phi+\xi^2+\eta^2+\zeta^2,$$

$$r^2 = \mathrm{R}^2-2\xi\mathrm{R}\sin\phi-2\zeta\mathrm{R}_1\cos\phi+\xi^2+\eta^2+\zeta^2,$$

and therefore

$$r_1 = \mathrm{R}_1+\xi\sin\phi+\zeta\cos\phi+\tfrac{1}{2}(\xi^2+\eta^2)/\mathrm{R}_1-\tfrac{1}{2}\xi^2\sin^2\phi/\mathrm{R}_1+\ldots,$$

$$r = \mathrm{R}-\xi\sin\phi-\zeta\cos\phi+\tfrac{1}{2}(\xi^2+\eta^2)/\mathrm{R}-\tfrac{1}{2}\xi^2\sin^2\phi/\mathrm{R}+\ldots,$$

whence

$$r_1+r = \mathrm{R}_1+\mathrm{R}+\tfrac{1}{2}(\xi^2\cos^2\phi+\eta^2)(\mathrm{R}_1^{\,-1}+\mathrm{R}^{-1})+\ldots,$$

the remaining terms involving higher powers of ξ and η.

Now

$$\iint e^{-\iota\kappa(r_1+r)}\,d\mathrm{S} = \iint e^{-\iota\kappa(r_1+r)}\sqrt{\left\{1+\left(\frac{\partial\zeta}{\partial\xi}\right)^2+\left(\frac{\partial\zeta}{\partial\eta}\right)^2\right\}}\,d\xi\,d\eta,$$

where the integral is taken throughout the area bounded by the projection on the tangent plane at Q to the conducting surface of the curve of contact of the tangent cone from the point O to the conducting surface. Hence the value of the principal part of

$$\iint e^{-\iota\kappa(r_1+r)}\,d\mathrm{S}$$

is the principal part of the integral

$$e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}\iint e^{-\frac{1}{2}\iota\kappa(\xi^2\cos^2\phi+\eta^2)(\mathrm{R}_1{}^{-1}+\mathrm{R}^{-1})+\ldots}\sqrt{\{1+(\mathrm{A}\xi+\mathrm{H}\eta+\,.)^2+(\mathrm{H}\xi+\mathrm{B}\eta+\,.)^2\}}\,d\xi\,d\eta,$$

that is, writing

$$\kappa\xi=\xi',\qquad \kappa\eta=\eta',$$

it follows that

$$\mathrm{I}=\kappa^{-2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})-\frac{\iota}{2\kappa}(\xi'^2\cos^2\phi+\eta'^2)(\mathrm{R}_1{}^{-1}+\mathrm{R}^{-1})}\,d\xi'\,d\eta',$$

provided that the point Q, in which OP cuts the conducting surface, is not near to the curve of contact of the tangent cone from O to the surface with the surface. Evaluating the above integral, the value of I is given by

$$\mathrm{I}=\frac{2\pi}{\iota\kappa\cos\phi}\,\frac{\mathrm{RR}_1}{\mathrm{R}+\mathrm{R}_1}\,e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})},$$

and therefore

$$\alpha_0=-\frac{\iota\kappa^2}{\mathrm{V}}\,\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{(\mathrm{R}_1+\mathrm{R})\cos\phi}\{(l\xi_0+m\eta_0+n\zeta_0)(y-\eta_0)+n(\eta_0z-\zeta_0y)\}/\mathrm{RR}_1,$$

$$\beta_0=\frac{\iota\kappa^2}{\mathrm{V}}\,\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{(\mathrm{R}_1+\mathrm{R})\cos\phi}\{(l\xi_0+m\eta_0+n\zeta_0)(x-\xi_0)+n(\xi_0z-\zeta_0x)\}/\mathrm{RR}_1,$$

$$\gamma_0=\frac{\iota\kappa^2}{\mathrm{V}}\,\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{(\mathrm{R}_1+\mathrm{R})\cos\phi}\{n(\eta_0x-\xi_0y)\}/\mathrm{RR}_1.$$

Now

$$\xi_0/\mathrm{R}_1=(x-\xi_0)/\mathrm{R},\qquad \eta_0/\mathrm{R}_1=(y-\eta_0)/\mathrm{R},\qquad \zeta_0/\mathrm{R}_1=(z-\zeta_0)/\mathrm{R},$$

and

$$(l\xi_0+m\eta_0+n\zeta_0)/\mathrm{R}_1=-\cos\phi,$$

whence, since

$$(y-\eta_0)/\mathrm{R}=y/(\mathrm{R}_1+\mathrm{R}),\qquad (x-\xi_0)/\mathrm{R}=x/(\mathrm{R}_1+\mathrm{R}),$$

$$\alpha_0=\frac{\iota\kappa^2}{\mathrm{V}}\,\frac{y}{\mathrm{R}_1+\mathrm{R}}\,\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}},$$

$$\beta_0=-\frac{\iota\kappa^2}{\mathrm{V}}\,\frac{x}{\mathrm{R}_1+\mathrm{R}}\,\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}},$$

$$\gamma_0=0.$$

Again, the components of the magnetic force at the point P due to the oscillator are

$$\alpha'=\frac{\kappa}{\mathrm{V}}\frac{\partial}{\partial y}\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}},\qquad \beta'=-\frac{\kappa}{\mathrm{V}}\frac{\partial}{\partial x}\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}},\qquad \gamma'=0,$$

hence, to the order of approximation adopted, the components of the total magnetic force at the point P are given by

$$\alpha = \frac{\iota\kappa^2}{\mathrm{V}}\frac{y}{\mathrm{R}_1+\mathrm{R}}\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}} - \frac{\iota\kappa^2}{\mathrm{V}}\frac{y}{\mathrm{R}_1+\mathrm{R}}\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}} = 0,$$

$$\beta = -\frac{\iota\kappa^2}{\mathrm{V}}\frac{x}{\mathrm{R}_1+\mathrm{R}}\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}} + \frac{\iota\kappa^2}{\mathrm{V}}\frac{x}{\mathrm{R}_1+\mathrm{R}}\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}} = 0,$$

$$\gamma = 0;$$

that is, the principal part of the magnetic force vanishes at all points inside the tangent cone from the point O to the surface which are on the side of the surface remote from O and not near to the boundary of the tangent cone. The principal part of the electric force also vanishes for these points, and therefore the surface condition, that the electric force tangential to the surface vanishes, is satisfied for points on the portion of the conducting surface remote from O inside the tangent cone and not near to the curve of contact of the tangent cone with the surface.

When the point P is external to the tangent cone or inside the tangent cone on the same side of the conducting surface as the point O, the relations to be satisfied are

$$x_1/\mathrm{R}_1+x_2/\mathrm{R} = 0, \qquad z_1/\mathrm{R}_1-z_2/\mathrm{R} = 0,$$

and, as above, writing

$$x_1 = -\mathrm{R}_1 \sin\phi, \qquad z_1 = -\mathrm{R}_1\cos\phi,$$

it follows that

$$x_2 = \mathrm{R}\sin\phi, \qquad y_2 = 0, \qquad z_2 = -\mathrm{R}\cos\phi,$$

and

$$r_1 = \mathrm{R}_1+\xi\sin\phi+\zeta\cos\phi+\tfrac{1}{2}(\xi^2\cos^2\phi+\eta^2)/\mathrm{R}_1+\ldots,$$

$$r = \mathrm{R}-\xi\sin\phi+\zeta\cos\phi+\tfrac{1}{2}(\xi^2\cos^2\phi+\eta^2)/\mathrm{R}\ldots,$$

whence

$$r_1+r = \mathrm{R}_1+\mathrm{R}+\tfrac{1}{2}(\xi^2\cos^2\phi+\eta^2)(\mathrm{R}_1^{-1}+\mathrm{R}^{-1})+2\zeta\cos\phi\ldots,$$

that is,

$$r_1+r = \mathrm{R}_1+\mathrm{R}+\tfrac{1}{2}\xi^2\{(\mathrm{R}_1^{-1}+\mathrm{R}^{-1})\cos^2\phi+2\mathrm{A}\cos\phi\}+2\mathrm{H}\cos\phi\,\xi\eta$$
$$+\tfrac{1}{2}\eta^2\{\mathrm{R}_1^{-1}+\mathrm{R}^{-1}+2\mathrm{B}\cos\phi\}+\ldots.$$

Writing

$$\xi = \xi_1\cos\theta-\eta_1\sin\theta, \qquad \eta = \xi_1\sin\theta+\eta_1\cos\theta,$$

and choosing θ so that the coefficient of ξ_1, η_1 vanishes, θ is given by

$$\cot 2\theta = \{2(\mathrm{A}-\mathrm{B})\cos\phi-(\mathrm{R}_1^{-1}+\mathrm{R}^{-1})\sin^2\phi\}/4\mathrm{H}\cos\phi,$$

and

$$r_1+r = \mathrm{R}_1+\mathrm{R}+\tfrac{1}{2}(\mathrm{A}_1\xi_1^2+\mathrm{B}_1\eta_1^2)+\ldots,$$

where

$$\mathrm{A}_1+\mathrm{B}_1 = (\mathrm{R}_1^{-1}+\mathrm{R}^{-1})(1+\cos^2\phi)+2(\mathrm{A}+\mathrm{B})\cos\phi,$$

$$\mathrm{A}_1\mathrm{B}_1 = (\mathrm{R}_1^{-1}+\mathrm{R}^{-1})^2\cos^2\phi+2(\mathrm{R}_1^{-1}+\mathrm{R}^{-1})(\mathrm{A}+\mathrm{B}\cos^2\phi)\cos\phi+4(\mathrm{AB}-\mathrm{H}^2)\cos^2\phi.$$

Now

$$\mathrm{A}_1\mathrm{B}_1 = \{(\mathrm{R}_1^{-1}+\mathrm{R}^{-1})\cos\phi+\mathrm{A}+\mathrm{B}\cos^2\phi\}^2-(\mathrm{A}-\mathrm{B}\cos^2\phi)^2-4\mathrm{H}^2\cos^2\phi,$$

and writing

$$\mathrm{A}-\mathrm{B}\cos^2\phi = 2\mathrm{H}\cos\phi\cot 2\psi,$$

this becomes

$$\mathrm{A}_1\mathrm{B}_1 = \cos^2\phi\,(\mathrm{R}^{-1}-f_1^{-1})\,(\mathrm{R}^{-1}-f_2^{-1}),$$

where

$$(\mathrm{R}_1^{-1}+f_1^{-1})\cos\phi+\mathrm{A}+\mathrm{B}\cos^2\phi-2\mathrm{H}\cos\phi\operatorname{cosec}2\psi = 0,$$

$$(\mathrm{R}_1^{-1}+f_2^{-1})\cos\phi+\mathrm{A}+\mathrm{B}\cos^2\phi+2\mathrm{H}\cos\phi\operatorname{cosec}2\psi = 0,$$

and

$$2\mathrm{H} = (f_1^{-1}-f_2^{-1})\sin\psi\cos\psi,$$

$$\mathrm{R}_1^{-1}+\cos^2\psi/f_1+\sin^2\psi/f_2+2\mathrm{B}\cos\phi = 0,$$

$$\mathrm{R}_1^{-1}+\sin^2\psi/f_1+\cos^2\psi/f_2+2\mathrm{A}\sec\phi = 0,$$

$$\cot 2\theta = \{(f_1^{-1}-\mathrm{R}^{-1})(\cos^2\psi-\sin^2\psi\cos^2\phi)$$
$$+(f_2^{-1}-\mathrm{R}^{-1})(\sin^2\psi-\cos^2\psi\cos^2\phi)\}/(f_1^{-1}-f_2^{-1})\sin^2\psi\cos\phi.$$

The value of the principal part of the integral

$$\iint e^{-\iota\kappa(r_1+r)}\,d\mathrm{S}$$

is now given by

$$\mathrm{I} = \kappa^{-2}e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{\iota}{2\kappa}(\mathrm{A}_1\xi'^2+\mathrm{B}_1\eta'^2)}\,d\xi'\,d\eta',$$

that is,

$$\mathrm{I} = \frac{2\pi}{\iota\kappa(\mathrm{A}_1\mathrm{B}_1)^{1/2}}\,e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}$$

or

$$\mathrm{I} = \frac{2\pi}{\iota\kappa\cos\phi}(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}\,e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})},$$

and therefore the principal parts of the components of the magnetic force at the point (x, y, z) due to the surface distribution are given by

$$\alpha_0 = -\frac{\iota\kappa^2}{\mathrm{V}\cos\phi}(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}\,e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}$$
$$\{(l\xi_0+m\eta_0+n\zeta_0)(y-\eta_0)+n(\eta_0 z-\zeta_0 y)\}/\mathrm{R}^2\mathrm{R}_1^2,$$

$$\beta_0 = \frac{\iota\kappa^2}{\mathrm{V}\cos\phi}(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}\,e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}$$
$$\{(l\xi_0+m\eta_0+n\zeta_0)(x-\xi_0)+n(\xi_0 z-\zeta_0 x)\}/\mathrm{R}^2\mathrm{R}_1^2,$$

$$\gamma_0 = \frac{\iota\kappa^2}{\mathrm{V}\cos\phi}(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}\,e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\{n(\eta_0 x-\xi_0 y)\}/\mathrm{R}^2\mathrm{R}_1^2.$$

Writing

$$\xi_0/\mathrm{R}_1 = \lambda_1, \qquad \eta_0/\mathrm{R}_1 = \mu_1, \qquad \zeta_0/\mathrm{R}_1 = \nu_1,$$
$$(x-\xi_0)/\mathrm{R} = \lambda_2, \qquad (y-\eta_0)/\mathrm{R} = \mu_2, \qquad (z-\zeta_0)/\mathrm{R} = \nu_2,$$

it follows that

$$l\lambda_1+m\mu_1+n\nu_1 = -\cos\phi,$$

and the relations satisfied at the point Q are equivalent to

$$\lambda_2 = \lambda_1+2l\cos\phi, \qquad \mu_2 = \mu_1+2m\cos\phi, \qquad \nu_2 = \nu_1+2n\cos\phi,$$

whence the above values of α_0, β_0, γ_0 may be written

$$\alpha_0 = \frac{\iota\kappa^2}{\mathrm{V}}(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\{\mu_2+2n(m\nu_1-n\mu_1)\}/\mathrm{RR}_1,$$

$$\beta_0 = \frac{\iota\kappa^2}{\mathrm{V}}(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\{-\lambda_2+2n(n\lambda_1-l\nu_1)\}/\mathrm{RR}_1,$$

$$\gamma_0 = \frac{\iota\kappa^2}{\mathrm{V}}(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\{2n(l\mu_1-m\lambda_1)\}/\mathrm{RR}_1.$$

The principal parts of the components of the electric force at the point (x, y, z) due to the surface distribution are therefore given by

$$\mathrm{X}_0 = -\iota\kappa^2(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\{\nu_1\lambda_1+2\nu_1 l\cos\phi+2nl\}/\mathrm{RR}_1,$$

$$\mathrm{Y}_0 = -\iota\kappa^2(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\{\mu_1\nu_1+2\nu_1 m\cos\phi+2mn\}/\mathrm{RR}_1,$$

$$\mathrm{Z}_0 = -\iota\kappa^2(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\{-\lambda_1^2-\mu_1^2+2\nu_1 n\cos\phi+2n^2\}/\mathrm{RR}_1,$$

and, writing

$$x = \lambda r, \qquad y = \mu r, \qquad z = \nu r,$$

where

$$r^2 = x^2+y^2+z^2,$$

the principal parts of the components of the electric force at the point (x, y, z) due to the oscillator are

$$\iota\kappa^2\nu\lambda\, e^{\iota\kappa(\mathrm{V}t-r)}/r, \qquad \iota\kappa^2\mu\nu\, e^{\iota\kappa(\mathrm{V}t-r)}/r, \qquad -\iota\kappa^2(\lambda^2+\mu^2)\,e^{\iota\kappa(\mathrm{V}t-r)}/r;$$

therefore the principal parts of the components of the total electric force at the point (x, y, z) are given by

$$\mathrm{X} = \iota\kappa^2\nu\lambda\, e^{\iota\kappa(\mathrm{V}t-r)}/r-\iota\kappa^2(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}$$
$$\{\nu_1\lambda_1+2\nu_1 l\cos\phi+2nl\}/\mathrm{RR}_1,$$

$$\mathrm{Y} = \iota\kappa^2\mu\nu\, e^{\iota\kappa(\mathrm{V}t-r)}/r-\iota\kappa^2(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}$$
$$\{\mu_1\nu_1+2\nu_1 m\cos\phi+2mn\}/\mathrm{RR}_1,$$

$$\mathrm{Z} = -\iota\kappa^2(\lambda^2+\mu^2)\,e^{\iota\kappa(\mathrm{V}t-r)}/r-\iota\kappa^2(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}$$
$$\{-\lambda_1^2-\mu_1^2+2\nu_1 n\cos\phi+2n^2\}/\mathrm{RR}_1.$$

When the point P is on the surface of the conductor,

$$\mathrm{R} = 0, \qquad r = \mathrm{R}_1, \qquad \lambda = \lambda_1, \qquad \mu = \mu_1, \qquad \nu = \nu_1,$$

and therefore the principal parts of the components of the electric force at a point on the surface are given by

$$\mathrm{X} = -2\iota\kappa^2 l\,(\nu_1 \cos\phi + n)\, e^{\iota\kappa(\mathrm{V}t - \mathrm{R}_1)}/\mathrm{R}_1,$$
$$\mathrm{Y} = -2\iota\kappa^2 m\,(\nu_1 \cos\phi + n)\, e^{\iota\kappa(\mathrm{V}t - \mathrm{R}_1)}/\mathrm{R}_1,$$
$$\mathrm{Z} = -2\iota\kappa^2 n\,(\nu_1 \cos\phi + n)\, e^{\iota\kappa(\mathrm{V}t - \mathrm{R}_1)}/\mathrm{R}_1,$$

hence the principal part of the electric force at a point on the surface is normal to the surface, and therefore the principal part of the electric force satisfies the condition that the electric force tangential to the surface vanishes. It follows from this that the principal parts of the components of the magnetic and electric forces at points not near to the boundary of the geometrical shadow are those given above.

To find the region within which the point P lies when the above values cease to represent the principal parts of the components of the magnetic and electric forces due to the obstacle, it is necessary to find the order of the terms neglected by taking the limits of the integral representing the principal part of the integral

$$\iint e^{-\iota\kappa(r_1 + r)}\, d\mathrm{S}$$

to be infinite. In the evaluation of I this integral was replaced by an integral taken throughout the area enclosed by the curve which is the projection on the tangent plane at the point Q of the curve of contact of the tangent cone from the point O to the surface of the obstacle with this surface. The actual limits of the integral

$$\iint e^{-\frac{\iota}{2\kappa}(\xi'^2 \cos^2\phi + \eta'^2)(\mathrm{R}_1{}^{-1} + \mathrm{R}^{-1})}\, d\xi'\, d\eta'$$

are quantities of the order κd or quantities of higher order, where d is the least distance of the point Q from the boundary of the curve throughout whose area the integration is taken; hence the part of the integral neglected by taking the limits to be infinite is at most of the order $(\kappa d^2/\mathrm{R}_1 + \kappa d^2/\mathrm{R})^{-1/2}$ compared with the part retained, when the point P is inside the tangent cone from the point O to the surface of the obstacle and on the side of the surface remote from the point O. Again, when the point P is outside the tangent cone from the point O to the surface, the actual limits of the corresponding integral are also quantities of the order κd or quantities of a higher order, and therefore, since $\mathrm{A} + \mathrm{B}$ and $\mathrm{AB} - \mathrm{H}^2$ are both positive, the part of the integral neglected by taking the limits to be infinite is at most of the order $(\kappa d^2/\mathrm{R}_1 + \kappa d^2/\mathrm{R})^{-1/2}$ compared with the part retained. The region within which the point P lies when the values obtained above for the principal parts of the magnetic and electric forces cease to represent them is determined by the condition that the point Q related to the point P in the manner already defined is so close to the curve of contact of the tangent cone from the point O to the surface of the obstacle with the surface that the quantity $(\kappa d^2/R_1+\kappa d^2/R)^{-1/2}$ is a quantity of the order of unity or of a higher order.

When the point P is sufficiently distant from the surface of the tangent cone from the point O to the surface of the obstacle, the limits of the integral may be taken to be infinite, and the order of the difference between the components of the actual magnetic and electric forces due to the obstacle and the components of the magnetic and electric forces due to the assumed electric current distribution may be obtained as follows. In the exponent of $e^{-\iota\kappa(r_1+r)}$ the terms up to and including those of the fourth degree in ξ and η must be retained, and in the other factors of the integrands the terms up to and including the terms of the second degree in ξ and η must be retained; this requires that in the equation to the surface

$$\zeta = \tfrac{1}{2}(A\xi^2+2H\xi\eta+B\eta^2)+\ldots+\ldots,$$

terms up to and including the terms of the fourth degree in ξ and η are retained, and the resulting integrals are now of the form

$$\iint(g_0+g_1+g_2+\kappa g_3+\kappa g_4)\,e^{-1/2\iota\kappa(A_1\xi^2+B_1\eta^2)}\,d\xi\,d\eta,$$

where g_n denotes a homogeneous function of ξ, η of degree n. The terms of odd degree in ξ, η contribute zero to the result and the integral is equal to

$$\iint(g_0+g_2+\kappa g_4)\,e^{-1/2\iota\kappa(A_1\xi^2+B_1\eta^2)}\,d\xi\,d\eta.$$

Now, if the conducting surface were the infinite plane coinciding with the tangent plane at the point Q to the surface of the obstacle, the corresponding integral would be

$$\iint(g_0+g'_2+\kappa g'_4)\,e^{-1/2\iota\kappa(A'_1\xi^2+B'_1\eta^2)}\,d\xi\,d\eta,$$

where this integral is equal to the value of the preceding integral when the quantities A, B, H, &c., in the equation to the surface are made zero. Further, for the surface $\zeta = 0$, the condition that the tangential electric force due to the assumed electric current distribution vanishes at the surface is accurately satisfied, and therefore the principal part of the electric force tangential to the surface of the obstacle at the point Q is the value at Q of the principal part of an integral of the form

$$\iint\left[(g_0+g_2+\kappa g_4)\,e^{-1/2\iota\kappa(A_1\xi^2+B_1\eta^2)}-(g_0+g'_2+\kappa g'_4)\right]e^{-1/2\iota\kappa(A'_1\xi^2+B'_1\eta^2)}\,d\xi\,d\eta,$$

which vanishes when A, B, H, &c., vanish, and hence is at most of the order $(\kappa\rho)^{-1}$, where ρ is the least radius of curvature of the surface at the point Q, it being assumed that the values of $\xi\frac{\partial^3\zeta}{\partial\xi^3}$, $\xi^2\frac{\partial^4\zeta}{\partial\xi^4}$, and the similar quantities in the immediate neighbourhood of the point Q are not of an order higher than ρ^{-1}. Therefore the difference between the components of the actual magnetic and electric forces due to the obstacle at the point P, not near to the surface of the tangent cone from the point O to the surface of the obstacle, and the components of the magnetic and electric forces due to the assumed electric current distribution on the surface of the obstacle is at most of the order $(\kappa\rho)^{-1}$, where ρ is the least radius of curvature of the surface at the point Q, which is related to the point P in the manner already defined.*

It has been shown above that the principal parts of the components of the magnetic force due to the assumed electric current distribution on the surface of the obstacle are

$$\frac{\iota\kappa^2}{\mathrm{V}}(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\{\mu_2+2n(m\nu_1-n\mu_1)\}/\mathrm{RR}_1,$$

$$\frac{\iota\kappa^2}{\mathrm{V}}(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\{-\lambda_2+2n(n\lambda_1-l\nu_1)\}/\mathrm{RR}_1,$$

$$\frac{\iota\kappa^2}{\mathrm{V}}(\mathrm{R}^{-1}-f_1^{-1})^{-1/2}(\mathrm{R}^{-1}-f_2^{-1})^{-1/2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\{2n(l\mu_1-m\lambda_1)\}/\mathrm{RR}_1\,;$$

in these expressions the quantities f_1, f_2 are both negative, since A+B and $\mathrm{AB}-\mathrm{H}^2$ are both positive, hence when the obstacle is a convex solid the principal parts of the components of the magnetic force in the reflected waves are given at all points P not near to the surface of the tangent cone from the point O to the surface of the obstacle by the above expressions which are everywhere finite. The points for which $\mathrm{R}-f_1$, $\mathrm{R}-f_2$ vanish are situated on the line PQ produced and determine the positions of virtual focal lines; the directions of these focal lines are given by

$$\tan\theta = \tan\psi\sec\phi, \qquad \text{when} \qquad \mathrm{R}=f_1,$$

and by

$$\tan\theta = \tan\psi\cos\phi, \qquad \text{when} \qquad \mathrm{R}=f_2.$$

If the obstacle is not a convex solid, provided that there is no point P on its surface such that a prolate spheroid whose foci are the points O and P can be drawn to touch the surface of the obstacle, the same analysis applies, but, P being now a point not on the surface of the obstacle, if the surface is concave towards O and P at

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* The value of the principal parts of these differences can be obtained by placing on the surface of the obstacle an electric current distribution of order $(\kappa\rho)^{-1}$ which will balance the unbalanced tangential electric force of this order.

the point Q (ξ_0, η_0, ζ_0) determined as before, the points P_1, P_2 on the straight line QP for which $R-f_1$ or $R-f_2$ vanish are both external to the surface of the obstacle if

$$A+B\cos^2\phi+\cos\phi/R_1$$

is negative, for then f_1 and f_2 are both positive. The principal parts of the magnetic force in the reflected waves given by the above expressions tend towards infinite values as either of the points P_1, P_2 is approached, and the points P_1, P_2 now determine the positions of actual focal lines whose directions are given by

$$\tan\theta = \tan\psi\sec\phi, \qquad R = f_1,$$
$$\tan\theta = \tan\psi\cos\phi, \qquad R = f_2.$$

The principal parts of the components of the magnetic force were evaluated above on the assumption that $R^{-1}-f_1^{-1}$, $R^{-1}-f_2^{-1}$ were both finite; if either of these quantities is very small, some of the terms neglected in that evaluation are of the same order as those retained, and it is necessary to calculate the principal part of the magnetic force taking account of these terms. In the equation of the surface in the neighbourhood of the point Q (ξ_0, η_0, ζ_0) the terms of the third order must be retained and the equation to the surface with Q as origin of co-ordinates and the same axes of reference as formerly is now

$$\zeta = \tfrac{1}{2}(A\xi^2+2H\xi\eta+B\eta^2)+\tfrac{1}{6}(C\xi^3+3L\xi^2\eta+3M\xi\eta^2+D\eta^3).$$

The value of r_1+r is now given by

$$r_1+r = R_1+R+\tfrac{1}{2}(A'\xi^2+2H'\xi\eta+B'\eta^2)+\tfrac{1}{6}(C'\xi^3+3L'\xi^2\eta+3M'\xi\eta^2+D'\eta^3)$$

where

$$A' = (R_1^{-1}+R^{-1})\cos^2\phi+2A\cos\phi, \quad B' = (R_1^{-1}+R^{-1})+2B\cos\phi, \quad H' = 2H\cos\phi,$$
$$C' = 2C\cos\phi+3A\sin\phi\cos\phi\,(R^{-1}-R_1^{-1})+3\sin\phi\cos^2\phi\,(1/R^2-1/R_1^2),$$
$$L' = 2L\cos\phi+2H\sin\phi\cos\phi\,(R^{-1}-R_1^{-1}),$$
$$M' = 2M\cos\phi+B\sin\phi\cos\phi\,(R^{-1}-R_1^{-1})+\sin\phi\,(1/R^2-1/R_1^2),$$
$$D' = 2D\cos\phi.$$

At the point P_1, for which $R = f_1$, these relations become

$$A' = K\cos^2\phi\cos^2\psi, \qquad B' = K\sin^2\psi, \qquad H' = K\sin\psi\cos\psi\cos\phi, \text{ \&c.},$$

where

$$f_1^{-1}-f_2^{-1} = K,$$

and, turning the axes of ξ and η through the angle θ given by $\tan\theta = \tan\psi\sec\phi$, r_1+r is given by

$$r_1+r = R_1+R+\tfrac{1}{2}(A_1\xi^2+B_1\eta^2)+\tfrac{1}{6}(C_1\xi^3+3L_1\xi^2\eta+3M_1\xi\eta^2+D_1\eta^3),$$

where

$$\mathrm{A}_1 = \mathrm{K}\,(\cos^2\phi\cos^2\psi+\sin^2\psi), \qquad \mathrm{B}_1 = 0,$$

$$\mathrm{D}_1 = [2\cos\phi(-\mathrm{C}\sin^3\psi+3\mathrm{L}\sin^2\psi\cos\phi\cos\psi+-3\mathrm{M}\sin\psi\cos^2\phi\cos^2\psi+\mathrm{D}\cos^3\phi\cos^3\psi) \\ +\tfrac{3}{2}(1/\mathrm{R}_1^2-1/\mathrm{R}^2)\sin\psi\sin\phi\cos^2\phi]\times(\cos^2\phi\cos^2\psi+\sin^2\psi)^{-3/2},$$

and the principal part of the integral

$$\iint e^{-\iota\kappa(r_1+r)}\,d\mathrm{S}$$

is equal to the principal part of the integral

$$e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}\iint e^{-1/2\,\iota\kappa\mathrm{A}_1\xi^2-1/6\,\iota\kappa(\mathrm{C}_1\xi^3+3\mathrm{L}_1\xi^2\eta+3\mathrm{M}_1\xi\eta^2+\mathrm{D}_1\eta^3)}\,d\xi\,d\eta,$$

that is to the integral

$$\kappa^{-2}e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-\frac{\iota}{\kappa}\mathrm{A}_1\xi_1^2-\frac{\iota}{6\kappa^2}\mathrm{D}_1\eta_1^3}\,d\xi_1\,d\eta_1,$$

which is equal to

$$\kappa^{-2}e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}\,\pi^{1/2}\left(\frac{\iota}{2\kappa}\mathrm{A}_1\right)^{-1/2}\int_{-\infty}^{\infty}e^{-\frac{\iota}{6\kappa^2}\mathrm{D}_1\eta_1^3}\,d\eta_1,$$

that is to

$$\pi^{1/2}\kappa^{-2}e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}\left(\frac{\iota}{2\kappa}\mathrm{A}_1\right)^{-1/2}\left[\left(\frac{\iota\mathrm{D}_1}{6\kappa^2}\right)^{-1/3}+\left(\frac{-\iota\mathrm{D}_1}{6\kappa^2}\right)^{-1/3}\right]\tfrac{1}{3}\Gamma\left(\tfrac{1}{3}\right),$$

whence

$$\mathrm{I} = \pi^{1/2}\kappa^{-5/6}2^{5/6}3^{-1/6}\Gamma\left(\tfrac{1}{3}\right)e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})+\frac{\pi\iota}{4}}\,\mathrm{A}_1^{-1/2}\mathrm{D}_1^{-1/3},$$

where A_1 and D_1 have the values given above. Therefore at the point P_1 the principal parts of the components of the magnetic force in the reflected waves are given by

$$\alpha_0 = -\frac{\kappa^{13/6}}{\pi\mathrm{V}}6^{-1/6}\Gamma\left(\tfrac{1}{2}\right)\Gamma\left(\tfrac{1}{3}\right)\mathrm{A}_1^{-1/2}\mathrm{D}_1^{-1/3}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})+\frac{\pi\iota}{4}}\cos\phi\,[\mu_2+2n\,(m\nu_1-n\mu_1)]/\mathrm{R}_1\mathrm{R},$$

$$\beta_0 = -\frac{\kappa^{13/6}}{\pi\mathrm{V}}6^{-1/6}\Gamma\left(\tfrac{1}{2}\right)\Gamma\left(\tfrac{1}{3}\right)\mathrm{A}_1^{-1/2}\mathrm{D}_1^{-1/3}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})+\frac{\pi\iota}{4}}\cos\phi\,[-\lambda_2+2n\,(n\lambda_1-l\nu_1)]/\mathrm{R}_1\mathrm{R},$$

$$\gamma_0 = -\frac{\kappa^{13/6}}{\pi\mathrm{V}}6^{-1/6}\Gamma\left(\tfrac{1}{2}\right)\Gamma\left(\tfrac{1}{3}\right)\mathrm{A}_1^{-1/2}\mathrm{D}_1^{-1/3}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})+\frac{\pi\iota}{4}}\cos\phi\,[2n\,(l\mu_1-m\lambda_1)]/\mathrm{R}_1\mathrm{R}.$$

Similarly, at the point P_2, for which $\mathrm{R} = f_2$, the principal parts of the components of the magnetic force are given by

$$\alpha_0 = -\frac{\kappa^{13/6}}{\pi\mathrm{V}}6^{-1/6}\Gamma\left(\tfrac{1}{2}\right)\Gamma\left(\tfrac{1}{3}\right)\mathrm{B}_1^{-1/2}\mathrm{C}_1^{-1/3}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})+\frac{\pi\iota}{4}}\cos\phi\,[\mu_2+2n\,(m\nu_1-n\mu_1)]/\mathrm{R}_1\mathrm{R},$$

$$\beta_0 = -\frac{\kappa^{13/6}}{\pi\mathrm{V}}6^{-1/6}\Gamma\left(\tfrac{1}{2}\right)\Gamma\left(\tfrac{1}{3}\right)\mathrm{B}_1^{-1/2}\mathrm{C}_1^{-1/3}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})+\frac{\pi\iota}{4}}\cos\phi\,[-\lambda_2+2n\,(n\lambda_1-l\nu_1)]/\mathrm{R}_1\mathrm{R},$$

$$\gamma_0 = -\frac{\kappa^{13/6}}{\pi\mathrm{V}}6^{-1/6}\Gamma\left(\tfrac{1}{2}\right)\Gamma\left(\tfrac{1}{3}\right)\mathrm{B}_1^{-1/2}\mathrm{C}_1^{-1/3}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})+\frac{\pi\iota}{4}}\cos\phi\,[2n\,(l\mu_1-m\lambda_1)]/\mathrm{R}_1\mathrm{R},$$

where

$$\mathrm{B}_1 = -\mathrm{K}\,(\sin^2\psi\cos^2\phi+\cos^2\psi),$$

$$\mathrm{C}_1 = [2\cos\phi\,(\mathrm{C}\cos^3\psi+3\mathrm{L}\sin\psi\cos^2\psi\cos\phi+3\mathrm{M}\sin^2\psi\cos\psi\cos^2\phi+\mathrm{D}\sin^3\psi\cos^3\phi)$$
$$+\tfrac{3}{2}(1/\mathrm{R}^2-1/\mathrm{R}_1{}^2)\sin\phi\cos^2\phi\cos\psi]\,[\cos^2\psi+\sin^2\psi\cos^2\phi]^{-3/2}.$$

From these results it follows that the intensity of the reflected waves at a point on a caustic is of a higher order than at an ordinary point, the ratio of the two intensities depending on $\lambda^{-1/3}$, where λ is the wave-length of the waves. In the above investigation it has been assumed that, when $\mathrm{R} = f_1$, D_1 and A_1 are finite, and that, when $\mathrm{R} = f_2$, C_1 and B_1 are finite; if, when $\mathrm{R} = f_1$, A_1 is finite and D_1 vanishes, terms of the fourth order must be retained and the ratio of the intensity at such a point on a caustic to the intensity at an ordinary point depends on $\lambda^{-1/2}$. Similarly, if, when $\mathrm{R} = f_2$, B_1 is finite and C_1 vanishes, the ratio of the intensity at the corresponding point on the caustic to the intensity at an ordinary point depends on $\lambda^{-1/2}$. Further, at a point on the intersection of the two sheets of the caustic A_1 and B_1 vanish simultaneously and, if C_1 and D_1 are both finite, the ratio of the intensity at this point to the intensity at an ordinary point depends on $\lambda^{-2/3}$. The other cases which depend on the vanishing of more of the constants A_1, B_1, C_1, &c., can be similarly treated.

At a point in the neighbourhood of the caustic either $\mathrm{R}-f_1$ or $\mathrm{R}-f_2$ is a small quantity; if $\mathrm{R}-f_1$ is small and $\mathrm{R}-f_2$ is not small, B_1 is a small quantity and the value of I the principal part of the integral

$$\iint e^{-\iota\kappa(r_1+r)}\,d\mathrm{S}$$

is given by

$$\mathrm{I} = \kappa^{-2}e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{\iota}{2\kappa}(\mathrm{A}_1\xi^2+\mathrm{B}_1\eta^2)-\frac{\iota}{6\kappa^2}\mathrm{D}_1\eta^3}\,d\xi\,d\eta,$$

that is

$$\mathrm{I} = \kappa^{-2}\pi^{1/2}\left(\frac{\iota}{2\kappa}\mathrm{A}_1\right)^{-1/2}\int_{-\infty}^{\infty} e^{-\frac{\iota}{2\kappa}\mathrm{B}_1\eta^2-\frac{\iota}{6\kappa^2}\mathrm{D}_1\eta^3}\,d\eta\, e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})},$$

or

$$\mathrm{I} = 2\pi^{1/2}\kappa^{-2}\left(\frac{\iota}{2\kappa}\mathrm{A}_1\right)^{-1/2}\left(\frac{3\pi\kappa^2}{\mathrm{D}_1}\right)^{1/3}\mathrm{W}\,e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})},$$

where

$$\mathrm{W} = \int_0^{\infty}\cos\tfrac{1}{2}\pi(\zeta^3-\mu\zeta)\,d\zeta, \qquad \text{and} \qquad \mu = 12^{1/3}\mathrm{B}_1{}^2\lambda^{-2/3}\mathrm{D}_1{}^{-4/3}.$$

Therefore at a point in the neighbourhood of a caustic the principal parts of the components of the magnetic force in the reflected waves are given by

$$\alpha_0 = -2^{1/2}3^{1/3}\pi^{-1/6}\mathrm{V}^{-1}\kappa^{13/6}\mathrm{A}_1{}^{-1/2}\mathrm{D}_1{}^{-1/3}\mathrm{W}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})-\frac{\pi\iota}{4}}\cos\phi\,[\mu_2+2n\,(m\nu_1-n\mu_1)]/\mathrm{R}_1\mathrm{R},$$

$$\beta_0 = -2^{1/2}3^{1/3}\pi^{-1/6}\mathrm{V}^{-1}\kappa^{13/6}\mathrm{A}_1{}^{-1/2}\mathrm{D}_1{}^{-1/3}\mathrm{W}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})-\frac{\pi\iota}{4}}\cos\phi\,[-\lambda_2+2n\,(n\lambda_1-l\nu_1)]/\mathrm{R}_1\mathrm{R},$$

$$\gamma_0 = -2^{1/2}3^{1/3}\pi^{-1/6}\mathrm{V}^{-1}\kappa^{13/6}\mathrm{A}_1{}^{-1/2}\mathrm{D}_1{}^{-1/3}\mathrm{W}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})-\frac{\pi\iota}{4}}\cos\phi\,[2n\,(l\mu_1-m\lambda_1)]/\mathrm{R}_1\mathrm{R},$$

where W has the value given above. When $\mathrm{R}-f_2$ is small and $\mathrm{R}-f_1$ is not small, the principal parts of the components of the magnetic force in the reflected waves are given by the corresponding expressions in which A_1 is replaced by B_1, B_1 is replaced by A_1, and D_1 is replaced by C_1. At a point in the neighbourhood of the intersection of the two sheets of the caustic, A_1 and B_1 are both small, and the expressions for the principal parts of the components of the magnetic force in the reflected waves will contain the product of two integrals which are values of W corresponding to two values of μ.

When the obstacle is of any form, if P is a point not inside the boundary of the geometrical shadow, there may be more than one point Q on the surface of the obstacle such that $\mathrm{OQ}+\mathrm{QP}$ is stationary, or there may be points Q, Q_1, Q_2, ... Q_n such that $\mathrm{OQ}+\mathrm{QQ}_1+\mathrm{Q}_1\mathrm{Q}_2+\ldots\mathrm{Q}_n\mathrm{P}$ is stationary; in the first of these cases the principal parts of the components of the magnetic force in the reflected waves is the same for all the different points Q; in the second case the principal parts of the magnetic force in the reflected waves at P is obtained by placing an electric current distribution on the surface in the neighbourhood of Q double that due to the tangential electric force from O, an electric current distribution in the neighbourhood of Q_1 double that due to the tangential electric force arising from the current distribution in the neighbourhood of Q and so on.

The magnetic and electric forces due to the assumed distribution over the surface of the obstacle have still to be obtained at points which are near to the boundary of the geometrical shadow. Taking first the case where the point P is inside the tangent cone from the point O to the surface of the obstacle, and on the side of the obstacle remote from the point O, the principal parts of α, β, γ, where

$$\alpha = -\frac{\kappa}{2\pi\mathrm{V}}\iint\left[\frac{y-\eta}{r}\,\frac{l\xi+m\eta+n\zeta}{r_1}+\frac{n\,(z\eta-y\zeta)}{rr_1}\right]\frac{\partial^2}{\partial r\,\partial r_1}\,\frac{e^{\iota\kappa(\mathrm{V}t-r_1-r)}}{rr_1}\,d\mathrm{S},$$

$$\beta = \frac{\kappa}{2\pi\mathrm{V}}\iint\left[\frac{x-\xi}{r}\,\frac{l\xi+m\eta+n\zeta}{r_1}+\frac{n\,(z\xi-x\zeta)}{rr_1}\right]\frac{\partial^2}{\partial r\,\partial r_1}\,\frac{e^{\iota\kappa(\mathrm{V}t-r_1-r)}}{rr_1}\,d\mathrm{S},$$

$$\gamma = \frac{\kappa}{2\pi\mathrm{V}}\iint\frac{n\,(x\eta-y\xi)}{rr_1}\,\frac{\partial^2}{\partial r\,\partial r_1}\,\frac{e^{\iota\kappa(\mathrm{V}t-r_1-r)}}{rr_1}\,d\mathrm{S},$$

have to be calculated when the limits can no longer be taken infinite for the purpose. As before, the principal parts of α, β, γ are given by

$$\alpha_0 = \frac{\kappa^3}{2\pi\mathrm{V}}\,\frac{y-\eta_0}{\mathrm{R}}\,\mathrm{I},\quad \beta_0 = -\frac{\kappa^3}{2\pi\mathrm{V}}\,\frac{x-\xi_0}{\mathrm{R}}\,\mathrm{I},\quad \gamma_0 = 0,$$

where I is the principal part of the integral

$$\iint\frac{l\xi_0+m\eta_0+n\zeta_0}{\mathrm{R}}\,\frac{e^{\iota\kappa(\mathrm{V}t-r_1-r)}}{\mathrm{R}_1\mathrm{R}}\,d\mathrm{S}.$$

Now

$$\iint \frac{l\xi_0+m\eta_0+n\zeta_0}{\mathrm{R}} \frac{e^{\iota\kappa(\mathrm{V}t-r_1-r)}}{\mathrm{R}_1\mathrm{R}}\,d\mathrm{S} = -\iint \frac{e^{\iota\kappa(\mathrm{V}t-r_1-r)}}{\mathrm{R}_1\mathrm{R}}\,d\sigma,$$

where $d\sigma$ is the projection of the element of area $d\mathrm{S}$ on a plane perpendicular to the straight line OP; to evaluate this integral let the axes of reference be OP the axis of z, the perpendicular to OP in the plane of incidence the axis of x, and the straight line perpendicular to these two the axis of y. Let ξ, η, ζ now denote the co-ordinates of a point on the surface, and ξ_1, 0_1, ζ_1 the co-ordinates of the point of contact R of the tangent from O to the surface in the plane of incidence; the co-ordinates of the point P are 0, 0, $\mathrm{R}_1+\mathrm{R}$, then

$$\iint e^{-\iota\kappa(r_1+r)}\,d\sigma = \int^{\xi_1}\!\!\int e^{-\iota\kappa(r_1+r)}\,d\xi\,d\eta,$$

that is, the principal part of this integral is given by

$$\int_{-\infty}^{\infty}\!\int_{-\infty}^{\infty} e^{-\iota\kappa(r_1+r)}\,d\xi\,d\eta - \int_{\xi_1}\!\!\int e^{-\iota\kappa(r_1+r)}\,d\xi\,d\eta.$$

It has already been proved that

$$\int_{-\infty}^{\infty}\!\int_{-\infty}^{\infty} e^{-\iota\kappa(r_1+r)}\,d\xi\,d\eta = \pi\left[\frac{\iota\kappa}{2}\left(\frac{1}{\mathrm{R}}+\frac{1}{\mathrm{R}_1}\right)\right]^{-1} e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})};$$

to obtain the value of the second integral

$$r_1^2 = \xi^2+\eta^2+\zeta^2, \qquad r^2 = \xi^2+\eta^2+(\mathrm{R}_1+\mathrm{R}-\zeta)^2,$$

and observing that ξ_1, ζ_1 correspond to the lower limit of the integral

$$r_1 = \zeta_1+\frac{1}{2\zeta_1}(\xi^2+\eta^2) + \&\mathrm{c}.,$$

$$r = \mathrm{R}_1+\mathrm{R}-\zeta_1+\frac{1}{2(\mathrm{R}_1+\mathrm{R}-\zeta_1)}(\xi^2+\eta^2) + \&\mathrm{c}.,$$

therefore

$$\int_{\xi_1}\!\!\int e^{-\iota\kappa(r_1+r)}\,d\sigma = e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}\int_{\xi_1}\!\!\int e^{-\frac{\iota\kappa}{2}\left(\frac{1}{\zeta_1}+\frac{1}{\mathrm{R}_1+\mathrm{R}-\zeta_1}\right)(\xi^2+\eta^2)}\,d\xi\,d\eta;$$

hence, unless the radius of curvature of the projection of the curve of contact of the tangent cone with the surface on the plane perpendicular to OP is a small quantity of the order of ξ_1, the principal part of the above integral is given by

$$\kappa^{-2}e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}\int_{\kappa\xi_1}^{\infty}\!\int_{-\infty}^{\infty} e^{-\frac{\iota}{2\kappa}\left(\frac{1}{\zeta_1}+\frac{1}{\mathrm{R}_1+\mathrm{R}-\zeta_1}\right)(u^2+v^2)}\,du\,dv,$$

that is, the principal part of

$$\int_{\xi_1}\!\!\int e^{-\iota\kappa(r_1+r)}\,d\sigma$$

is given by

$$\pi\kappa^{-1}\iota^{-1/2}2^{1/2}e^{-\iota\kappa(\mathrm{R}_1+\mathrm{R})}\frac{\mathrm{R}_1\mathrm{R}}{\mathrm{R}_1+\mathrm{R}}\int_{u_0}^{\infty}e^{-1/2\pi\iota u^2}\,du,$$

where

$$u_0 = \left\{\frac{\kappa}{\pi}\left(\frac{1}{\zeta_1}+\frac{1}{\mathrm{R}_1+\mathrm{R}-\zeta_1}\right)\right\}^{1/2}\xi_1.$$

Therefore

$$\mathrm{I} = -\frac{2\pi}{\iota\kappa}\frac{\mathrm{R}_1\mathrm{R}}{\mathrm{R}_1+\mathrm{R}}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\left\{1-2^{-1/2}\iota^{1/2}\int_{u_0}^{\infty}e^{-1/2\pi\iota u^2}\,du\right\},$$

whence, writing

$$2^{-1/2}e^{\frac{\pi\iota}{4}}\int_{u_0}^{\infty}e^{-1/2\pi\iota u^2\,du} = \mathrm{L},$$

it follows that the principal parts of the components of the magnetic force due to the assumed surface distribution are given by

$$\alpha_0 = \frac{\iota\kappa^2}{\mathrm{V}}\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}}\frac{y-\eta_0}{\mathrm{R}}(1-\mathrm{L}),$$

$$\beta_0 = -\frac{\iota\kappa^2}{\mathrm{V}}\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}}\frac{x-\xi_0}{\mathrm{R}}(1-\mathrm{L}),$$

$$\gamma_0 = 0.$$

Now, α', β', γ', the principal parts of the components of the magnetic force due to the oscillator at the point O are given by

$$\alpha' = -\frac{\iota\kappa^2 y}{\mathrm{V}(\mathrm{R}_1+\mathrm{R})^2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})} = -\frac{\iota\kappa^2}{\mathrm{V}}\frac{y-\eta_0}{\mathrm{R}}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}/(\mathrm{R}_1+\mathrm{R}),$$

$$\beta' = \frac{\iota\kappa^2 x}{\mathrm{V}(\mathrm{R}_1+\mathrm{R})^2}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})} = \frac{\iota\kappa^2}{\mathrm{V}}\frac{x-\xi_0}{\mathrm{R}}e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}/(\mathrm{R}_1+\mathrm{R}),$$

$$\gamma' = 0,$$

for

$$\frac{x}{\mathrm{R}_1+\mathrm{R}} = \frac{x-\xi_0}{\mathrm{R}}, \qquad \frac{y}{\mathrm{R}_1+\mathrm{R}} = \frac{y-\eta_0}{\mathrm{R}};$$

therefore

$$\alpha_0 = -\alpha'(1-\mathrm{L}), \qquad \beta_0 = -\beta'(1-\mathrm{L}), \qquad \gamma_0 = 0,$$

and the principal parts of the components of the magnetic force at the point P due to the oscillator and the assumed surface distribution are given by

$$\alpha = \mathrm{L}\alpha', \qquad \beta = \mathrm{L}\beta', \qquad \gamma = 0,$$

where

$$\mathrm{L} = 2^{-1/2}e^{1/4\pi\iota}\int_{u_0}^{\infty}e^{-1/2\pi\iota u^2}\,du,$$

and

$$u_0 = \left[\frac{2}{\lambda}\left(\frac{1}{\mathrm{OM}} + \frac{1}{\mathrm{PM}}\right)\right]^{1/2} \mathrm{RM},$$

where λ is the wave-length of the oscillations and M is the foot of the perpendicular from R on OP.

When the point P is outside the tangent cone from O to the surface and near to the tangent cone and at a distance from O greater than OR it appears that the focal lines as determined above are situated one of them close to the surface of the obstacle and the other near to the source, hence the same analysis applies as in the immediately preceding case, and the components of the magnetic force at P due to the assumed surface distribution are given by

$$\alpha_0 = -\mathrm{L}\alpha', \qquad \beta_0 = -\mathrm{L}\beta', \qquad \gamma_0 = 0,$$

where

$$\mathrm{L} = \int^{-\xi_1}\!\!\int e^{-\iota\kappa(r_1+r)}\, d\sigma \Big/ \iint e^{-\iota\kappa(r_1+r)}\, d\sigma,$$

and in the integral in the denominator the limits are indefinitely extended, while in the integral in the numerator the upper limit is $-\xi_1$ where ξ_1 denotes the perpendicular from R on OP. Evaluating the above, the value of L is given by

$$\mathrm{L} = 2^{-1/2} e^{1/4\pi\iota} \int_{-\infty}^{-u_0} e^{-1/2\pi\iota u^2}\, du = 2^{-1/2} e^{1/4\pi\iota} \int_{u_0}^{\infty} e^{-1/2\pi\iota u^2}\, du,$$

where

$$u_0 = \left[\frac{2}{\lambda}\left(\frac{1}{\mathrm{OM}} + \frac{1}{\mathrm{PM}}\right)\right]^{1/2} \mathrm{RM},$$

and therefore the principal parts of the components of the magnetic force at the point P outside the tangent cone and near to it are given by

$$\alpha = (1-\mathrm{L})\,\alpha', \qquad \beta = (1-\mathrm{L})\,\beta', \qquad \gamma = 0,$$

where L has the value given above.

Considering now a point P on the surface of the obstacle near to the curve of contact of the tangent cone and on the side of the surface remote from O it appears that the principal parts of the components of the magnetic force due to the oscillator and the assumed surface distribution are $\mathrm{L}\alpha'$, $\mathrm{L}\beta'$, 0, and there will be a corresponding tangential electric force involving the factor L, therefore the surface condition is not satisfied at such points; the same result holds for points near the curve of contact on the side of the surface next O. It is therefore now necessary to determine what the effect of the electric current distribution on the surface which would reduce this unbalanced electric force to zero is. Taking first the case of a point P inside the tangent cone on the side of the surface of the obstacle remote from O and near to the boundary of the cone, with the same notation as above, the components of the magnetic force at P due to the electric current distribution necessary to balance the unbalanced tangential electric force in the neighbourhood of the curve of contact of the tangent cone are, compared with the components of the magnetic force at P due to the oscillator, of the order

$$\mathrm{K} = \frac{\iota\kappa}{2\pi\mathrm{R}} \iint e^{-\iota\kappa(\xi^2+\eta^2)/2\mathrm{R}}\, \mathrm{L}\, d\sigma,$$

where L varies from point to point of the surface.*

The integration with respect to η can be effected and it follows that

$$\mathrm{K} = \frac{\iota\kappa}{2\pi\mathrm{R}} \left(\frac{\iota\kappa}{2\mathrm{R}}\right)^{-1/2} \pi^{1/2} \int^{\xi_1} e^{-\iota\kappa\xi^2/2\mathrm{R}}\, \mathrm{L}\, d\xi.$$

Let ξ_1 denote the perpendicular from R on OP, ξ the perpendicular from a point P_1 on the surface on OP, then

$$\mathrm{L} = 2^{-1/2} e^{1/4\pi\iota} \int_{u_0}^{\infty} e^{-1/2\pi\iota u^2}\, du,$$

where

$$u_0 = \left(\frac{2}{\lambda \mathrm{P}_1\mathrm{M}_1}\right)^{1/2} \mathrm{RM}_1 = \left[\frac{2(\xi_1-\xi)^{3/2}}{\lambda(2\rho)^{1/2}}\right]^{1/2},$$

in which ρ denotes the radius of curvature of the normal section of the surface through OR, hence

$$\mathrm{L} = 2^{-3/4} e^{1/4\pi\iota} \pi^{-1/2} \kappa^{1/2} \rho^{-1/4} (\xi_1-\xi)^{3/4} \int_1^{\infty} e^{-1/2\iota\kappa(\xi_1-\xi)^{3/2} v^2 (2\rho)^{-1/2}}\, dv.$$

Therefore K is at most of the order

$$\left(\frac{\iota\kappa}{2\mathrm{R}}\right)^{1/2} \kappa^{1/2} \rho^{-1/4} \xi_1^{3/4} \int_1^{\infty} \left(\frac{\iota\kappa}{2\mathrm{R}} + \frac{3\iota\kappa v^2}{16(2\rho\xi_1)^{1/2}}\right)^{-1/2} e^{-1/2\iota\kappa\xi_1^{3/2} v^2 (2\rho)^{-1/2}}\, dv,$$

if

$$\left[\frac{\iota\kappa}{2\mathrm{R}} + \frac{3\iota\kappa v^2}{16(2\rho\xi_1)^{1/2}}\right]^{1/2} \xi_1$$

is of the same or higher order than unity, that is, provided R is of the same or higher order than $(\rho\xi_1)^{1/2}$, if $\kappa^{1/2}\xi_1$ is of the same or higher order than $(\rho\xi_1)^{1/4}$, that is, if ξ_1 is of the same or higher order than $\rho(\kappa\rho)^{-2/3}$. Hence, when R is of the same or higher order than $(\rho\xi_1)^{1/2}$, and ξ_1 is of the same or higher order than $\rho(\kappa\rho)^{-2/3}$, the quantity K is at most of the order

$$\kappa^{1/2} \xi_1^{3/4} \rho^{-1/4} \int_1^{\infty} e^{-1/2\iota\kappa\xi_1^{3/2}(2\rho)^{-1/2} v^2}\, dv,$$

which is at most of the order $\kappa^{-1/2}\xi_1^{-3/4}\rho^{1/4}$, for $\kappa\xi_1^{3/2}$ is of the same or higher order than

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* To simplify the analysis R_1 is taken infinite as the result is not affected provided the oscillator is at a distance from the surface of the obstacle comparable with a wave-length.

$\rho^{1/2}$; therefore, when R is of the same or higher order than $(\rho\xi_1)^{1/2}$, and ξ_1 is of higher order than $\rho(\kappa\rho)^{-2/3}$, K is of lower order than unity. When R is of higher order than $(\rho\xi_1)^{1/2}$, and ξ_1 is of the same or higher order than $\rho(\kappa\rho)^{-2/3}$, the quantity K is at most of the order

$$\kappa^{1/2}\xi_1\mathrm{R}^{-1/2}\int_1^\infty e^{-1/2\,\iota\kappa\xi_1{}^{3/2}(2\rho)^{-1/2}v^2}\,dv,$$

which is at most of the order $(\rho\xi_1)^{1/4}\mathrm{R}^{-1/2}$, and therefore, when R is of higher order than $(\rho\xi_1)^{1/2}$, and ξ_1 is of the same or higher order than $\rho(\kappa\rho)^{-2/3}$, K is of lower order than unity. Hence, at a point P inside the tangent cone from O to the surface of the obstacle, the effect of the electric current distribution which balances the unbalanced tangential electric force due to the oscillator and the assumed surface distribution, and is on the part of the surface inside the tangent cone and remote from O, is of lower order than that due to the oscillator, provided that the perpendicular distance ξ_1 of the point of contact R of the tangent from O to the surface in the plane of incidence is of the same or higher order than $\rho(\kappa\rho)^{-2/3}$, and that the distance of the point P from the surface of the obstacle measured along OP is of higher order than $\rho(\kappa\rho)^{-1/3}$, or provided that ξ_1 is of higher order than $\rho(\kappa\rho)^{-2/3}$, and the distance of P from the surface is of the same order as $\rho(\kappa\rho)^{-1/3}$. In a similar way it may be shown that the effect of the electric current distribution on the part of the surface of the obstacle next the oscillator which balances the unbalanced tangential electric force there, due to the oscillator and the assumed surface distribution, is of lower order than that due to the oscillator at a point P satisfying similar conditions to those in the previous case. Therefore, at a point P inside the tangent cone from O which satisfies the above conditions the principal parts of the components of the magnetic and electric forces are equal to the principal parts of the components of the magnetic and electric forces due to the oscillator and the assumed electric current surface distribution. The same result holds for points P outside the tangent cone similarly restricted; the region omitted in the neighbourhood of the tangent cone is that lying between the cone through O which cuts the surface of the obstacle in a curve inside the tangent cone on the side of the surface next O and at a distance from the curve of contact of the tangent cone of the order $\rho(\kappa\rho)^{-1/3}$ and a surface touching the obstacle along this surface and generated by straight lines in the plane of incidence at each point of the curve.

The principal parts of the magnetic and electric forces at points on the surface of the obstacle which are at a distance from the curve of contact of the tangent cone of order greater than $\rho(\kappa\rho)^{-1/3}$ can now be found. Let P be a point on the surface inside the tangent cone and on the side of the surface remote from O, and let OP cut the surface between O and P in the point Q, then PQ is of higher order than $\rho(\kappa\rho)^{-1/3}$ if P is at a distance along the surface from the curve of contact of the tangent cone which is of higher order than $\rho(\kappa\rho)^{-1/3}$, and therefore the effects at P of the surface distribution on the part of the surface inside the tangent cone and nearest to O which balances the unbalanced tangential electric force there, due to the oscillator and the assumed surface distribution, is of lower order than that due to the oscillator. Further, if M is the actual magnetic force at P tangential to the surface, the magnetic force at P due to the distribution in the neighbourhood of P is $\frac{1}{2}$M tangential to the surface; now it has been shown that the magnetic force tangential to the surface at P, due to the oscillator and the assumed surface distribution, is LM′, where M′ is the tangential magnetic force due to the oscillator alone and L has the value previously determined, therefore

$$\mathrm{M} = \tfrac{1}{2}\mathrm{M}+\mathrm{LM}', \quad \text{that is,} \quad \mathrm{M} = 2\mathrm{LM}'.$$

Hence, at points P inside the tangent cone on the side of the surface remote from O, the principal part of the magnetic force tangential to the surface is 2LM′, and the principal part of the electric force perpendicular to the surface is 2LE′, where M′, E′ are the principal parts of the magnetic force tangential to the surface and of the electric force perpendicular to the surface due to the oscillator. Similarly at points on the surface on the side nearest to the oscillator the principal part of the tangential magnetic force is $2(1-\mathrm{L})\,\mathrm{M}'$, and the principal part of the electric force perpendicular to the surface is $2(1-\mathrm{L})\,\mathrm{E}'$.

The preceding analysis can be adapted to the case of a conducting screen when the radii of curvature of the screen are large compared with the wave-length of the oscillations. The same assumed distribution as above on the two surfaces of the screen, viz., double the electric current distribution that would produce the magnetic force tangential to the screen on the side on which the waves are incident and a zero electric current distribution on the other side, give the important part of the asymptotic solution of the problem. The analysis only differs from the preceding owing to the presence of edges, and it will be proved that the effect of the actual distribution at the edge differs from that due to the oscillator and the assumed distribution by a quantity of lower order than the corresponding component in the waves due to the oscillator. At an edge the radius of curvature is zero, and therefore the distribution in the neighbourhood of the edge is the same as if the wave-length were indefinitely great; hence the electric current distribution in the immediate neighbourhood if the edge varies as $r_1^{-1/2}$, where r_1 is the distance along the screen perpendicular to the edge, that is, the electric current distribution in the neighbourhood of the edge is $(\kappa r_1)^{-1/2}$ multiplied by a quantity of the order of the magnetic force in the incident waves. The effect of this distribution in the neighbourhood of the edge is of the order

$$\mathrm{K}' = \kappa \iint \frac{e^{-\iota\kappa r}}{r\,(\kappa r_1)^{1/2}}\, d\mathrm{S}$$

at a point P compared with the corresponding component in the waves due to the oscillator. Let Q be the point on the edge such that QP is at right angles to the edge, and let QP make an angle θ with the line QR through Q in the screen perpendicular to the edge, then

$$\mathrm{K}' = \kappa \int \left(\frac{\iota\kappa}{2r}\right)^{-1/2} \frac{e^{-\iota\kappa r}}{r\,(\kappa r_1)^{1/2}}\, dr_1,$$

where r now denotes the distance of P from a point in the line QR; for points near to Q

$$r^2 = \mathrm{R}^2 + r_1^2 - 2r_1\mathrm{R}\cos\theta,$$

where R is the distance QP, and therefore the principal part of K′ is

$$\left(\frac{\iota}{2}\right)^{-1/2} \frac{e^{-\iota\kappa\mathrm{R}}}{\mathrm{R}^{1/2}} \int_0^\infty \frac{e^{\iota\kappa r_1\cos\vartheta}}{r_1^{1/2}}\, dr_1,$$

that is, K′ is a quantity of the order $(\kappa\mathrm{R})^{-1/2}$; hence at points which are at a distance from the nearest edge great compared to a wave-length the effect of the edges is negligible in comparison with the waves due to the oscillator. Therefore the principal parts of the components of the electric and magnetic forces at such points are equal to the principal parts of the electric and magnetic forces due to the assumed electric current distribution and the oscillator.

It may be verified that this agrees with the known solution of the problem of the semi-infinite conducting plane. Taking the case where the electric force in the incident waves is parallel to the edge, let the origin be in the edge, the axis of z along the edge, the axis of y perpendicular to the plane of the edge, and let the direction of the incident waves make an angle ϑ_1 with the conducting plane, then the components of the electric force in the incident waves are

$$\mathrm{X} = \mathrm{Y} = 0, \qquad \mathrm{Z} = e^{\iota\kappa(\mathrm{V}t + x\cos\vartheta_1 + y\sin\vartheta_1)}$$

and the components of the assumed electric current distribution on the upper face of the plane are

$$\bar{\alpha} = 0, \qquad \bar{\beta} = 0, \qquad \bar{\gamma} = 2\mathrm{V}^{-1} e^{\iota\kappa(\mathrm{V}t + x\cos\vartheta_1)},$$

and on the lower face

$$\bar{\alpha} = 0, \qquad \bar{\beta} = 0, \qquad \bar{\gamma} = 0.$$

Hence the components of the electric force due to the assumed distribution are

$$\mathrm{X} = 0, \qquad \mathrm{Y} = 0, \qquad \mathrm{Z} = -(2\pi)^{-1}\iota\kappa\sin\vartheta_1 \int_0^\infty \int_{-\infty}^\infty e^{\iota\kappa(\mathrm{V}t + x_1\cos\vartheta_1 - r)}\, r^{-1}\, d\mathrm{S},$$

where $(x_1, 0, z_1)$ is any point on the screen, r is the distance of the point P $(x, y, 0)$ from the point on the screen, and the integration is taken over the conducting plane. Now

$$r^2 = (x - x_1)^2 + y^2 + z_1^2 = \rho^2 + z_1^2,$$

where

$$\rho^2 = (x-x_1)^2+y^2,$$

therefore

$$Z = -(2\pi)^{-1}\iota\kappa \sin \vartheta_1 \int_0^\infty \int_{-\infty}^\infty e^{\iota\kappa(Vt+x_1 \cos \vartheta_1-\rho-{}^1\!/_2 z_1^2/\rho-)}\, \rho^{-1}\, dx_1\, dz_1,$$

whence the principal part of Z is given by the principal part of Z_0, where

$$Z_0 = -(2\pi)^{-1}\iota\kappa \sin \vartheta_1 \int_0^\infty (\iota\kappa/2\rho)^{-1/2} \rho^{-1}\, e^{\iota\kappa(Vt+x_1 \cos \vartheta_1-\rho)}\, dx_1\, ;$$

now $x_1 \cos \vartheta_1-\rho$ is stationary when

$$x = x_1-\rho \cos \vartheta_1, \qquad y = \pm\rho \sin \vartheta_1,$$

the upper sign corresponds to the case where P is on the positive side of the screen and the lower sign to the case where P is on the negative side of the screen. When P is on the negative side of the screen, let the line through P parallel to the direction of the waves cut the screen or the plane of the screen produced at the point Q $(\xi_1, 0, 0)$, then, writing $x_1 = \xi+\xi_1$ and R for the distance QP,

$$\rho^2 = R^2+2\xi R \cos \vartheta_1+\xi^2,$$
$$x_1 \cos \vartheta_1-\rho = \xi_1 \cos \vartheta_1-R-\tfrac{1}{2}\xi^2 \sin^2 \vartheta_1/R,$$

and the principal part of Z_0 is given by

$$-(2\pi)^{-1} (2\iota\kappa)^{1/2} R^{-1/2} \sin \vartheta_1\, e^{\iota\kappa(Vt-R+\xi_1 \cos \vartheta_1)} \int_{-\xi_1}^\infty e^{-1/2\,\iota\kappa\xi^2 \sin^2 \vartheta_1/R}\, d\xi,$$

that is, by

$$-2^{-1/2}\, e^{1/4\,\pi\iota}\, e^{\iota\kappa(Vt+x \cos \vartheta_1+y \sin \vartheta_1)} \int_{-u_0}^\infty e^{-1/2\,\pi\iota u^2}\, du,$$

where

$$u_0 = 2^{1/2} (\lambda R)^{-1/2}\, \xi_1 \sin \vartheta_1,$$

and therefore the electric force at a point on the negative side of the screen is given by

$$Z = 2^{-1/2}\, e^{1/4\,\pi\iota}\, e^{\iota\kappa(Vt+x \cos \vartheta_1+y \sin \vartheta_1)} \int_{-\infty}^{-u_0} e^{-1/2\,\pi\iota u^2}\, du.$$

When the point P is on the positive side of the screen, the principal part of the electric force due to the assumed distribution is found in the same way to be

$$-2^{-1/2}\, e^{1/4\,\pi\iota}\, e^{\iota\kappa(Vt+x \cos \vartheta_1-y \sin \vartheta_1)} \int_{-u_0}^\infty e^{-1/2\,\pi\iota u^2}\, du,$$

where the point Q $(\xi_1, 0)$ is the point where the line through P in the plane perpendicular to the edge making an angle $\pi-\vartheta_1$, with the plane of the screen meets it and therefore the electric force at a point P on the positive side of the screen is given by

$$Z = e^{\iota\kappa(Vt+x \cos \vartheta_1+y \sin \vartheta_1)}-2^{-1/2}\, e^{1/4\,\pi\iota}\, e^{\iota\kappa(Vt+x \cos \vartheta_1-y \sin \vartheta_1)} \int_{-u_0}^\infty e^{-1/2\,\pi\iota u^2}\, du.$$

When the point P is at a distance from the edge of the screen great compared with a wave-length these expressions are sensibly the same as those of the known accurate solution, as u_0 is very large unless the line OP makes an angle which is very small with the line through O making an angle $\pi+\vartheta_1$ with the plane of the screen, or with the line through O making an angle $\pi-\vartheta_1$ with the plane of the screen, and in these cases the results are the same.

When the magnetic force in the incident waves is parallel to the edge of the conducting screen

$$\alpha = 0, \qquad \beta = 0, \qquad \gamma = e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1+y\sin\vartheta_1)}$$

in the incident waves, and the assumed electric current distribution on the positive side of the screen is given by

$$\bar{\alpha} = 2e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1)}, \qquad \bar{\beta} = 0, \qquad \bar{\gamma} = 0,$$

and on the negative side of the screen by

$$\bar{\alpha} = 0, \qquad \bar{\beta} = 0, \qquad \bar{\gamma} = 0,$$

whence the components of the magnetic force due to the assumed surface distribution at a point P (x, y, z) are

$$\alpha = 0, \qquad \beta = 0, \qquad \gamma = -\frac{1}{2\pi}\int_0^\infty\int_{-\infty}^\infty \frac{\partial}{\partial y}\frac{e^{\iota\kappa(\mathrm{V}t+x_1\cos\vartheta_1-r)}}{r}\,dx_1,\, dz_1,$$

and, by a similar analysis to that in the preceding case, when the point P is on the negative side of the screen

$$\gamma = -e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1+y\sin\vartheta_1)}\,2^{-1/2}\,e^{1/4\pi\iota}\int_{-u_0}^\infty e^{-1/2\pi\iota u^2}\,du,$$

where

$$u_0 = 2^{1/2}(\lambda\mathrm{R})^{-1/2}\,\xi_1\sin\vartheta_1,$$

ξ_1 having the same meaning as above, and therefore the resultant magnetic force on the negative side of the screen is given by

$$e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1+y\sin\vartheta_1)}\,2^{-1/2}\,e^{1/4\pi\iota}\int_{-\infty}^{-u_0} e^{-1/2\pi\iota u^2}\,du.$$

When the point P is on the positive side of the screen the magnetic force is given by

$$e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1+y\sin\vartheta_1)}+e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1-y\sin\vartheta_1)}\,2^{-1/2}\,e^{1/4\pi\iota}\int_{-u_0}^\infty e^{-1/2\pi\iota u^2}\,du,$$

these results again agreeing with the known accurate solution when the point P is at a distance from the edge great compared with a wave-length. Again, when the conducting screen is an infinite plane with a slit in it of breadth $2d$ bounded by parallel edges, taking the origin in the middle line of the slit, this line being the axis of z, and the straight line in the plane of the screen perpendicular to it the axis of x, the same analysis shows that, when the electric force in the incident waves is parallel to the edges of the slit and is given by

$$\mathrm{Z} = e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1+y\sin\vartheta_1)}$$

the electric force at a point P on the negative side of the screen is given by

$$\mathrm{Z} = e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1+y\sin\vartheta_1)}\,2^{-1/2}\,e^{1/4\,\pi\iota}\int_{-u_0}^{-u_1} e^{-1/2\,\pi\iota u^2}\,du,$$

where

$$u_0 = 2^{1/2}(\lambda\mathrm{R})^{-1/2}(\xi_0+d)\sin\vartheta_1,$$
$$u_1 = 2^{1/2}(\lambda\mathrm{R})^{-1/2}(\xi_1-d)\sin\vartheta_1,$$

and $(\xi_1, 0)$ are the co-ordinates of the point Q where the straight line through P parallel to the direction of the incident waves cuts the plane of the screen. The electric force at a point P on the positive side of the screen is given by

$$\mathrm{Z} = e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1+y\sin\vartheta_1)} - e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1-y\sin\vartheta_1)} + e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1-y\sin\vartheta_1)}\,2^{-1/2}\,e^{1/4\,\pi\iota}\int_{-u_0}^{-u_1} e^{-1/2\,\pi\iota u^2}\,du,$$

where u_0, u_1 are the same as above and ξ_1, 0 are the co-ordinates of the point where the straight line through P in a plane perpendicular to the edges making an angle $\pi-\vartheta_1$ with the plane of the screen cuts the screen.

When the magnetic force in the incident waves is parallel to the edges and is given by

$$\gamma = e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1+y\sin\vartheta_1)},$$

the magnetic force at a point P on the negative side of the screen is given by

$$\gamma = e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1+y\sin\vartheta_1)}\,2^{-1/2}\,e^{1/4\pi\iota}\int_{-u_0}^{-u_1} e^{-1/2\pi\iota u^2}\,du,$$

and at a point P on the positive side of the screen by

$$\gamma = e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1+y\sin\vartheta_1)} + e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1-y\sin\vartheta_1)} - e^{\iota\kappa(\mathrm{V}t+x\cos\vartheta_1-y\sin\vartheta_1)}\,2^{-1/2}e^{1/4\,\pi\iota}\int_{-u_0}^{-u_1} e^{-1/2\,\pi\iota u^2}\,du,$$

where u_0, u_1 in each case have the same meanings as in the corresponding case in the preceding. The discussion of these results is similar to that given by GILBERT[*] for an absorbing screen.

The corresponding results for a plane conducting screen in which there is any number of parallel slits can be written down immediately, provided the breadth of the portion of the screen between every two consecutive slits is great compared with a wave-length; when the number of conducting strips in the breadth of a wave-length is large the effect of the edges becomes the most important.

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[*] ‘Memoires couronnés de l'Acad. de Bruxelles,’ t. xxxi., p. 29, 1863.

As a further example, the case of an infinite plane conducting screen with a circular aperture of radius a will be worked out. As above, let a straight line through the centre of the aperture perpendicular to the plane of the screen be the axis of y, the axes of x and z being in the plane of the screen, and let the incident waves be given by

$$\alpha = 0, \qquad \beta = 0, \qquad \gamma = e^{\iota\kappa(\mathrm{V}t+y)},$$

the magnetic force being parallel to the plane of the screen and the direction of the waves perpendicular to it; then the components of the magnetic force due to the distribution to be assumed over the screen are

$$\alpha_0 = 0, \qquad \beta_0 = \frac{1}{2\pi}e^{\iota\kappa\mathrm{V}t}\iint\frac{\partial}{\partial z}\frac{e^{-\iota\kappa r}}{r}\,d\mathrm{S}, \qquad \gamma_0 = -\frac{1}{2\pi}e^{\iota\kappa\mathrm{V}t}\iint\frac{\partial}{\partial y}\frac{e^{-\iota\kappa r}}{r}\,d\mathrm{S},$$

where r is the distance of the point from a point in the plane of the screen and the integrals are taken over the conducting part of it. Transforming to cylindrical co-ordinates

$$r^2 = y^2+\rho^2+\rho_1^{\,2}-2\rho\rho_1\cos(\phi_1-\phi),$$

where the co-ordinates of the point P are (ρ, ϕ, y) and of a point in the plane $(\rho_1, \phi_1, 0)$. The principal parts of the integrals are contributed by the elements in the neighbourhood of the point for which r is stationary, that is, when

$$\phi_1 = \phi, \qquad \rho_1 = \rho,$$

and then, provided ρ is not small,

$$\iint\frac{e^{-\iota\kappa r}}{r}\,d\mathrm{S} = \int_a^\infty\int_0^{2\pi}\frac{e^{-\iota\kappa r}}{r}\rho_1\,d\rho_1\,d\phi_1 = \pi^{1/2}\left(\frac{\iota\kappa\rho}{2}\right)^{-1/2}\int_a^\infty e^{-\iota\kappa r_1}r_1^{\,-1/2}\rho_1^{\,1/2}\,d\rho_1,$$

where $r_1^{\,2} = y^2+(\rho_1+\rho)^2$.

For a point on the negative side of the screen $y = -d$, and writing $\rho_1 = \rho+\rho'$, the principal part of the integral $\iint e^{-\iota\kappa r}r^{-1}\,d\mathrm{S}$ is given by

$$(2\pi)^{1/2}(\iota\kappa\rho)^{-1/2}\int_{a-\rho}^{\infty}e^{-\iota\kappa d-1/2\,\iota\kappa\rho'^2/d}\,d^{-1/2}(\rho+\rho')^{1/2}\,d\rho',$$

that is, provided $\kappa\rho^2$ is great compared with d, by

$$2\pi(\iota\kappa)^{-1}2^{-1/2}e^{1/4\,\pi\iota}e^{\iota\kappa y}\int_{u_0}^{\infty}e^{-1/2\,\pi\iota u^2}\,du,$$

where $u_0 = 2^{1/2}(\lambda d)^{-1/2}(a-\rho)$.

Hence, at a point P on the negative side of screen, the principal parts of the components of the magnetic force due to the assumed distribution are

$$\alpha_0 = 0,$$

$$\beta_0 = (\iota\kappa)^{-1} 2^{-1/2} e^{1/4\pi\iota} e^{\iota\kappa(\mathrm{V}t+y)} \frac{\partial}{\partial z} \int_{u_0}^{\infty} e^{-1/2\pi\iota u^2}\, du,$$

$$\gamma_0 = -2^{-1/2} e^{1/4\pi\iota} e^{\iota\kappa(\mathrm{V}t+y)} \int_{u_0}^{\infty} e^{-1/2\pi\iota u^2}\, du,$$

and therefore the principal parts of the components of the magnetic force at the point P are

$$\alpha = 0, \qquad \beta = 0, \qquad \gamma = 2^{-1/2} e^{1/4\pi\iota} e^{\iota\kappa(\mathrm{V}t+y)} \int_{-\infty}^{u_0} e^{-1/4\pi\iota u^2}\, du,$$

for β_0 is of order $(\kappa d)^{-1/2}$ compared with the magnetic force in the incident waves. When ρ is small compared with a,

$$\int_a^{\infty}\int_0^{2\pi} e^{-\iota\kappa r} r^{-1} \rho_1\, d\rho_1\, d\phi_1 = d^{-1} \int_a^{\infty}\int_0^{2\pi} e^{-\iota\kappa d + \iota\kappa\rho\rho_1 d^{-1}\cos(\phi_1-\phi) - 1/2\iota\kappa\rho_1^2/d} \rho_1\, d\rho_1\, d\phi_1,$$

that is, the principal part only being retained,

$$\iint e^{-\iota\kappa r} r^{-1}\, d\mathrm{S} = 2\pi d^{-1} e^{\iota\kappa y} \int_a^{\infty} e^{-1/2\iota\kappa\rho_1^2/d} \mathrm{J}_0(\kappa\rho\rho_1/d)\, \rho_1\, d\rho_1,$$

or

$$\iint e^{-\iota\kappa r} r^{-1}\, d\mathrm{S} = 2\pi(\iota\kappa)^{-1} e^{\iota\kappa y} - 2\pi d^{-1} e^{\iota\kappa y} \int_0^{a} e^{-1/2\iota\kappa\rho_1^2/d} \mathrm{J}_0(\kappa\rho\rho_1/d)\, \rho_1\, d\rho_1.$$

Therefore, when ρ is small, the principal parts of the components of the magnetic force at a point near the axis of y on the negative side of the screen are given by

$$\alpha = 0,$$

$$\beta = \kappa z \rho^{-1} d^{-2} e^{\iota\kappa(\mathrm{V}t+y)} \int_0^{a} e^{-1/2\iota\kappa\rho_1^2/d} \mathrm{J}_1(\kappa\rho\rho_1/d)\, \rho_1^2\, d\rho_1,$$

$$\gamma = \iota\kappa d^{-1} e^{\iota\kappa(\mathrm{V}t+y)} \int_0^{a} e^{-1/2\iota\kappa\rho_1^2/d} \mathrm{J}_0(\kappa\rho\rho_1/d)\, \rho_1\, d\rho_1.$$

As an example illustrating the phenomenon of the bright spot, the case of a conducting circular disc of radius a with a Hertzian oscillator on the axis will be treated. Let the axis of the disc be the axis of z, the origin being at the oscillator and the equation of the plane of the disc $z = z_0$; the components of the magnetic force due to the oscillator are

$$\alpha' = \frac{\kappa}{\mathrm{V}} \frac{\partial}{\partial\eta} \frac{e^{\iota\kappa(\mathrm{V}t-r_1)}}{r_1}, \qquad \beta' = -\frac{\kappa}{\mathrm{V}} \frac{\partial}{\partial\xi} \frac{e^{\iota\kappa(\mathrm{V}t-r_1)}}{r_1}. \qquad \gamma' = 0,$$

where ξ, η, ζ are the co-ordinates of any point and

$$r_1^2 = \xi^2 + \eta^2 + \zeta^2,$$

and the components of the electric current distribution to be assumed on the lower side of the disc are

$$\bar{\alpha} = -\frac{2\kappa}{\mathrm{V}}\frac{\partial}{\partial\xi}\frac{e^{\iota\kappa(\mathrm{V}t-r_1)}}{r_1}, \qquad \bar{\beta} = -\frac{2\kappa}{\mathrm{V}}\frac{\partial}{\partial\eta}\frac{e^{\iota\kappa(\mathrm{V}t-r_1)}}{r_1}, \qquad \bar{\gamma} = 0,$$

where ξ, η, z_0 are now the co-ordinates of a point on the disc. Therefore the components of the magnetic force at a point x, y, z due to this distribution are

$$\alpha = \frac{\kappa}{2\pi\mathrm{V}}\iint \frac{\partial}{\partial z}\frac{1}{r}\frac{\partial}{\partial\xi}\frac{1}{r_1}\, e^{\iota\kappa(\mathrm{V}t-r_1-r)}\, d\mathrm{S},$$

$$\beta = -\frac{\kappa}{2\pi\mathrm{V}}\iint \frac{\partial}{\partial z}\frac{1}{r}\frac{\partial}{\partial\eta}\frac{1}{r_1}\, e^{\iota\kappa(\mathrm{V}t-r_1-r)}\, d\mathrm{S},$$

$$\gamma = 0,$$

where

$$r^2 = (x-\xi)^2+(y-\eta)^2+(z-z_0)^2,$$

writing

$$x = \rho\cos\phi, \qquad y = \rho\sin\phi, \qquad \xi = \rho_1\cos\phi_1, \qquad \eta = \rho_1\sin\phi_1,$$

the resultant magnetic force due to the distribution is

$$\beta\cos\phi-\alpha\sin\phi = \frac{\iota\kappa^2}{2\pi\mathrm{V}}\frac{\partial}{\partial z}\int_0^a\int_0^{2\pi}\sin(\phi_1+\phi)\,\frac{\rho_1^{\,2}}{r_1^{\,2}r}\,e^{\iota\kappa(\mathrm{V}t-r_1-r)}\,d\rho_1\,d\phi_1,$$

where

$$r^2 = (z-z_0)^2+\rho^2+\rho_1^{\,2}-2\rho\rho_1\cos(\phi_1-\phi), \qquad r_1^{\,2} = z_0^{\,2}+\rho_1^{\,2}.$$

Now r_1+r is stationary when

$$\phi_1 = \phi, \qquad (\rho-\rho_1)/r = \rho_1/r_1,$$

and, writing R, R_1 for the corresponding values of r, r_1 and $\sin\vartheta = \rho_1/r_1$, the principal value of the magnetic force is given by

$$\frac{\iota\kappa^2}{2\pi\mathrm{V}}\left(\frac{\iota\kappa}{2}\right)^{-1/2}\pi^{1/2}\sin 2\phi\,\frac{\partial}{\partial z}\,e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}\int_{-\rho_1}^{a-\rho_1}\rho^{-1/2}\rho_1^{\,3/2}\mathrm{R}_1^{\,-2}\mathrm{R}^{-1/2}\,e^{-1/2\,\iota\kappa\cos^2\vartheta\,(\mathrm{R}_1^{\,-1}+\mathrm{R}^{-1})\rho'^2}\,d\rho'.$$

When $a-\rho_1$ is not small, the principal value of the above expression is

$$\frac{\kappa}{\mathrm{V}}\frac{\partial}{\partial z}\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}}\sin 2\phi\tan\vartheta,$$

that is, when the point x, y, z is on the upper side of the disc

$$-\frac{\iota\kappa^2}{\mathrm{V}}\sin\vartheta\sin 2\phi\,\frac{e^{\iota\kappa(\mathrm{V}t-\mathrm{R}_1-\mathrm{R})}}{\mathrm{R}_1+\mathrm{R}},$$

which is the value, with the opposite sign, of the resultant magnetic force due to the oscillator, and therefore at these points the principal part of the magnetic force vanishes. When $a-\rho_1$ is small, the principal value of the magnetic force due to the assumed distribution is

$$\frac{\kappa}{V} 2^{-1/2} e^{1/4\pi\iota} \frac{\partial}{\partial z} \frac{e^{\iota\kappa(Vt-R_1-R)}}{R_1+R} \sin 2\phi \tan \vartheta \int_{-\infty}^{u_0} e^{-1/2\pi\iota u^2} du,$$

where

$$u_0 = \left[\frac{2}{\lambda}\left(\frac{1}{R_1}+\frac{1}{R}\right)\right]^{1/2} (a-\rho_1) \cos \vartheta,$$

ρ_1 being the distance from the axis of the point where the line OP cuts the plane of the disc; whence, if the point P (x, y, z) is on the upper side of the disc, the above has the value

$$-\frac{\iota\kappa^2}{V} \sin \vartheta \sin 2\phi \frac{e^{\iota\kappa(Vt-R_1-R)}}{R_1+R} 2^{-1/2} e^{1/4\pi\iota} \int_{-\infty}^{u_0} e^{-1/2\pi\iota u^2} du,$$

and therefore the resultant magnetic force at the point P is

$$\frac{\iota\kappa^2}{V} \sin \vartheta \sin 2\phi \frac{e^{\iota\kappa(Vt-R_1-R)}}{R_1+R} 2^{-1/2} e^{1/4\pi\iota} \int_{u_0}^{\infty} e^{-1/2\pi\iota u^2} du.$$

In the immediately preceding investigation it has been assumed that ρ is not small; when ρ is small and $z > z_0$,

$$r = z-z_0+\tfrac{1}{2}\rho_1^2/(z-z_0)-\{\rho\rho_1 \cos(\phi_1-\phi)\}/(z-z_0)\ldots,$$
$$r_1 = z_0+\tfrac{1}{2}\rho_1^2/z_0,$$

and

$$\beta \cos \phi-\alpha \sin \phi$$
$$= \frac{\iota\kappa^2}{2\pi V} \frac{\partial}{\partial z} \int_0^a \int_0^{2\pi} \sin(\phi_1+\phi)\rho_1^2 r_1^{-2} r^{-1} e^{\iota\kappa\{Vt-z+[\rho\rho_1 \cos(\phi_1-\phi)]/(z-z_0)-1/2\rho_1^2 [1/z_0+1/(z-z_0)\}} d\rho_1\, d\phi_1,$$

that is

$$\beta \cos \phi-\alpha \sin \phi$$
$$= \frac{\iota\kappa^2}{2\pi V} \frac{\partial}{\partial z} \int_0^a 2\pi\iota \sin 2\phi\, e^{\iota\kappa\{Vt-z-1/2\rho_1^2[1/z_0+1/(z-z_0)]\}} \rho_1^2 (z-z_0)^{-1} z_0^{-2} J_1\{\kappa\rho\rho_1/(z-z_0)\}\, d\rho_1,$$

or

$$\beta \cos \phi-\alpha \sin \phi = \frac{\iota\kappa^3}{V} e^{\iota\kappa(Vt-z)} \sin 2\phi \,.\, z_0^{-2}(z-z_0)^{-1} \int_0^a e^{-1/2\iota\kappa\rho_1^2[1/z_0+1/(z-z_0)]} J_1\{\kappa\rho\rho_1/(z-z_0)\}\rho_1^2\, d\rho_1.$$

This quantity tends to zero with ρ, but increases rapidly as ρ increases from zero, thus the resultant magnetic and electric forces at a point on the axis have the same principal values as if there were no disc, and diminish rapidly in the neighbourhood of the axis. Similar results hold for any surface of revolution or for a cylindrical obstacle with a line source parallel to its axis.

A Perfectly Absorbing Obstacle.

When the obstacle is perfectly absorbing, the conditions to be satisfied at its surface are that the electric and magnetic forces in the incident waves are annihilated there. This requires an electric current distribution on the surface which will produce the magnetic force tangential to the surface of the obstacle in the incident waves and a magnetic current distribution on the surface which will produce the electric force tangential to the surface of the obstacle in the incident waves. As in the former case, it is sufficient to discuss the case of a Hertzian oscillator at a point outside the obstacle. Taking the origin of co-ordinates at the oscillator and the axis of z coincident with the axis of the oscillator, the components of the electric and magnetic forces at a point ξ, η, ζ due to the oscillator are given by

$$\mathrm{X}' = -\iota\frac{\partial^2}{\partial\xi\,\partial\zeta}\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1, \qquad \mathrm{Y}' = -\iota\frac{\partial^2}{\partial\eta\,\partial\zeta}\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1, \qquad \mathrm{Z}' = \iota\left(\frac{\partial^2}{\partial\xi^2}+\frac{\partial^2}{\partial\eta^2}\right)e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1\,;$$

$$\alpha' = \frac{\kappa}{\mathrm{V}}\frac{\partial}{\partial\eta}\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1, \qquad \beta' = -\frac{\kappa}{\mathrm{V}}\frac{\partial}{\partial\xi}\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1, \qquad \gamma' = 0,$$

where

$$r_1^{\,2} = \xi^2+\eta^2+\zeta^2,$$

and therefore the components of the electric current and magnetic current distributions to be assumed on the portion of the surface of the obstacle on which waves are incident are given by

$$(m\gamma'-n\beta'), \qquad (n\alpha'-l\gamma'), \qquad (l\beta'-m\alpha')\,;$$
$$(m\mathrm{Z}'-n\mathrm{Y}'), \qquad (n\mathrm{X}'-l\mathrm{Z}'), \qquad (l\mathrm{Y}'-m\mathrm{X}')\,;$$

where l, m, n are the direction cosines of the normal to the surface, these are equivalent to

$$-\iota\kappa^2 n\xi e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1^{\,2}\mathrm{V}, \qquad -\iota\kappa^2 n\eta e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1^{\,2}\mathrm{V}, \qquad \iota\kappa^2(l\xi+m\eta)\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1^{\,2}\mathrm{V}\,;$$

$$-\iota\kappa^2\{m(\xi^2+\eta^2)+n\eta\zeta\}\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1^{\,2}, \qquad \iota\kappa^2\{n\zeta\xi+l(\xi^2+\eta^2)\}\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1^{\,2},$$
$$\iota\kappa^2(l\eta\zeta-m\zeta\xi)\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1^{\,2},$$

where only the principal parts have been retained; writing

$$\xi_1/r_1 = \lambda_1, \qquad \eta_1/r_1 = \mu_1, \qquad \zeta/r_1 = \nu_1,$$

these become

$$-\iota\kappa^2 n\lambda_1\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1\mathrm{V}, \qquad -\iota\kappa^2 n\mu_1\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1\mathrm{V}, \qquad \iota\kappa^2(l\lambda_1+m\mu_1)\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1,$$

$$-\iota\kappa^2\{m(\lambda_1^{\,2}+\mu_1^{\,2})+n\mu_1\nu_1\}\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1, \qquad \iota\kappa^2\{n\nu_1\lambda_1+l(\lambda_1^{\,2}+\mu_1^{\,2})\}\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1,$$
$$\iota\kappa^2(l\mu_1-m\lambda_1)\,\nu_1\,e^{\iota\kappa(\mathrm{V}t-r_1)}/r_1.$$

The components of the electric force at the point x, y, z due to this distribution are

$$\begin{aligned} \mathrm{X} = &-\frac{\mathrm{V}}{4\pi\iota\kappa}\iint\left[\frac{\partial^2}{\partial x^2}n\lambda_1+\frac{\partial^2}{\partial x\,\partial y}n\mu_1-\frac{\partial^2}{\partial x\,\partial z}(l\lambda_1+m\mu_1)-\frac{1}{\mathrm{V}^2}\frac{\partial^2}{\partial t^2}n\lambda_1\right]\frac{\iota\kappa^2}{rr_1\mathrm{V}}e^{\iota\kappa(\mathrm{V}t-r_1-r)}\,d\mathrm{S} \\ &-\frac{1}{4\pi}\iint\left[-\frac{\partial}{\partial y}\nu_1(l\mu_1-m\lambda_1)+\frac{\partial}{\partial z}\{n\nu_1\lambda_1+l(\lambda_1^2+\mu_1^2)\}\right]\frac{\iota\kappa^2}{rr_1}e^{\iota\kappa(\mathrm{V}t-r_1-r)}\,d\mathrm{S}, \end{aligned}$$

$$\begin{aligned} \mathrm{Y} = &-\frac{\mathrm{V}}{4\pi\iota\kappa}\iint\left[\frac{\partial^2}{\partial x\,\partial y}n\lambda_1+\frac{\partial^2}{\partial y^2}n\mu_1-\frac{\partial^2}{\partial y\,\partial z}(l\lambda_1+m\mu_1)-\frac{1}{\mathrm{V}^2}\frac{\partial^2}{\partial t^2}n\mu_1\right]\frac{\iota\kappa^2}{rr_1\mathrm{V}}e^{\iota\kappa(\mathrm{V}t-r_1-r)}\,d\mathrm{S} \\ &-\frac{1}{4\pi}\iint\left[\frac{\partial}{\partial z}\{m(\lambda_1^2+\mu_1^2)+n\mu_1\nu_1\}+\frac{\partial}{\partial x}\nu_1(l\mu_1-m\lambda_1)\right]\frac{\iota\kappa^2}{rr_1}e^{\iota\kappa(\mathrm{V}t-r_1-r)}\,d\mathrm{S}, \end{aligned}$$

$$\begin{aligned} \mathrm{Z} = &-\frac{\mathrm{V}}{4\pi\iota\kappa}\iint\left[\frac{\partial^2}{\partial x\,\partial z}n\lambda_1+\frac{\partial^2}{\partial y\,\partial z}n\mu_1-\frac{\partial^2}{\partial z^2}(l\lambda_1+m\mu_1)+\frac{1}{\mathrm{V}^2}\frac{\partial^2}{\partial t^2}(l\lambda_1+m\mu_1)\right]\frac{\iota\kappa^2}{rr_1\mathrm{V}}e^{\iota\kappa(\mathrm{V}t-r_1-r)}\,d\mathrm{S} \\ &-\frac{1}{4\pi}\iint\left[-\frac{\partial}{\partial x}\{n\nu_1\lambda_1+l(\lambda_1^2+\mu_1^2)\}-\frac{\partial}{\partial y}\{m(\lambda_1^2+\mu_1^2)+n\mu_1\nu_1\}\right]\frac{\iota\kappa^2}{rr_1}e^{\iota\kappa(\mathrm{V}t-r_1-r)}\,d\mathrm{S}; \end{aligned}$$

retaining only the principal parts and writing

$$(x-\xi)/r = \lambda_2, \qquad (y-\eta)/r = \mu_2, \qquad (z-\zeta)/r = \nu_2,$$

these are equivalent to

$$\begin{aligned} \mathrm{X} = \frac{\kappa^3}{4\pi}\iint[&-\nu_2(\lambda_1+\lambda_2)(l\lambda_1+m\mu_1+n\nu_1)+n\lambda_2(\lambda_1\lambda_2+\mu_1\mu_2+\nu_1\nu_2)-n\lambda_1 \\ &+(l\mu_1-m\lambda_1)(\mu_2\nu_1-\mu_1\nu_2)]\frac{e^{\iota\kappa(\mathrm{V}t-r_1-r)}}{r_1r}\,d\mathrm{S}, \end{aligned}$$

$$\begin{aligned} \mathrm{Y} = \frac{\kappa^3}{4\pi}\iint[&-\nu_2(\mu_1+\mu_2)(l\lambda_1+m\mu_1+n\nu_1)+n\mu_2(\lambda_1\lambda_2+\mu_1\mu_2+\nu_1\nu_2)-n\mu_1 \\ &+(l\mu_1-m\lambda_1)(\nu_2\lambda_1-\nu_1\lambda_2)]\frac{e^{\iota\kappa(\mathrm{V}t-r_1-r)}}{r_1r}\,d\mathrm{S}, \end{aligned}$$

$$\begin{aligned} \mathrm{Z} = \frac{\kappa^3}{4\pi}\iint[&\{\lambda_2(\lambda_1+\lambda_2)+\mu_2(\mu_1+\mu_2)\}(l\lambda_1+m\mu_1+n\nu_1)+n\nu_2(\lambda_1\lambda_2+\mu_1\mu_2+\nu_1\nu_2)-n\nu_1 \\ &+(l\mu_1-m\lambda_1)(\lambda_2\mu_1-\mu_2\lambda_1)]\frac{e^{\iota\kappa(\mathrm{V}t-r_1-r)}}{r_1r}\,d\mathrm{S}. \end{aligned}$$

The principal parts of these integrals are contributed by the elements in the neighbourhood of the points for which r_1+r is stationary, and, as in the case of the conducting obstacle, there are the two cases when the point Q, for which $r+r_1$ is stationary, is on the straight line OP and when the lines OQ, QP make equal angles with the normal to the surface at Q. In the first case, the point P is on the side of the obstacle remote from the oscillator and at the point Q

$$\lambda_2 = \lambda_1, \qquad \mu_2 = \mu_1, \qquad \nu_2 = \nu_1,$$

and the principal parts of the components of the electric force due to the distribution are

$$X = -\frac{\kappa^3\nu_1\lambda_1}{2\pi}\iint (l\lambda_1+m\mu_1+n\nu_1)\,\frac{e^{\iota\kappa(Vt-r_1-r)}}{rr_1}\,dS,$$

$$Y = -\frac{\kappa^3\nu_1\mu_1}{2\pi}\iint (l\lambda_1+m\mu_1+n\nu_1)\,\frac{e^{\iota\kappa(Vt-r_1-r)}}{rr_1}\,dS,$$

$$Z = \frac{\kappa^3(\lambda_1^2+\mu_1^2)}{2\pi}\iint (l\lambda_1+m\mu_1+n\nu_1)\,\frac{e^{\iota\kappa(Vt-r_1-r)}}{rr_1}\,dS,$$

that is

$$X = \frac{\kappa^3\nu_1\lambda_1}{2\pi R_1 R}\iint e^{\iota\kappa(Vt-r_1-r)}\,d\sigma,$$

$$Y = \frac{\kappa^3\nu_1\mu_1}{2\pi R_1 R}\iint e^{\iota\kappa(Vt-r_1-r)}\,d\sigma,$$

$$Z = -\frac{\kappa^3(\lambda_1^2+\mu_1^2)}{2\pi R_1 R}\iint e^{\iota\kappa(Vt-r_1-r)}\,d\sigma,$$

where $OP = R_1$, $QP = R$, and $d\sigma$ is the projection of an element of the surface on a plane perpendicular to OP.

The integral involved in these expressions has been already evaluated and gives when the point Q is not near to the curve of contact of the tangent cone from O to the surface of the obstacle

$$X = -\iota\kappa^2\nu_1\lambda_1\,e^{\iota\kappa(Vt-R_1-R)}/(R_1+R),$$

$$Y = -\iota\kappa^2\nu_1\mu_1\,e^{\iota\kappa(Vt-R_1-R)}/(R_1+R),$$

$$Z = \iota\kappa^2(\lambda_1^2+\mu_1^2)\,e^{\iota\kappa(Vt-R_1-R)}/(R_1+R);$$

that is

$$X = -X', \qquad Y = -Y', \qquad Z = -Z',$$

and therefore at points inside the boundary of the geometrical shadow and not close to it the principal part of the electric force vanishes and consequently the principal part of the magnetic force vanishes. In the second case when OQ, QP made equal angles with the normal at Q the coefficients

$$-\nu_2(\lambda_1+\lambda_2)(l\lambda_1+m\mu_1+n\nu_1)+n\lambda_2(\lambda_1\lambda_2+\mu_1\mu_2+\nu_1\nu_2)-n\lambda_1+(l\mu_1-m\lambda_1)(\mu_2\nu_1-\mu_1\nu_2),$$

$$-\nu_2(\mu_1+\mu_2)(l\lambda_1+m\mu_1+n\nu_1)+n\mu_2(\lambda_1\lambda_2+\mu_1\mu_2+\nu_1\nu_2)-n\mu_1+(l\mu_1-m\lambda_1)(\nu_2\lambda_1-\nu_1\lambda_2),$$

$$\{\lambda_2(\lambda_1+\lambda_2)+\mu_2(\mu_1+\mu_2)\}(l\lambda_1+m\mu_1+n\nu_1)+n\nu_2(\lambda_1\lambda_2+\mu_1\mu_2+\nu_1\nu_2)-n\nu_1 + (l\mu_1-m\lambda_1)(\lambda_2\mu_1-\lambda_1\mu_2),$$

vanish at Q and therefore the principal parts of X, Y, Z vanish at P, provided the point Q is not near to the curve of contact of the tangent cone. These results might have been obtained by observing that when the limits of the integral can be taken infinite the effect is the same as if the surface on which this distribution of electric and magnetic currents is placed surrounded the source and therefore at a point inside this surface the effect of the distribution is zero and at a point outside it equal and opposite to that of the source.

When the point P is inside the boundary of the geometrical shadow and so near to it that the limits of integration cannot be taken to be infinite the values of X, Y, Z as in the case of the conducting surface are given by

$$X = -(1-L)X', \qquad Y = -(1-L)Y', \qquad Z = -(1-L)Z',$$

where

$$L = 2^{-1/2}e^{1/4\pi\iota}\int_{u_0}^{\infty} e^{-1/2\pi\iota u^2}\,du,$$

and

$$u_0 = \left\{\frac{2}{\lambda}\left(\frac{1}{OM}+\frac{1}{PM}\right)\right\}^{1/2} RM,$$

where the letters have the same signification as in the case of the conducting surface. Hence, at points inside the boundary of the geometrical shadow, the components of the electric force are

$$LX', \quad LY', \quad LZ',$$

where X', Y', Z' are the components of the electric force at the point due to the oscillator when there is no obstacle, and the components of the magnetic force are

$$L\alpha', \quad L\beta', \quad L\gamma',$$

where α', β', γ' are the components of the magnetic force due to the oscillator. In this case these values of the components of the magnetic and electric forces are valid up to the boundary of the obstacle, therefore the principal parts of the components of the magnetic and electric forces at a point P inside the boundary of the geometrical shadow are the same whether the obstacle is perfectly conducting or perfectly absorbing, provided the point P is at a distance from the surface of the obstacle measured along OP of a higher order than $\rho(\kappa\rho)^{-1/3}$, where ρ is the radius of curvature of the section of the surface through the tangent in the plane of incidence, and the value of the principal part of the magnetic force tangential to the surface of the obstacle at a point on it inside the boundary of the geometrical shadow when the obstacle is perfectly conducting is double the value it has when the obstacle is perfectly absorbing; the value of the principal part of the component of the electric force normal to the surface of the obstacle at a point inside the boundary of the geometrical shadow when the obstacle is perfectly conducting is also double the value it has when the obstacle is perfectly absorbing.

When the point P is near to the boundary of the geometrical shadow and outside it the principal parts of the components of the electric and magnetic forces at the point P are

$$\mathrm{L}X', \quad \mathrm{L}Y', \quad \mathrm{L}Z', \quad \mathrm{L}\alpha', \quad \mathrm{L}\beta', \quad \mathrm{L}\gamma',$$

where

$$\mathrm{L} = 2^{-1/2} e^{1/4 \pi\iota} \int_{-u_0}^{\infty} e^{-1/2 \pi\iota u^2} du,$$

and u_0 has the same meaning as above.

An Imperfectly Conducting Obstacle.

When the obstacle is an imperfectly conducting body the conditions to be satisfied at the surface of the obstacle are that the components of the electric and magnetic forces tangential to the surface are continuous. The electric and magnetic current distributions to be placed on the surface to effect this can be obtained from the following considerations. At a point on the surface of the obstacle not near to the point where the axis of the oscillator meets it the incident waves may be treated as if they were plane waves; let M_1 and M_2 be the components of the magnetic force in the incident waves tangential to the surface, M_1 being in the plane of incidence and M_2 perpendicular to it, and let E_1 and E_2 be the components of the electric force in the incident waves tangential to the surface, E_1 being in the plane of incidence and E_2 perpendicular to it, then, if ϕ is the acute angle between the direction of the incident waves and the normal to the surface at a point Q on it, writing

$$\epsilon = (\kappa' + \iota\kappa \cos\phi)/(\kappa' - \iota\kappa \cos\phi), \qquad \epsilon' = (\kappa' \cos\phi + \iota\kappa)/(\kappa' \cos\phi - \iota\kappa),^*$$

where

$$\kappa'^2 = \kappa^2 \sin^2\phi + 4\pi\iota\kappa V/\sigma,$$

and σ is the specific resistance of the obstacle, the electric current distribution to be placed on the surface has components

$$M_2(1+\epsilon'), \quad M_1(1+\epsilon),$$

and the magnetic current distribution to be placed on the surface has components

$$E_2(1-\epsilon), \quad E_1(1-\epsilon').$$

The effect of this distribution can be immediately obtained from the previous calculations by superposing the two distributions

$$2M_2\epsilon', \quad 2M_1\epsilon,$$

and the two distributions

$$M_2(1-\epsilon'), \quad E_1(1-\epsilon'); \qquad M_1(1-\epsilon), \quad E_2(1-\epsilon);$$

the first two involve the same calculation as in the case of the perfectly conducting

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[*] The general value of ϵ' is $(4\pi V/\sigma + \kappa' \sec\phi)/(4\pi V/\sigma - \kappa' \sec\phi)$, which has the approximate value in the text when the wave-length λ of the oscillations is great compared with σ/V.

obstacle, and the second two involve the same calculation as in the case of the perfectly absorbing obstacle, hence, at points inside the tangent cone from the oscillator to the surface of the obstacle, the principal parts of the components of the electric and magnetic forces vanish when the point is not near to the boundary of the geometrical shadow, at a point P outside the boundary of the geometrical shadow and not near to it, the principal parts of the components of the electric and magnetic forces in the reflected waves at P are given by multiplying the components due to $2M_2$ at Q in the case of perfect reflection by ϵ' and the components due to $2M_1$ at Q by ϵ, where OQ, QP make equal angles with the normal at Q to the surface. When the point P is inside the tangent cone and near to the boundary of the geometrical shadow, the distribution $2M_2\epsilon'$ gives the corresponding components multiplied of $-(1-L)\epsilon'$ and the distribution $M_2(1-\epsilon')$, $E_1(1-\epsilon')$ the corresponding components multiplied by $-(1-L)(1-\epsilon')$, that is these two distributions give the corresponding components multiplied by $-(1-L)$ and the other two distributions give the corresponding components multiplied by $-(1-L)$; therefore the principal parts of the components of the electric and magnetic forces at the point P due to the oscillator and to the assumed distribution on the surface are

$$LX', \quad LY', \quad LZ', \quad L\alpha', \quad L\beta', \quad L\gamma',$$

where X', Y', Z', α', β', γ' are the principal parts of the components of the electric and magnetic forces due to the oscillator at the point P and L has the value defined above. It may be verified as in the case of the perfect conductor that the boundary conditions at points on the surface of the obstacle not near to the curve of contact of the tangent cone from the oscillator are satisfied by this assumed distribution on the surface. It also follows from the investigation for the case of the perfectly conducting obstacle that the principal parts of the components of the electric and magnetic forces at a point P inside the boundary of the geometrical shadow are given by

$$LX', \quad LY', \quad LZ', \quad L\alpha', \quad L\beta', \quad L\gamma',$$

provided P is at a distance from the surface of the obstacle which is of an order higher than $\rho(\kappa\rho)^{-1/3}$ and the perpendicular distance of OP from the point R on the curve of contact of the tangent cone from O to the surface is of the same or higher order than $\rho(\kappa\rho)^{-2/3}$, where ρ is the radius of curvature of the normal section of the surface through OR. The principal parts of the components of the electric and magnetic forces at points on the surface of the obstacle near the curve of contact but at a distance along the surface from it of higher order than $\rho(\kappa\rho)^{-1/3}$ can be determined as follows. Let M'_1, M'_2 be the principal parts of the components of the magnetic force due to the oscillator tangential to the surface at the point P on it inside the boundary of the geometrical shadow, M'_1 being in the plane containing OP and the normal to the surface at P, and M'_2 perpendicular to this plane. Further, let M_1, M_2

be the principal parts of the components of the actual magnetic force at P in these directions, then P being at a distance along the surface from the curve of contact of higher order than $\rho\,(\kappa\rho)^{-1/3}$, the principal part of the component of the magnetic force in the plane of OP and the normal to the surface at P which is due to the oscillator and the actual distribution on the part of the surface inside the tangent cone from O and nearest to O is LM'_1, and the principal part of the corresponding component of the magnetic force due to the local distribution at P is $\epsilon\mathrm{M}_1/(1+\epsilon)$, where $\epsilon = (\kappa'+\iota\kappa\cos\phi)/(\kappa'-\iota\kappa\cos\phi)$, and ϕ is the acute angle between the normal at P and OP.

Therefore

$$\mathrm{M}_1 = \epsilon\mathrm{M}_1/(1+\epsilon)+\mathrm{LM}'_1,$$

that is

$$\mathrm{M}_1 = (1+\epsilon^1)\,\mathrm{LM}'_1.$$

Similarly

$$\mathrm{M}_2 = (1+\epsilon')\,\mathrm{LM}'_2,$$

where

$$\epsilon' = (\kappa'\cos\phi+\iota\kappa)/(\kappa'\cos\phi-\iota\kappa),$$

and the principal parts of the components of the electric force at P can be similarly obtained. When κ is small compared with $4\pi\mathrm{V}/\sigma$, κ' is approximately given by $\kappa' = \kappa_1(1+\iota)$, where $\kappa_1 = (2\pi\kappa\mathrm{V}/\sigma)^{1/2}$, the modulus of $1+\epsilon$, is greater than 2, and the modulus of $1+\epsilon'$ is greater than 2 provided $\cos\phi$ is greater than $\kappa/2\kappa_1$; therefore at a point P on the part of the surface next the oscillator the amplitude of the tangential magnetic force is greater than in the case of a perfectly conducting obstacle, and at a point on the part of the surface of the obstacle remote from the oscillator the tangential magnetic force is greater than in the case of a perfectly conducting obstacle, provided $\cos\phi$ is greater than $\kappa/2\kappa_1$. The same results hold for the components of the electric force normal to the surface of the obstacle.

It appears from the foregoing investigations that at a point P inside the boundary of the geometrical shadow formed by any opaque obstacle the principal parts of the components of the electric and magnetic forces are

$$\mathrm{LX}',\quad \mathrm{LY}',\quad \mathrm{LZ}',\quad \mathrm{L}\alpha',\quad \mathrm{L}\beta',\quad \mathrm{L}\gamma',$$

where X', Y', Z', α', β', γ' are the principal parts of the components of the electric and magnetic forces at the point P due to the oscillator, when the point P is at a distance measured along OP from the surface of the obstacle of a higher order than $\rho\,(\kappa\rho)^{-1/3}$, that when the obstacle is perfectly absorbing the principal parts of the components of the electric and magnetic forces at a point P on the surface of the obstacle inside the boundary of the geometrical shadow have the above values, that when the obstacle is perfectly conducting the ratio of the electric force normal to the surface at the point P on it to the electric force normal to the surface of a perfectly absorbing obstacle occupying the same space at the same point on it is 2, and that when the obstacle is imperfectly conducting this ratio is greater than 2,* but decreases as the distance along the surface of the point P from the edge of the shadow increases when the magnetic force in the incident waves is perpendicular to the plane of incidence.

The same methods as have been applied in the foregoing can be used to solve the problem of the case of a transparent obstacle; it is convenient in this case to treat separately the components of the electric and magnetic forces tangential to the surface in and perpendicular to the plane of incidence.

[*October 17.*—The investigation given above of the effect of a perfectly absorbing obstacle assumes that the electric and magnetic forces on the surface change abruptly at the curve of contact of the tangent cone from the point O to the surface. When the creeping effect at the edge is taken into account, the quantity L gives the ratio of the forces at a point P inside the geometrical shadow to the forces at that point due to the oscillator alone, only if the point P is subject to the same restrictions as in the case of the perfectly conducting obstacle, that the distance of the point P along OP from the surface of the obstacle is of higher order than $\rho(\kappa\rho)^{-1/3}$, and that OM is of higher order than $\rho(\kappa\rho)^{-1/3}$. The theorem, that the electric force normal to the surface of the obstacle at a point on it when the obstacle is perfectly conducting has double the value it has when the obstacle is perfectly absorbing, can be established generally as follows: Let E and M be the electric and magnetic forces in the incident waves tangential to the surface of the obstacle at a point on it. If the surface is perfectly conducting there is an electric current distribution $2M\omega$ on it and a zero magnetic current distribution, and if the obstacle is incapable of supporting magnetic force there is a zero electric current distribution on it and a magnetic current distribution $2E\omega'$; the superposition of these two distributions gives the solution for the case when the obstacle is perfectly absorbing and the electric and magnetic forces in the incident waves tangential to the surface at a point on it are 2E, 2M. Hence the electric current distribution on the surface of the obstacle when it is perfectly absorbing is $M\omega$, and when it is perfectly conducting $2M\omega$, the electric and magnetic forces in the incident waves tangential to the surface being E, M; and therefore the magnetic force tangential to the surface and the electric force normal to the surface of the obstacle when it is perfectly conducting have each double the value they have when the obstacle is perfectly absorbing. Similar reasoning applies to the case of the imperfectly conducting obstacle, the ratio in this case being $1+\epsilon$ for the component of magnetic force tangential to the surface in the plane of incidence and $1+\epsilon'$ for the component perpendicular to the plane of incidence.]

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* For the case of waves of the wave-lengths used in wireless telegraphy, the conducting body being the sea, the value of this ratio at a distance of 150 miles is not greater than 2·06 and decreases as the distance increases.

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ON THE FOUNDATIONS OF THE THEORY OF ALGEBRAIC FUNCTIONS OF ONE VARIABLE.

BY

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XI. *On the Foundations of the Theory of Algebraic Functions of One Variable.*

By J. C. Fields, *Ph.D., Associate Professor of Mathematics in the University of Toronto.*

Communicated by A. R. Forsyth, *Sc.D., LL.D., F.R.S.*

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§ 1. Some years ago the writer published a book* in which he developed a new theory of the algebraic functions of a complex variable. The theory in question was purely algebraic in its character and perfectly general. The higher singularities gave rise to no specific difficulties due to their greater complexity and no exceptional cases had to be reserved for separate treatment. The capital result of the theory might be said to be the "Complementary Theorem"—a theorem which is considerably more general than the Riemann-Roch Theorem.

The book, however, presents its difficulties for the reader, and, in particular, the sixth chapter would seem to have been a stumbling-block. For this chapter the writer has already given several comparatively simple substitutes, and the reader of the present paper will find that, among other results, those of the chapter in question follow in very easy fashion from the representation of a rational function in the form (8). The method of the "deformation of a product," which plays a conspicuous part in the earlier chapters of the book, is here dispensed with. The residues of what we call the *principal coefficient* of the reduced form of a rational function will be found to play an important *rôle*—a *rôle* which is already implied in the argument of the book and which is brought into evidence in a paper by the writer published in Vol. XXXII. of the 'American Journal of Mathematics' under the title "The Complementary Theorem." In the present paper the apparatus for handling the residues in question will be greatly simplified. We have no need of the function $R(z, v)$ defined in Chapter IX. of the book, and at the same time we are able to dispense with the functions $\zeta_s^{(i)}(z, v)$ and the more or less complicated formulæ connected with these functions in the earlier presentation of the theory.

Let

$$f(z, u) = u^n + f_{n-1}u^{n-1} + \ldots + f_0 = 0 \quad \ldots \ldots \ldots \quad (1)$$

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* 'Theory of the Algebraic Functions of a Complex Variable,' Mayer and Müller, Berlin, 1906.

Published separately, January 29, 1913.

be an equation in which we shall ultimately suppose the coefficients $f_{n-1}, \ldots, f_0$ to be rational functions of z. For the moment, however, it will suffice to assume that these coefficients have the character of rational functions for the value $z = a$ (or $z = \infty$), that is, that they are developable in series of integral powers of $z-a$ (or $1/z$) in which, at most, a finite number of terms have negative exponents. We say that a function has the character of a rational function of (z, u) for the value $z=a$ (or $z = \infty$) if it is built up by rational operations out of u and functions of z which have the character of rational functions for the value $z = a$ (or $z = \infty$). Here it is to be understood that the function is to have a meaning for each of the branches of the equation (1), corresponding to the value of the variable z in question—otherwise said, that the rational operations do not involve division by a factor of $f(z, u)$. The equation (1) may or may not be reducible in the domain of functions of rational character for the value $z = a$ (or $z = \infty$). In any case, however, without detriment to the generality of our theory, we may assume that the equation does not involve a repeated factor.

Any function possessing the character of a rational function of (z, u) for the value $z = a$ (or $z = \infty$) can evidently be written in one, and only one, way in the form

$$\mathrm{H}(z, u) = h_{n-1}u^{n-1}+h_{n-2}u^{n-2}+\ldots+h_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the coefficients h_s possess the character of rational functions for the value of the variable z in question. This form we call the *reduced form* of the function. The coefficient of u^{n-1} in the reduced form of a function of (z, u) we call the *principal coefficient* of the function. The term $h_{n-1}u^{n-1}$ itself we call the *principal term.* In what follows we shall take for granted that a function of (z, u) is expressed in its reduced form where nothing in the context implies the contrary.

Corresponding to the value $z = a$ (or $z = \infty$) we have a representation of the equation (1) in the form

$$f(z, u) = (u-\mathrm{P}_1)(u-\mathrm{P}_2)\ldots(u-\mathrm{P}_n) = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\mathrm{P}_1, \ldots, \mathrm{P}_n$ are series in powers of $z-a$ (or $1/z$) with exponents, integral or fractional, of which, it may be, a finite number are negative. These power-series group themselves into a number, r, of cycles of orders $\nu_1, \ldots, \nu_r$ respectively where the series of a cycle of order ν_s proceed according to ascending integral powers of the element $(z-a)^{1/\nu_s}$, or z^{-1/ν_s}, as the case may be. As a general rule we have $\nu_s = 1$.

We shall speak of the order of coincidence of a function $\mathrm{H}(z, u)$ with a branch $u-\mathrm{P}_s = 0$, or of the order of coincidence of the branch with the function, meaning thereby the lowest exponent in $\mathrm{H}(z, \mathrm{P}_s)$ arranged according to ascending powers of $z-a$ (or $1/z$). The order of coincidence of the branch $u-\mathrm{P}_s = 0$ with the product

$$\mathrm{Q}_s(z, u) = (u-\mathrm{P}_1)\ldots(u-\mathrm{P}_{s-1})(u-\mathrm{P}_{s+1})\ldots(u-\mathrm{P}_n) \quad . \quad . \quad . \quad . \quad (4)$$

we shall indicate by the symbol $\bar{\mu}_s$. This is plainly also the order of coincidence of the branch with the function $f'_u(z,u)$. The order of coincidence of the branch $u-\mathrm{P}_s=0$ with the factor $u-\mathrm{P}_t$ we shall briefly refer to also as the order of coincidence of the branch $u-\mathrm{P}_s=0$ with the branch $u-\mathrm{P}_t=0$, and we shall indicate this order of coincidence by the symbol $\mu_{s,t}$. It is evident that $\mu_{s,t}=\mu_{t,s}$. Furthermore, $\bar{\mu}_s$ is equal to the sum of the orders of coincidence of the branch $u-\mathrm{P}_s=0$ with its $n-1$ conjugate branches, and we therefore have

$$\bar{\mu}_s=\mu_{s,1}+\ldots+\mu_{s,s-1}+\mu_{s,s+1}+\ldots+\mu_{s,n}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It is readily seen that the numbers $\bar{\mu}_s$ corresponding to the several branches of the same cycle are all equal. The r numbers thus defined for the branches of the r cycles we shall indicate by the symbols

$$\mu_1, \mu_2, \ldots, \mu_r. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The functions $\mathrm{Q}_s(z,u)$ in (4) are defined by the identities

$$f(z,u)=(u-\mathrm{P}_s)\,\mathrm{Q}_s(z,u),\ s=1,2,\ldots,n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

We can then represent any function $\mathrm{H}(z,u)$, of rational character for the value $z=a$ (or $z=\infty$), in the form*

$$\mathrm{H}(z,u)=\theta_1\mathrm{Q}_1(z,u)+\ldots+\theta_s\mathrm{Q}_s(z,u)+\ldots+\theta_n\mathrm{Q}_n(z,u) \quad . \quad . \quad . \quad . \quad (8)$$

where $\theta_1,\ldots,\theta_n$ are series in powers of $z-a$ (or $1/z$) involving integral or fractional exponents, of which a finite number only can be negative. The necessary and sufficient condition that the function $\mathrm{H}(z,u)$ should be represented by the expression on the right-hand side of (8) is

$$\theta_s=\frac{\mathrm{H}(z,\mathrm{P}_s)}{\mathrm{Q}_s(z,\mathrm{P}_s)},\ s=1,2,\ldots,n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

To see this it is only necessary to note that the functions

$$\mathrm{Q}_1(z,u),\ \ldots,\ \mathrm{Q}_{s-1}(z,u),\ \mathrm{Q}_{s+1}(z,u),\ \ldots,\ \mathrm{Q}_n(z,u)$$

all vanish identically on substituting in them $u=\mathrm{P}_s$. The representation of the function $\mathrm{H}(z,u)$ in the form (8) then exists and is unique. This representation evidently also gives the function in its reduced form since u^{n-1} is the highest power of u which presents itself.

The order of coincidence of the branch $u-\mathrm{P}_s=0$ with the function $\mathrm{H}(z,u)$ is plainly the same as its order of coincidence with the element $\theta_s\mathrm{Q}_s(z,u)$ in (8) and is,

---

* This form of representation was suggested to the writer by formula (3) in Chapter XIII. of his book on the algebraic functions, already cited. It may be pointed out, however, that the same form was derived by CHRISTOFFEL from LAGRANGE'S interpolation formula and employed in his paper, "Algebraischer Beweis des Satzes von der Anzahl der linearunabhängigen Integrale erster Gattung," 'Annali di Matematica,' ser. II., t. X., pp. 81–100.

therefore, obtained on adding the lowest exponent in the series θ_s to $\bar{\mu}_s$, the order of coincidence of the function $Q_s(z, u)$ with the branch in question. If, then, the order of coincidence of the function $H(z, u)$ with the branch $u - P_s = 0$ is $\geqq \bar{\mu}_s$, the series θ_s can involve no negative exponent. If the order of coincidence of the function $H(z, u)$ with the branch $u - P_s = 0$ is $> \bar{\mu}_s - 1$ the lowest exponent in the series θ_s must be > -1. Now the coefficient of u^{n-1} in the reduced form of $H(z, u)$, as given in (8), is

$$\sum_{s=1}^{n} \theta_s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

a function which is evidently of rational character for the value of the variable z in question. If, then, the orders of coincidence of the function $H(z, u)$ with the branches $u - P_1 = 0, \ldots, u - P_n = 0$ are greater than the corresponding numbers in the set $\bar{\mu}_1 - 1, \ldots, \bar{\mu}_n - 1$, the lowest exponent in the principal coefficient is > -1 and must therefore be $\geqq 0$, because of the rational character of the coefficient for the value $z = a$ (or $z = \infty$). We shall say of a function of z that it is *integral with regard to the element* $z - a$ (or $1/z$) if its expansion in powers of the element involves no negative exponents. The principal coefficient in a function $H(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) is then integral with regard to the element $z - a$ (or $1/z$) if the orders of coincidence of the function with the branches of the corresponding cycles are greater than the numbers $\mu_1 - 1, \ldots, \mu_r - 1$ respectively. Otherwise stated, the principal coefficient in a function $H(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) must be integral with regard to the element $z - a$ (or $1/z$) if the orders of coincidence of the function with the branches of the several cycles do not fall short of the numbers

$$\mu_1 - 1 + \frac{1}{\nu_1}, \ldots, \mu_r - 1 + \frac{1}{\nu_r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

respectively. A set of orders of coincidence which do not fall short of the numbers given in (11) we call a *set of adjoint orders of coincidence*, and, if a function possess such a set of orders of coincidence, we say that it is *adjoint* for the value of the variable z in question. The theorem which we have just proved may then be briefly stated as follows:—If a function $H(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) is adjoint for this value of the variable its principal coefficient must be integral with regard to the element $z - a$ (or $1/z$). This theorem, so far as it has reference to the value $z = \infty$, is evidently also embodied in the statement that the degree in (z, u) of the principal term in a function $H(z, u)$ of rational character for the value $z = \infty$ must be $\leqq n - 1$ if the function is adjoint for this value of z.

If a function $H(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) is conditioned for this value of the variable by a certain set of adjoint orders of coincidence $\mu'_1, \ldots, \mu'_r$, and if for a single one of these orders of coincidence μ'_s we have $\mu'_s \gtreqqless \mu_s$, the principal coefficient, already integral, will in the *general* function so conditioned have a constant term which is $\neq 0$. This we can readily see from the form of representation for the function given in (8). If, namely, we suppose $u-P_1 = 0, \ldots, u-P_{\nu_s} = 0$ to be the ν_s branches of the cycle of order ν_s, the ν_s series $\theta_1, \ldots, \theta_{\nu_s}$ in (8) will be conjugate series in which the lowest exponent is > -1, and in each of which the constant term is the same and unconditioned by the orders of coincidence here in question. The constant term in the principal coefficient of the partial sum

$$\theta_1 Q_1(z, u) + \ldots + \theta_{\nu_s} Q_{\nu_s}(z, u), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

on the right-hand side of (8), is then arbitrary, and this is, therefore, also the case for the constant term in the total sum on the right-hand side of (8), since the series $\theta_{\nu_s+1}, \ldots, \theta_n$ are determined independently of the ν_s series $\theta_1, \ldots, \theta_{\nu_s}$.

The theorem just stated, together with the theorem preceding, may be included in the one statement:—In the *general* function $H(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) and conditioned for this value by a set of adjoint orders of coincidence $\mu'_1, \ldots, \mu'_r$, the principal coefficient must be integral with regard to the element $z-a$ (or $1/z$), and, furthermore, will involve an arbitrary constant term unless $\mu'_1, \ldots, \mu'_r$ are simultaneously greater than the corresponding numbers in the set $\mu_1, \ldots, \mu_r$.

Let $H(z, u)$ be the general function of rational character for the value $z = a$ (or $z = \infty$), which is conditioned by a set of orders of coincidence

$$i+\mu'_1, \ldots, i+\mu'_r, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where i is a positive or negative integer or 0, and where $\mu'_1, \ldots, \mu'_r$ constitute a set of adjoint orders of coincidence which, however, are not simultaneously greater than the numbers $\mu_1, \ldots, \mu_r$. The function $(z-a)^{-i} H(z, u)$, or $z^i H(z, u)$, is then evidently the general function of rational character for the value $z = a$ (or $z = \infty$), which is conditioned by the set of adjoint orders of coincidence $\mu'_1, \ldots, \mu'_r$, and its principal coefficient, by the theorem last stated, must therefore be integral in the element $z-a$ (or $1/z$) and involve an arbitrary constant. It follows that the lowest term in the principal coefficient of the general function $H(z, u)$, conditioned by the set of orders of coincidence (13), is $\alpha (z-a)^i$, or αz^{-i}, where α is an arbitrary constant.

Evidently any set of orders of coincidence corresponding to the value $z = a$ (or $z = \infty$) can be written in the form (13), so that we may also state the last theorem as follows:—The lowest term in the principal coefficient of the general function $H(z, u)$ of rational character for the value $z = a$ (or $z = \infty$), and conditioned by a given set of orders of coincidence for this value of z, is $\alpha (z-a)^i$, or αz^{-i}, where α is an arbitrary constant, and where i is the greatest integer whose subtraction from each number of the set leaves a set of adjoint orders of coincidence.

From the form (8) it is readily seen that we can construct a function $H(z, u)$ of rational character for the value $z = a$ (or $z = \infty$), which possesses an arbitrarily assigned set of orders of coincidence $\tau_1, \ldots, \tau_r$, for the branches of the corresponding cycles. Here $\tau_1, \ldots, \tau_r$ may be any integral multiples—positive, negative, or zero—of the numbers $1/\nu_1, \ldots, 1/\nu_r$ respectively. We can write

$$\tau_s = \mu_s + \frac{n_s}{\nu_s}, \quad s = 1, 2, \ldots, r, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where the numbers n_s are integral. In the form (8) each of the n elements on the right-hand side corresponds to a different one of the n branches. In the ν_s elements corresponding to the conjugate branches of the cycle of order ν_s substitute for the coefficients θ corresponding conjugate series beginning with a term in $(z-a)^{n_s/\nu_s}$, or z^{-n_s/ν_s}. Do this for each of the r cycles and the resulting function $H(z, u)$ will have precisely the set of orders of coincidence $\tau_1, \ldots, \tau_r$ here in question, and will at the same time evidently be of rational character for the value $z = a$ (or $z = \infty$).

Not only can we construct a function $H(z, u)$ of rational character for the value $z = a$ (or $z = \infty$), which possesses the arbitrary set of orders of coincidence $\tau_1, \ldots, \tau_r$, but we can in particular construct a *rational* function of (z, u) which possesses precisely this set of orders of coincidence for the value of the variable in question. To obtain such a rational function, in fact, it evidently suffices in the function $H(z, u)$, already constructed, to cut off in the series in powers of $z-a$ (or $1/z$), which constitute the coefficients of the powers of u, terms of order sufficiently high to be unaffected by the orders of coincidence $\tau_1, \ldots, \tau_r$, required of the function.

Let us now suppose for the moment that the equation (1) has reference to the value $z = \infty$, so that the coefficients $f_{n-1}, \ldots, f_0$ are series in powers of $1/z$ involving, it may be, a finite number of positive powers of z. The aggregate degree of the equation in (z, u) we shall indicate by the letter N. Referring to the identities (7), then, we see that the degrees of the functions $Q_s(z, u)$ can in no case exceed $N-1$. If now the function $H(z, u)$ in (8) be adjoint for the value $z = \infty$, the lowest exponents in the series $\theta_s(1/z)$ must, as we have already noted, be > -1, and the degrees in z of these series must therefore all be < 1. The degrees in (z, u) of the elements $\theta_s Q_s(z, u)$ in (8) will consequently all be $< N$, and the same will be true of the degree of the function $H(z, u)$. It follows that the degree of the function $H(z, u)$ must be $\leqq N-1$, because of the rational character of the function for the value $z = \infty$. We have just proved then that a function $H(z, u)$ which is of rational character for the value $z = \infty$, and which is also adjoint for this value of the variable z, must be of degree $\leqq N-1$, and we had already proved that the degree of the principal term in such a function must be $\leqq n-1$.

§ 2. If a function $H(z, u)$, of rational character for the value $z = a$ (or $z = \infty$), is also adjoint for this value of the variable z, we have seen that its principal coefficient must be integral with regard to the element $z-a$ (or $1/z$). We have also seen, in the case of a set of orders of coincidence corresponding to the value $z = a$ (or $z = \infty$), of which some one at least falls short of what is requisite to adjointness, that a rational function of (z, u) can be constructed possessing precisely the orders of coincidence here in question and having a principal coefficient which is not integral with regard to the element $z-a$ (or $1/z$).

We say of two sets of orders of coincidence $\tau_1, \ldots, \tau_r$, and $\bar{\tau}_1, \ldots, \bar{\tau}_r$, corresponding to a value $z = a$ (or $z = \infty$), that they are complementary adjoint to each other if they satisfy the inequalities

$$\tau_1+\bar{\tau}_1 \geqq \mu_1-1+\frac{1}{\nu_1}, \ldots, \tau_r+\bar{\tau}_r \geqq \mu_r-1+\frac{1}{\nu_r}. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

When they satisfy the inequalities

$$\tau_1+\bar{\tau}_1 \geqq i+\mu_1-1+\frac{1}{\nu_1}, \ldots, \tau_r+\bar{\tau}_r \geqq i+\mu_r-1+\frac{1}{\nu_r}, \quad . \quad . \quad . \quad . \quad (16)$$

they are said to be complementary adjoint to the order i. If the sets of orders of coincidence of two functions for a given value of the variable z are complementary adjoint, we say also that the functions are complementary adjoint to each other for the value of the variable in question. The orders of coincidence of the product of the two functions are evidently obtained on adding the corresponding orders of coincidence of the functions. If the functions $\Phi(z, u)$ and $\Psi(z, u)$ are complementary adjoint for the value $z = a$ (or $z = \infty$) their product is adjoint for the value of the variable in question, and the coefficient of the principal term in the product must therefore be integral with regard to the element $z-a$ (or $1/z$). When we speak of the principal term in a product it is, of course, to be understood that we mean the principal term in the product expressed in its reduced form.

In order that a function $\Psi(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) shall have orders of coincidence which are complementary adjoint to a given set of orders of coincidence $\tau_1, \ldots, \tau_r$, the necessary and sufficient condition is that the coefficient of the principal term in the product $\Phi(z, u)\, \Psi(z, u)$ shall be integral with regard to the element $z-a$ (or $1/z$), where $\Phi(z, u)$ represents the most general function of (z, u) of rational character for the value $z = a$ (or $z = \infty$) whose orders of coincidence with the branches of the corresponding cycles do not fall short of the numbers $\tau_1, \ldots, \tau_r$ respectively. That this is a necessary condition has been seen in what just precedes. That it is a sufficient condition may be proved as follows :—Suppose $\Psi(z, u)$ to be a specific function of (z, u) of rational character for the value $z = a$ (or $z = \infty$), and suppose its orders of coincidence for this value of the variable to be $\bar{\tau}_1, \ldots, \bar{\tau}_r$. Furthermore, suppose this set of orders of coincidence not to be complementary adjoint to the set $\tau_1, \ldots, \tau_r$. The numbers $\tau_1+\bar{\tau}_1, \ldots, \tau_r+\bar{\tau}_r$, then do not constitute a set of adjoint orders of coincidence, and we can therefore construct a function $\mathrm{H}(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) which possesses precisely this set of orders of coincidence and whose principal term is not integral in regard to the element $z-a$ (or $1/z$).

For the moment we shall suppose that all of the orders of coincidence $\bar{\tau}_1, \ldots, \bar{\tau}_r$, are finite. The quotient $\mathrm{H}(z, u)/\Psi(z, u)$ is then a function of rational character for the value $z = a$ (or $z = \infty$) whose orders of coincidence for this value of the variable are $\tau_1, \ldots, \tau_r$, and yet in its product by the function $\Psi(z, u)$ the principal term is not integral in character. If then the set of orders of coincidence $\bar{\tau}_1, \ldots, \bar{\tau}_r$, of the function $\Psi(z, u)$ be not complementary adjoint to the set of orders of coincidence $\tau_1, \ldots, \tau_r$, the principal term in the product of $\Psi(z, u)$ by the general function $\Phi(z, u)$, which possesses the latter set of orders of coincidence, is not integral in character with regard to the element $z-a$ (or $1/z$). It follows, therefore, that the sufficient, as well as the necessary condition, in order that the orders of coincidence of a function $\Psi(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) shall be complementary adjoint to a given set of orders of coincidence $\tau_1, \ldots, \tau_r$, is contained in the statement that the coefficient of the principal term in the product of $\Psi(z, u)$ by $\Phi(z, u)$ is integral with regard to the element $z-a$ (or $1/z$), where $\Phi(z, u)$ is the general function of rational character for the value $z = a$ (or $z = \infty$) whose orders of coincidence with the branches of the corresponding cycles do not fall short of the numbers $\tau_1, \ldots, \tau_r$.

In what precedes we have assumed that the orders of coincidence $\bar{\tau}_1, \ldots, \bar{\tau}_r$ of the function $\Psi(z, u)$ are all finite. Suppose now that certain of these orders of coincidence are infinite, and that nevertheless the set is not complementary adjoint to the set of orders of coincidence $\tau_1, \ldots, \tau_r$. As before, let $\Phi(z, u)$ be the general function of rational character for the value $z = a$ (or $z = \infty$) conditioned by the set of orders of coincidence $\tau_1, \ldots, \tau_r$. Construct a function $\Psi'(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) which possesses for this value of the variable a set of orders of coincidence which is complementary adjoint to the set $\tau_1, \ldots, \tau_r$, all of its orders of coincidence being at the same time finite, and each one of them different from the corresponding order of coincidence in the set $\bar{\tau}_1, \ldots, \bar{\tau}_r$. It is evident that the orders of coincidence of the function

$$\Psi''(z, u) = \Psi(z, u) + \Psi'(z, u)$$

for the value of the variable z in question are all finite, and that they constitute a set which is not complementary adjoint to the set $\tau_1, \ldots, \tau_r$. By what we have already seen, then, the principal coefficient in the product $\Phi(z, u)\ \Psi''(z, u)$ will not be integral. The principal coefficient in the product $\Phi(z, u)\ \Psi'(z, u)$, however, is integral, since $\Psi'(z, u)$ has orders of coincidence which are complementary adjoint to those of the set $\tau_1, \ldots, \tau_r$. It follows that the principal coefficient in the product $\Phi(z, u)\ \Psi(z, u)$ is not integral. If then the orders of coincidence of a function $\Psi(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) be not complementary adjoint to the orders of coincidence $\tau_1, \ldots, \tau_r$, it follows that in the product $\Phi(z, u)\ \Psi(z, u)$ the principal coefficient is not integral, where $\Phi(z, u)$ is the general function of rational character for the value $z = a$ (or $z = \infty$) conditioned by the set of orders of coincidence $\tau_1, \ldots, \tau_r$. The necessary and sufficient condition then that a function $\Psi(z, u)$ of rational character for the value $z = a$ (or $z = \infty$) should have, for this value of the variable z, a set of orders of coincidence complementary adjoint to a given set of orders of coincidence $\tau_1, \ldots, \tau_r$, is that the principal coefficient in the product $\Phi(z, u)\Psi(z, u)$ should be integral with regard to the element $z-a$ (or $1/z$), where $\Phi(z, u)$ is the general function of rational character for the value $z = a$ (or $z = \infty$) conditioned by the set of orders of coincidence $\tau_1, \ldots, \tau_r$.

Without detriment to the truth of the statement just made the expression *function of rational character for the value $z = a$ (or $z = \infty$)* employed with reference to the functions $\Phi(z, u)$ and $\Psi(z, u)$ can, in connection with either or both of these functions, be replaced by the expression rational function of (z, u).

If in the product of a function $\Psi(z, u)$ by the function $\Phi(z, u)$ the coefficient of the principal term is integral with regard to the element $z-a$, the residue of this coefficient for the value $z = a$ is of course zero. Conversely, however, if the residue of the principal coefficient for the value $z = a$ vanishes in the product of a function $\Psi(z, u)$ by the general function $\Phi(z, u)$ whose orders of coincidence for this value of the variable z do not fall short of the numbers $\tau_1, \ldots, \tau_r$ respectively, it follows that the principal coefficient in question must be integral with regard to the element $z-a$. For if the function $\Phi'(z, u)$ is included under the general function $\Phi(z, u)$ conditioned by the orders of coincidence $\tau_1, \ldots, \tau_r$, and if the principal coefficient in the product $\Phi'(z, u)\Psi(z, u)$ actually contains a negative power $(z-a)^{-i}$, then also is the residue relative to the value $z = a$ in the principal coefficient of the product $(z-a)^{i-1}\Phi'(z, u)$ $\Psi(z, u)$ different from 0, while the function $(z-a)^{i-1}\Phi'(z, u)$ is evidently included under the general function $\Phi(z, u)$ above conditioned by the orders of coincidence $\tau_1, \ldots, \tau_r$. If then the residue of the principal coefficient for the value $z = a$ vanishes in the product of a function $\Psi(z, u)$ by the general function $\Phi(z, u)$, it follows that the principal coefficient in question must be integral with regard to the element $z-a$.

We may then say, in the case of a finite value $z = a$, that the necessary and sufficient condition in order that a function $\Psi(z, u)$ should be complementary adjoint to a set of orders of coincidence $\tau_1, \ldots, \tau_r$ for the value of z in question, is contained in the statement that the residue relative to the value $z = a$ in the principal coefficient of the product $\Phi(z, u)\Psi(z, u)$ should vanish, where $\Phi(z, u)$ represents the most general function of (z, u) of rational character for $z = a$ whose orders of coincidence with the branches of the corresponding cycles do not fall short of the numbers $\tau_1, \ldots, \tau_r$ respectively.

In like manner for the value $z = \infty$ we may evidently say that the necessary and sufficient condition in order that a function $\Psi(z, u)$ should be complementary adjoint to a set of orders of coincidence $\tau_1, \ldots, \tau_r$, corresponding to the value of the variable in question, is contained in the statement that the constant coefficient of the element zu^{n-1} in the principal term of the product $\Phi(z, u)\Psi(z, u)$ should vanish, where $\Phi(z, u)$ represents the most general function of (z, u) of rational character for the value $z = \infty$, whose orders of coincidence with the branches of the corresponding cycles do not fall short of the numbers $\tau_1, \ldots, \tau_r$ respectively. The vanishing of the constant coefficient of the element zu^{n-1} in the principal term of the product $\Phi(z, u)\, z^2\Psi(z, u)$ then gives the condition that the function $z^2\Psi(z, u)$ should have a set of orders of coincidence which is complementary adjoint to the set of orders of coincidence $\tau_1, \ldots, \tau_r$. This, therefore, is the condition that the function $\Psi(z, u)$ should have orders of coincidence which are complementary adjoint to the order 2 to the orders of coincidence $\tau_1, \ldots, \tau_r$. Also the vanishing of the coefficient of the element zu^{n-1} in the principal term of the product $\Phi(z, u)\, z^2\Psi(z, u)$ is equivalent to the vanishing of the coefficient of the element $z^{-1}u^{n-1}$ in the principal term of the product $\Phi(z, u)\Psi(z, u)$. The vanishing of the residue relative to the value $z = \infty$ in the coefficient of the principal term in the product $\Phi(z, u)\Psi(z, u)$ consequently gives the necessary and sufficient condition that the function $\Psi(z, u)$ should have a set of orders of coincidence for the value $z = \infty$ which is complementary adjoint to the order 2 to the set of orders of coincidence $\tau_1, \ldots, \tau_r$, where $\Phi(z, u)$ is the most general function of (z, u) of rational character for the value $z = \infty$ whose orders of coincidence with the branches of the several cycles do not fall short of the numbers $\tau_1, \ldots, \tau_r$ respectively. If then $\Phi(z, u)$ represents the most general function of (z, u) of rational character for the value $z = a$ (or $z = \infty$) whose orders of coincidence with the branches of the corresponding cycles do not fall short of the numbers $\tau_1, \ldots, \tau_r$ respectively, the vanishing of the residue, for the value of the variable z in question, in the coefficient of the principal term in the product $\Phi(z, u)\Psi(z, u)$ gives, in the case of a finite value $z = a$, the necessary and sufficient condition that the orders of coincidence of the function $\Psi(z, u)$ should be complementary adjoint to the numbers $\tau_1, \ldots, \tau_r$, while, if the functions and numbers here in question have reference to the value $z = \infty$, the vanishing of the corresponding residue in the product $\Phi(z, u)\Psi(z, u)$ gives the necessary and sufficient condition that the orders of coincidence of the function $\Psi(z, u)$ should be complementary adjoint to the order 2 to the numbers $\tau_1, \ldots, \tau_r$.

In the foregoing statement it would evidently suffice to let $\Phi(z, u)$ represent the general *rational* function of (z, u) whose orders of coincidence for the value of z in question do not fall short of the number $\tau_1, \ldots, \tau_r$ respectively—at least so long as these numbers are all finite. Where we are concerned with the finite value $z = a$ we might, without detriment to the truth of our statement, further impose on the rational function $\Phi(z, u)$ the condition that its coefficients should be integral with regard to all finite values of z save only the value $z = a$, with regard to which value the coefficients will or will not be integral according as this is or is not required by the set of orders of coincidence $\tau_1, \ldots, \tau_r$. In the statement here in question the function $\Psi(z, u)$ was simply assumed to be a function of (z, u) of rational character for the value $z = a$ (or $z = \infty$), and the statement therefore holds good in particular when $\Psi(z, u)$ is a rational function of (z, u).

The product of any two functions $\Phi(z, u)$ and $\Psi(z, u)$ can be written in the form

$$\Phi(z, u)\Psi(z, u) = \vartheta(z, u) f(z, u) + \chi(z, u), \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where $\chi(z, u)$ is the reduced form of the product on the left-hand side of this identity. The factors $\Phi(z, u)$ and $\Psi(z, u)$ of this product are also supposed to be expressed in their reduced forms, so that the degree in u of the product is $\leqq 2n-2$ and the degree of $\vartheta(z, u)$ in u as a consequence is $\leqq n-2$. If $\Phi(z, u)$ represents the most general function of (z, u) of rational character for a given value $z = a$ (or $z = \infty$) conditioned by a given set of orders of coincidence $\tau_1, \ldots, \tau_r$ for this value of the variable z, the vanishing of the corresponding residue in the principal coefficient of $\chi(z, u)$ gives, in the case of a finite value $z = a$, the necessary and sufficient condition that the orders of coincidence of the function $\Psi(z, u)$ for this value of z should be complementary adjoint to the orders of coincidence $\tau_1, \ldots, \tau_r$, while, in the case of the value $z = \infty$, the vanishing of the corresponding residue in the principal coefficient of $\chi(z, u)$ gives the necessary and sufficient condition that the orders of coincidence of the function $\Psi(z, u)$ for the value $z = \infty$ should be complementary adjoint to the order 2 to the orders of coincidence $\tau_1, \ldots, \tau_r$.

§ 3. We shall now assume the equation (1) to be an integral algebraic equation. The series representing the branches of the equation for any finite value $z = a$ will then involve no negative exponents. In the representation of a rational function $H(z, u)$ in the form (8) corresponding to the value $z = a$, the functions $Q_s(z, u)$ will therefore evidently be integral with regard to the element $z-a$. If the function $H(z, u)$ be adjoint for the value $z = a$ it is readily seen that it must be integral with regard to the element $z-a$. For in this case the lowest exponent in each of the series θ_s in (8) is > -1 and the same is therefore true of the lowest exponent in each of the coefficients of the several products $\theta_s Q_s(z, u)$. It follows that, in the coefficients of the rational function $H(z, u)$ represented by the sum on the right-hand side of (8), the lowest exponent is $\geqq 0$. A rational function $H(z, u)$, which is adjoint for the value $z = a$, must then be integral with regard to the element $z-a$. Furthermore, a rational function of (z, u), which is adjoint for all finite values of the variable z, must evidently be an integral rational function of (z, u).

While a rational function $H(z, u)$ must be integral with regard to the element $z-a$ if its orders of coincidence are to be adjoint for the value $z = a$, divisibility* by $z-a$ is required from it by a set of orders of coincidence $\tau_1, \ldots, \tau_r$ corresponding to the value $z = a$ when these orders of coincidence severally exceed the corresponding numbers $\mu_1, \ldots, \mu_r$—but not otherwise. If, namely, the orders of coincidence of $H(z, u)$ severally exceed the corresponding numbers $\mu_1, \ldots, \mu_r$, the quotient of the function by $z-a$ will be adjoint for the value $z = a$, and must, therefore, be integral with regard to the element $z-a$. If, however, a single one, τ_s, of the orders of coincidence which condition the rational function $H(z, u)$ is not greater than the corresponding number μ_s, then in the representation of the general function in the form (8) the ν_s corre-

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* We here find it convenient to say of a rational function of (z, u) that it is divisible by the element $z-a$ if the function can be represented as the product of $z-a$ and a function of (z, u) in which the coefficients of the powers of u are power-series in $z-a$ not involving negative exponents.

sponding conjugate series θ will not be divisible by $z-a$ and will involve an arbitrary constant term which is independent of the coefficients in the remaining $n-\nu_s$ series θ. In this case, then, the coefficient of the principal term in the general function $\mathrm{H}(z, u)$ contains an arbitrary constant. The principal term in $\mathrm{H}(z, u)$ is, therefore, not divisible by $z-a$ and the same is consequently true of $\mathrm{H}(z, u)$ itself.

We see, then, that the general rational function conditioned by a certain set of orders of coincidence for the value $z = a$ is or is not divisible by the element $z-a$ according as its principal term is or is not divisible by this element, and we furthermore see that the principal term is or is not divisible by $z-a$ according as the orders of coincidence in question severally exceed the corresponding numbers μ_s or not. From this it follows in particular that the general rational function conditioned by a certain set of adjoint orders of coincidence for the value $z = a$ is divisible by precisely the same power of the element $z-a$ as the coefficient of its principal term.

We shall employ the letter A to designate the number of the independent conditions which must be imposed on the coefficients of the general integral rational function of (z, u) in order that it may be adjoint for the finite value $z = a$. Every extra coincidence over and above adjointness required from the function will impose an extra condition on its coefficients, for we have seen that we can construct a rational function which actually possesses an arbitrarily assigned set of orders of coincidence corresponding to a value $z = a$, and we have also seen that an adjoint set of orders of coincidence already requires that the function be integral with regard to the element $z-a$. The number of the independent conditions then which are imposed on the coefficients of the general integral rational function of (z, u) by a set of orders of coincidence $\mu'_1, \ldots, \mu'_r$, adjoint for the value $z = a$, is given by the sum

$$\mathrm{A}+\sum_{s=1}^{r}\left(\mu'_s-\mu_s+1-\frac{1}{\nu_s}\right)\nu_s, \quad \ldots \ldots \ldots \quad (18)$$

where we still have to determine the value of A.

We have seen in § 2 that the necessary and sufficient conditions, in order that a function $\Psi(z, u)$ may have a set of orders of coincidence complementary adjoint to a given set of orders of coincidence $\tau_1, \ldots, \tau_r$, corresponding to a finite value $z = a$, are obtained on equating to 0 the residue relative to this value of z in the coefficient of the principal term in the product $\Phi(z, u)\Psi(z, u)$, where $\Phi(z, u)$ is the general rational function of (z, u) conditioned by the orders of coincidence $\tau_1, \ldots, \tau_r$ for the value $z = a$. If in this theorem we give to each of the numbers $\tau_1, \ldots, \tau_r$ the value 0 and take for $\Psi(z, u)$ the general integral rational function of (z, u), we evidently obtain the necessary and sufficient conditions which must be imposed on the coefficients of the general integral rational function in order that it may be adjoint for the value $z = a$, on equating to 0 the residue relative to this value of z in the coefficient of the principal term in the product $\Phi(z, u)\Psi(z, u)$, where $\Phi(z, u)$ is the general rational function of (z, u), which is algebraically integral in character for the value $z = a$.

We may write $\Phi(z, u)$ in the form

$$\Phi(z, u) = \frac{\phi^{(i)}(z, u)}{(z-a)^i} + ((z-a, u)), \quad \dots \dots \dots \quad (19)$$

where the notation $\phi^{(i)}(z, u)$ indicates a polynomial in (z, u) of degree $i-1$ in z, and where by the notation $((z-a, u))$ we designate a polynomial in u in which the coefficients expanded in powers of $(z-a)$ present no negative exponents. Here, since $\Phi(z, u)$ is to be of integral algebraic character for the value $z = a$, the orders of coincidence of the function $\phi^{(i)}(z, u)$ with the n branches of the equation (1), corresponding to the value $z = a$, must each be $\gtreqless i$. On assuming, as we are free to do, that $\phi^{(i)}(z, u)$ is not divisible by the factor $z-a$, we are forced to take for i the greatest of the r integers $[\mu_1], \dots, [\mu_r]$, for this is evidently the greatest value which we can give to i without forcing the function $\phi^{(i)}(z, u)$ to be divisible by the factor $z-a$. Orders of coincidence, namely, which are simultaneously greater than the numbers $\mu_1, \dots, \mu_r$ require divisibility by $z-a$.

The orders of coincidence i which we here require from the function $\phi^{(i)}(z, u)$ are adjoint, and the number of the conditions which they impose on the otherwise arbitrary constant coefficients of the function is evidently obtained on substituting i for each of the r numbers $\mu'_1, \dots, \mu'_r$ in the expression (18). This gives us

$$\mathrm{A} + ni - \sum_{s=1}^{r} \left(\mu_s - 1 + \frac{1}{\nu_s}\right)\nu_s$$

for the number of the conditions to which we subject the ni coefficients of the otherwise unconditioned function $\phi^{(i)}(z, u)$. For the number of the arbitrary constants involved in the expression of the conditioned function $\phi^{(i)}(z, u)$ here in question we then have

$$l_{\mathrm{A}} = \sum_{s=1}^{r} \left(\mu_s - 1 + \frac{1}{\nu_s}\right)\nu_s - \mathrm{A}, \quad \dots \dots \dots \quad (20)$$

and we can write

$$\phi^{(i)}(z, u) = \sum_{s=1}^{l_{\mathrm{A}}} \delta_s \phi_s^{(i)}(z, u), \quad \dots \dots \dots \quad (21)$$

where the l_{A} quantities δ_s are arbitrary constants, and where the l_{A} functions $\phi_s^{(i)}(z, u)$ are specific linearly independent functions.

Now we have seen that we impose on the coefficients of the general integral rational function $\Psi(z, u)$ the conditions necessary and sufficient for adjointness relative to the value $z = a$ on equating to 0 the residue relative to this value in the coefficient of the principal term in the product $\Phi(z, u) \,.\, \Psi(z, u)$. This, however, from (19), is evidently equivalent to equating to 0 the residue relative to the value $z = a$ in the coefficient of the principal term in the product

$$\frac{\phi^{(i)}(z, u)}{(z-a)^i} \,.\, \Psi(z, u) = \sum_{s=1}^{l_{\mathrm{A}}} \frac{\delta_s \phi_s^{(i)}(z, u)}{(z-a)^i} \,.\, \Psi(z, u).$$

We then impose on the coefficients of the function $\Psi(z, u)$ just those conditions which are necessary and sufficient for adjointness relative to the value $z = a$ on equating to 0 the residue relative to this value of z in the principal coefficient of each one of the l_{A} products

$$\frac{\phi_s^{(i)}(z, u)}{(z-a)^i} \cdot \Psi(z, u)\,; \quad s = 1, 2, \ldots, l_{\mathrm{A}}. \qquad \qquad (22)$$

That the l_{A} conditions on the coefficients of the function $\Psi(z, u)$ which we have just obtained are linearly independent of one another may readily be seen. For if the residues relative to the value $z = a$ in the principal coefficients of the l_{A} products (22) were connected by a linear relation with constant multipliers, the linear expression in the functions $\phi_s^{(i)}(z, u)$ with the like multipliers would be a function $\phi^{(i)}(z, u)$ such that the residue relative to the value $z = a$ in the principal coefficient of the product

$$\frac{\phi^{(i)}(z, u)}{(z-a)^i} \cdot \Psi(z, u) \qquad \qquad (23)$$

would be 0, no matter what the coefficients of $\Psi(z, u)$ might happen to be. The function $\phi^{(i)}(z, u)$ cannot vanish identically, since by hypothesis the l_{A} functions $\phi_s^{(i)}(z, u)$ are linearly independent of one another. Suppose u^s to be the highest power of u which appears in the expression of the function $\phi^{(i)}(z, u)$, and suppose, furthermore, that a term $\beta(z-a)^{i-r}u^s$ actually presents itself. On choosing for $\Psi(z, u)$ the function $\alpha(z-a)^{r-1}u^{n-1-s}$ the residue of the principal coefficient in the product (23) will evidently be $\beta\alpha$, and this residue is not equal to 0 unless we have $\alpha = 0$. There does not exist a function $\phi^{(i)}(z, u)$ then such that the residue relative to the value $z = a$ in the product (23) is equal to 0 independently of the values of the coefficients of $\Psi(z, u)$. It follows that the l_{A} equations in the coefficients of the function $\Psi(z, u)$ obtained on equating to 0 the residues relative to the value $z = a$ in the principal coefficients of the l_{A} products (22) are independent of one another. These equations, however, give the necessary and sufficient conditions for the adjointness of $\Psi(z, u)$ relative to the value $z = a$, and we therefore have $l_{\mathrm{A}} = \mathrm{A}$. From (20) we then derive

$$l_{\mathrm{A}} = \mathrm{A} = \tfrac{1}{2}\sum_{s=1}^{r}\left(\mu_s - 1 + \frac{1}{\nu_s}\right)\nu_s. \qquad \qquad (24)$$

For the number of the independent conditions which are imposed on the coefficients of the general integral rational function $\Psi(z, u)$ by a set of orders of coincidence $\mu'_1, \ldots, \mu'_r$, which are adjoint for the value $z = a$, we obtain from (18) and (24) the expression

$$\sum_{s=1}^{r}\mu'_s\nu_s - \mathrm{A} = \sum_{s=1}^{r}\mu'_s\nu_s - \tfrac{1}{2}\sum_{s=1}^{r}\left(\mu_s - 1 + \frac{1}{\nu_s}\right)\nu_s. \qquad \qquad (25)$$

Representing in the form (19) the general rational function $\Phi(z, u)$ conditioned by a set of orders of coincidence $\tau_1, \ldots, \tau_r$ for the value $z = a$ and equating to 0 the principal residue relative to the value $z = a$ in the product $\Phi(z, u)\Psi(z, u)$ we obtain the necessary and sufficient conditions that the rational function $\Psi(z, u)$ may have orders of coincidence for the value $z = a$ which are complementary adjoint to the orders of coincidence $\tau_1, \ldots, \tau_r$. If $\Psi(z, u)$ is an integral rational function, these conditions are evidently all obtained on equating to 0 the principal residue relative to the value $z = a$ in the product

$$\frac{\phi^{(i)}(z, u)}{(z-a)^i} \cdot \Psi(z, u). \qquad (26)$$

This, however, is equivalent to equating to 0 in this product the principal residue relative to the value $z = \infty$, since in the principal coefficient of the product the sum of the residues must be 0 and the only residues which could here present themselves would have to correspond to the values $z = a$ and $z = \infty$. The necessary and sufficient conditions, then, that $\Psi(z, u)$ should have orders of coincidence for the value $z = a$, which are complementary adjoint to the orders of coincidence $\tau_1, \ldots, \tau_r$, are obtained on equating to 0 the principal residue relative to the value $z = \infty$ in the product (26).

Supposing the integral rational function $\Psi(z, u)$ to have a definite degree M, and representing the first factor of the product (26) in the form

$$\frac{\phi^{(i)}(z, u)}{(z-a)^i} = \sum_{t=1}^{n} \sum_{r=1}^{j-1} \gamma_{-r, n-t} z^{-r} u^{n-t} + z^{-j}\left(\left(\frac{1}{z}, u\right)\right), \qquad (27)$$

we see that, on choosing j sufficiently large, the residue relative to the value $z = \infty$ of the principal coefficient in the product (26) will be the same as the residue of the principal coefficient in the product

$$\sum_{t=1}^{n} \sum_{r=1}^{j-1} \gamma_{-r, n-t} z^{-r} u^{n-t} \cdot \Psi(z, u). \qquad (28)$$

The vanishing of the principal residue in the product (28), independently of the values of the arbitrary parameters involved in the expression of the coefficients $\gamma_{-r, n-t}$, then gives the necessary and sufficient conditions in order that the function $\Psi(z, u)$ may have orders of coincidence for the value $z = a$ which are complementary adjoint to the orders of coincidence $\tau_1, \ldots, \tau_r$, the integer j being supposed to be chosen sufficiently large.

If the orders of coincidence $\tau_1, \ldots, \tau_r$ were all adjoint the index i in (26) would be 0 and the function $\phi^{(i)}(z, u)$ would not exist. In this case the orders of coincidence of $\Psi(z, u)$ would simply have to be 0, or positive, in order that they might be complementary adjoint to the orders of coincidence $\tau_1, \ldots, \tau_r$, and that is already the case for the function $\Psi(z, u)$ since it is integral, and because we are here assuming the fundamental equation (1) to be integral. We might remark that where we have occasion later on in this paper to make explicit use of the results just obtained the orders of coincidence $\tau_1, \ldots, \tau_r$ will be none of them positive. On writing

$$\tau_s = -\sigma_s, \; s = 1, 2, \ldots, r,$$

the numbers σ_s will then be 0 or positive. To say in this case that a rational function of (z, u) is conditioned by the set of orders of coincidence $\tau_1, \ldots, \tau_r$ for the value $z = a$ is equivalent to saying that it becomes infinite for the branches of the several cycles corresponding to the value $z = a$ to orders which do not exceed the numbers $\sigma_1, \ldots, \sigma_r$ respectively.

§ 4. We shall now consider the connection between the form of a rational function of (z, u) and its orders of coincidence for the value $z = \infty$. Indicating by r_∞ the number of the cycles of the equation (1) for the value $z = \infty$ and by $\nu_1^{(\infty)}, \ldots, \nu_{r_\infty}^{(\infty)}$ the orders of these cycles, we represent by the notation

$$\mu_1^{(\infty)}-1+\frac{1}{\nu_1^{(\infty)}}, \ldots, \mu_{r_\infty}^{(\infty)}-1+\frac{1}{\nu_{r_\infty}^{(\infty)}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

the orders of coincidence which define adjointness for the branches of the several cycles. On introducing two new variables, $\xi = z^{-1}$, $\eta = z^{-m}u$, where m is a properly chosen integer, the equation (1) goes over into an equation

$$g(\xi, \eta) = \eta^n + g_{n-1}\eta^{n-1} + \ldots + g_0 = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

in which the coefficients g_s are integral rational functions of ξ. Rational functions of (ξ, η) are rational functions of (z, u), and conversely. The branches of the equation (30) for the value $\xi = 0$ correspond individually to the branches of the equation (1) for the value $z = \infty$ and group themselves in like manner into cycles of orders $\nu_1^{(\infty)}, \ldots, \nu_{r_\infty}^{(\infty)}$ respectively. Also it is evident that adjointness relative to the equation (30) for the value $\xi = 0$ is defined by the orders of coincidence

$$m(n-1)+\mu_1^{(\infty)}-1+\frac{1}{\nu_1^{(\infty)}}, \ldots, m(n-1)+\mu_{r_\infty}^{(\infty)}-1+\frac{1}{\nu_{r_\infty}^{(\infty)}}, \quad . \quad . \quad . \quad (31)$$

obtained on adding $m(n-1)$ to each of the numbers given in (29). The general rational function of (ξ, η), which is adjoint relatively to the equation (30) for the value $\xi = 0$, is integral with regard to the element ξ since the equation is an integral algebraic equation. Furthermore, on referring to formulæ (24) and (31) we obtain immediately the expression

$$\tfrac{1}{2}mn(n-1)+\tfrac{1}{2}\sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)}-1+\frac{1}{\nu_s^{(\infty)}}\right)\nu_s^{(\infty)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

for the number of the conditions which must be imposed on the coefficients of the general rational function of $(\xi, \eta)_\eta$ of integral character for the value $\xi = 0$, in order that it may be adjoint relatively to the equation (30) for this value of the variable.

Represent the general rational function of (ξ, η), of integral character for the value $\xi = 0$, by the expression

$$\rho_{n-1}(\xi)\eta^{n-1}+\rho_{n-2}(\xi)\eta^{n-2}+\ldots+\rho_0(\xi). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

The number of the conditions which must be imposed on its coefficients in order that it may have the orders of coincidence indicated in (31) is given by the formula (32). This same formula, then, gives the number of the conditions which must be satisfied by the coefficients in the expression

$$\xi^{-m(n-1)}\{\rho_{n-1}(\xi)\eta^{n-1}+\rho_{n-2}(\xi)\eta^{n-2}+\ldots+\rho_0(\xi)\} \quad . \quad . \quad . \quad . \quad . \quad (34)$$

in order that it may have, for the value $\xi = 0$, the orders of coincidence indicated in (29). Also the general rational function of (ξ, η), conditioned by the set of orders of coincidence (29), must be included under the form (34) since the general rational function of (ξ, η), conditioned by the set of orders of coincidence (31), is included under the form (33).

Transforming the expression (34) to terms of (z, u) we see that the general rational function of (z, u), conditioned for the value $z = \infty$ by the set of orders of coincidence (29), is included under the form

$$\rho_{n-1}\left(\frac{1}{z}\right)u^{n-1}+z^m\rho_{n-2}\left(\frac{1}{z}\right)u^{n-2}+\ldots+z^{m(n-1)}\rho_0\left(\frac{1}{z}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Furthermore, it is obtained from this form on subjecting the coefficients to a succession of conditions whose number is given by the expression (32).

Let us now consider, in its reduced form, the general rational function of (z, u) with its coefficients represented as series in powers of $1/z$. The general rational function so represented, whose coefficients involve no exponent which is $<-\lambda$ we shall indicate by the notation* $R_{-\lambda}(1/z, u)$. Taking $\lambda \gtreqless m(n-1)$ the general function $R_{-\lambda}(1/z, u)$ will certainly include all rational functions of the form (35) and will, therefore, in particular include all rational functions of (z, u) which are adjoint for the value $z = \infty$. To pass from the general function $R_{-\lambda}(1/z, u)$ to the general form given in (35) we must, for $s = 1, 2, \ldots, n$, reduce the degree in z of the coefficient of u^{n-s} in the function from λ to $m(s-1)$. In reducing the general function $R_{-\lambda}(1/z, u)$ to the form (35) then we impose on the coefficients of the function a succession of conditions whose number is given by the sum

$$\sum_{s=1}^{n}\{\lambda-m(s-1)\} = n\lambda-\tfrac{1}{2}mn(n-1). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

To this number we evidently only have to add the number given in (32) in order to obtain the total number of the conditions which we must impose on the coefficients of the general function $R_{-\lambda}(1/z, u)$ in order that it may be adjoint for the value $z = \infty$. We therefore impose just

$$n\lambda+\tfrac{1}{2}\sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)}-1+\frac{1}{\nu_s^{(\infty)}}\right)\nu_s^{(\infty)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

conditions on the constant coefficients in the general function $R_{-\lambda}(1/z, u)$ in order that it may be adjoint for the value $z = \infty$.

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* It may be noted that a suffix will have the significance here attached to $-\lambda$ only in connection with the letter R.

It is evident that the statement just made holds not only for $\lambda \underset{>}{\equiv} m(n-1)$ but also for any value of the integer λ so long as it is at least as great as the greatest degree λ' in z which a coefficient of a power of u in the reduced form of a rational function of (z, u) can have consistently with adjointness for the value $z = \infty$. We see, namely, that among the conditions whose number is given in (37) are included the $n(\lambda-\lambda')$ conditions, which dispose of the terms of degree $>\lambda'$ in the coefficients of the powers of u.

Let us now denote by i an integer which is at least as great as the greatest of the integers $[\mu_1^{(\infty)}], \ldots, [\mu_{r_\infty}^{(\infty)}]$ and impose on the general function $R_{-\lambda}(1/z, u)$ the order of coincidence i with each of the branches of the fundamental equation corresponding to the value $z = \infty$. The orders of coincidence i here in question are evidently adjoint and over and above the conditions requisite to adjointness, whose number is given in (37), impose on the coefficients of the function $R_{-\lambda}(1/z, u)$ further conditions, whose number is given by the sum

$$\sum_{s=1}^{r_\infty}\left(i-\mu_s^{(\infty)}+1-\frac{1}{\nu_s^{(\infty)}}\right)\nu_s^{(\infty)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (38)$$

The total number of the conditions here imposed on the coefficients of the general function $R_{-\lambda}(1/z, u)$ by the orders of coincidence i is therefore

$$n(i+\lambda)-\tfrac{1}{2}\sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)}-1+\frac{1}{\nu_s^{(\infty)}}\right)\nu_s^{(\infty)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (39)$$

We shall now assume not only that λ has been chosen at least as large as the greatest degree of a coefficient in a rational function $R(z, u)$ which is consistent with adjointness relative to the value $z = \infty$ on the part of the function, but also, where this is not already implied, that it has been chosen at least as large as the greatest degree of a coefficient which is consistent with orders of coincidence relative to the value $z = \infty$, which are none of them negative. Let us assume for the moment, too, that we have chosen i positive—what is not necessarily implied for all cases in what precedes. Now impose on the coefficients of the general function $R_{-\lambda}(1/z, u)$ first the conditions required by a set of orders of coincidence for the value $z = \infty$, each one of which is 0. Thereafter imposing on the coefficients the ni further conditions required by a set of orders of coincidence, each one of which is i, we arrive at the total number of the conditions given in (39). Substracting ni then from this number we obtain the expression

$$n\lambda-\tfrac{1}{2}\sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)}-1+\frac{1}{\nu_s^{(\infty)}}\right)\nu_s^{(\infty)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (40)$$

for the total number of the conditions imposed on the coefficients of the general function $R_{-\lambda}(1/z, u)$ by a set of orders of coincidence for the value $z = \infty$, each one of which has the value 0.

From (40) we see, where i is an integer positive or negative, that the expression

(39) gives the number of the conditions imposed on the coefficients of the general function $\mathrm{R}_{-\lambda}(1/z, u)$ by the orders of coincidence i for all n branches, so long as λ has been chosen at least as large as the greatest degree of a coefficient in a rational function $\mathrm{R}(z, u)$ which is consistent with the orders of coincidence i here in question. For i positive this is evident. For negative $i = -j$ it is plain that the coefficients of the general function $\mathrm{R}_{-\lambda}(1/z, u)$, already conditioned by the orders of coincidence $-j$ for all n branches, must be subjected to nj further conditions if we would increase its orders of coincidence to 0 for all n branches. These nj conditions are counted in the expression (40), which gives the number of the conditions required by the orders of coincidence 0 for all n branches. Subtracting nj then from this expression, we obtain, for the number of the conditions imposed on the coefficients of the general function $\mathrm{R}_{-\lambda}(1/z, u)$ by the negative orders of coincidence $i = -j$ for all n branches, the expression given in (39).

Indicate by $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ any set of orders of coincidence with the branches of the r_∞ cycles corresponding to the value $z = \infty$, and take the integer i equal to or less than the least of these. We have in (39) an expression for the number of the conditions imposed on the coefficients of the general function $\mathrm{R}_{-\lambda}(1/z, u)$ by the orders of coincidence i for all n branches, where we assume that λ has been chosen at least as large as the greatest degree of a coefficient in a rational function $\mathrm{R}(z, u)$ which is consistent with the orders of coincidence i here in question. To obtain the number of the conditions imposed on the coefficients of the general function $\mathrm{R}_{-\lambda}(1/z, u)$ by the set of orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$, we must evidently add to the expression (39) the number represented by the sum

$$\sum_{s=1}^{r_\infty} \left(\tau_s^{(\infty)} - i\right) \nu_s^{(\infty)}.$$

This gives us for the number of the conditions imposed on the coefficients of the general function $\mathrm{R}_{-\lambda}(1/z, u)$ by the set of orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$, the expression

$$n\lambda + \sum_{s=1}^{r_\infty} \tau_s^{(\infty)} \nu_s^{(\infty)} - \tfrac{1}{2} \sum_{s=1}^{r_\infty} \left(\mu_s^{(\infty)} - 1 + \frac{1}{\nu_s^{(\infty)}}\right) \nu_s^{(\infty)}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (41)$$

We have derived this formula on assuming that λ has been chosen at least as large as the greatest degree of a coefficient in a rational function $\mathrm{R}(z, u)$ which is consistent with the orders of coincidence i for all n branches. It is now evident, however, that the formula holds so long as λ is not less than the greatest degree λ' in z which a coefficient in a rational function $\mathrm{R}(z, u)$ can have consistently with the possession by the function of the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$. For among the conditions whose number is given in (41) are included the $n(\lambda - \lambda')$ conditions which make the terms of degree $> \lambda'$ in the coefficients of the powers of u vanish.

Under the general rational function $\mathrm{R}_{-\lambda}(1/z, u)$, with coefficients of degree λ in z, is evidently included the general rational function of degree λ in (z, u). To pass from the former function to the latter function we should have, for $s = 1, \ldots, n-1$, to reduce the degree of the coefficient of u^s from λ to $\lambda - s$. This would impose on the coefficients of the function $\mathrm{R}_{-\lambda}(1/z, u)$ in all $\frac{1}{2}n(n-1)$ conditions. Now we have seen in § 1 that the degree of a rational function of (z, u), which is adjoint for the value $z = \infty$, must be $\leqq \mathrm{N}-1$. Taking $\lambda = \mathrm{N}-1$, formula (37) gives us

$$n(\mathrm{N}-1)+\tfrac{1}{2}\sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)}-1+\frac{1}{\nu_s^{(\infty)}}\right)\nu_s^{(\infty)}$$

for the number of the conditions which must be imposed on the coefficients of the general function $\mathrm{R}_{-\mathrm{N}+1}(1/z, u)$ in order that it may be adjoint for the value $z = \infty$. Among these conditions are included the $\frac{1}{2}n(n-1)$ conditions requisite to reduce the general function here in question to degree $\mathrm{N}-1$. For the number of the conditions which must be imposed on the coefficients of the general reduced rational function of (z, u) of degree $\mathrm{N}-1$, in order that it may be adjoint for the value $z = \infty$, we then obtain the expression

$$n(\mathrm{N}-1)-\tfrac{1}{2}n(n-1)+\tfrac{1}{2}\sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)}-1+\frac{1}{\nu_s^{(\infty)}}\right)\nu_s^{(\infty)}. \quad . \quad . \quad . \quad . \quad . \quad (42)$$

More generally, on subtracting $\frac{1}{2}n(n-1)$ from the expression given in (41), we obtain

$$n\lambda-\tfrac{1}{2}n(n-1)+\sum_{s=1}^{r_\infty}\tau_s^{(\infty)}\nu_s^{(\infty)}-\tfrac{1}{2}\sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)}-1+\frac{1}{\nu_s^{(\infty)}}\right)\nu_s^{(\infty)} \quad . \quad . \quad . \quad . \quad (43)$$

for the number of the conditions imposed on the coefficients of the general rational function of (z, u) of degree λ by the set of orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$, where λ is not less than the greatest degree which a rational function can have and yet possess these orders of coincidence.

The general rational function of (z, u), whose coefficients are of degree λ in z, we shall represent in the form

$$\mathrm{R}_{-\lambda}\left(\frac{1}{z}, u\right) = \mathrm{R}^{(i)}{}_{-\lambda}\left(\frac{1}{z}, u\right)+z^{-i}\left(\left(\frac{1}{z}, u\right)\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

where in the first element the index (i) signifies that in the coefficients, arranged according to powers of $1/z$, the highest power which may appear is $(1/z)^{i-1}$, while in the second element the notation $((1/z, u))$ signifies a reduced polynomial in u whose coefficients, expanded in powers of $1/z$, present no negative exponents. Taking i sufficiently large and imposing on the function $\mathrm{R}_{-\lambda}(1/z, u)$ the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ for the value $z = \infty$ the coefficients of the second element in the sum on the right of (44) will be unaffected. The number of the conditions to which the coefficients of the function $\mathrm{R}_{-\lambda}(1/z, u)$ are thereby subjected, and therefore the number of the conditions imposed on the coefficients of the function $\mathrm{R}^{(i)}{}_{-\lambda}(1/z, u)$ by the orders of coincidence here in question, is given by the expression (41) on assuming that λ has been chosen sufficiently large. Subtracting this expression from $n(\lambda+i)$, the total number of the constant coefficients in the general function $R^{(i)}_{-\lambda}(1/z, u)$, we obtain the expression

$$l_\infty = ni - \sum_{s=1}^{r_\infty} \tau_s^{(\infty)}\nu_s^{(\infty)} + \tfrac{1}{2}\sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)} - 1 + \frac{1}{\nu_s^{(\infty)}}\right)\nu_s^{(\infty)}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (45)$$

for the total number of the arbitrary constants involved in the function $R^{(i)}_{-\lambda}(1/z, u)$, conditioned by the set of orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$. Dropping the now superfluous suffix, $-\lambda$, we may say that the expression (45) gives the number of the arbitrary constants involved in the general rational function $R^{(i)}(1/z, u)$, conditioned by the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$, where the index (i) still implies that the coefficients of the rational function expanded in powers of $1/z$ involve no powers as high as $(1/z)^i$.

In the representation

$$R\left(\frac{1}{z}, u\right) = R^{(i)}\left(\frac{1}{z}, u\right) + z^{-i}\left(\left(\frac{1}{z}, u\right)\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (46)$$

of the general rational function of (z, u) conditioned by the set of orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ corresponding to the value $z = \infty$ we shall find it convenient to write

$$R^{(i)}\left(\frac{1}{z}, u\right) = -\sum_{s=1}^{l_\infty} \delta_s^{(\infty)}\phi_s^{(i)}\left(\frac{1}{z}, u\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (47)$$

so as to bring into evidence the l_∞ arbitrary constants $\delta_s^{(\infty)}$ involved in the element $R^{(i)}(1/z, u)$. The l_∞ functions $\phi_s^{(i)}(1/z, u)$ are specific linearly independent functions of the form implied by the index (i) and possessing for the value $z = \infty$ orders of coincidence which do not fall short of the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ respectively. The number l_∞, it is to be borne in mind, depends not alone on the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ here in question, but also on the particular value chosen for the integer i. It is, also, not to be forgotten that i is taken so large that terms involving powers of $1/z$ higher than $(1/z)^{i-1}$ are not conditioned* by the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$. The general rational function of (z, u), conditioned by the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$, we shall then represent in the form

$$R\left(\frac{1}{z}, u\right) = -\sum_{s=1}^{l_\infty} \delta_s^{(\infty)}\phi_s^{(i)}\left(\frac{1}{z}, u\right) + z^{-i}\left(\left(\frac{1}{z}, u\right)\right) \quad . \quad . \quad . \quad . \quad . \qquad (48)$$

where the number l_∞ is given by the expression in (45) and where the constant coefficients in $((1/z, u))$ are all arbitrary.

In order that a rational function $\Psi(z, u)$ may be complementary adjoint to the general function $R(1/z, u)$ here in question, for the value $z = \infty$, we know it is

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* When we here say that a term is not conditioned by the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ we mean that it already possesses orders of coincidence at least as great as these.

necessary and sufficient that the constant coefficient of zu^{n-1} should be 0 in the reduced form of the product

$$\mathrm{R}\left(\frac{1}{z}, u\right) \Psi(z, u) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

with the coefficients of the powers of u expanded in powers of $1/z$. In order that the orders of coincidence of a rational function $\Psi(z, u)$ for the value $z = \infty$ may be complementary adjoint to the order 2 to the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$, it is necessary and sufficient that the principal residue, relative to the value $z = \infty$, in the product (49), should be 0. This we have seen in § 2. In order, then, that the orders of coincidence of the function $\Psi(z, u)$ for the value $z = \infty$ should not fall short of the orders of coincidence $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$ defined by the equalities

$$\tau_s^{(\infty)} + \bar{\tau}_s^{(\infty)} = \mu_s^{(\infty)} + 1 + \frac{1}{\nu_s^{(\infty)}}, \; s = 1, 2, \ldots, r_\infty \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

it is necessary and sufficient that the principal residue in the product (49) should be 0. Among the conditions imposed on the constants in the function $\Psi(z, u)$ by the orders of coincidence here in question are included those obtained on equating to 0 the principal residue relative to $z = \infty$ in the product

$$\mathrm{R}^{(i)}\left(\frac{1}{z}, u\right) \Psi(z, u). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

To the function $\Psi(z, u)$ we shall now give the form

$$\Psi(z, u) = \sum_{t=1}^{n} \sum_{q=-i+2}^{i-1} \alpha_{q-1, t-1} z^{q-1} u^{t-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

We shall assume that the integer i has been chosen so large that terms involving z^{-i} and higher powers of $1/z$ are unconditioned by either of the sets of orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$, or $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$. Furthermore, we shall assume, where this is not already implied, that i has been chosen so large that a rational function of (z, u), conditioned by either of these sets of orders of coincidence, cannot involve a power of z higher than z^{i-2}. The function $\mathrm{R}^{(i)}(1/z, u)$ is then of the type $\mathrm{R}^{(i)}_{-i+2}(1/z, u)$.

Write the product (51) in the form

$$\mathrm{R}^{(i)}_{-i+2}\left(\frac{1}{z}, u\right) \sum_{t=1}^{n} \sum_{q=-i+2}^{i-1} \alpha_{q-1, t-1} z^{q-1} u^{t-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

with the constants $\alpha_{q-1, t-1}$ as yet arbitrary. Now equate to 0 the principal residue in this product. We thus subject the constants $\alpha_{q-1, t-1}$ to l_∞ independent conditions, that is to say, we subject these constants to as many conditions as there are arbitrary constants involved in $\mathrm{R}^{(i)}_{-i+2}(1/z, u)$. To see this we note first that the principal residue in a product

$$\phi^{(i)}\left(\frac{1}{z}, u\right) \sum_{t=1}^{n} \sum_{q=-i+2}^{i-1} \alpha_{q-1, t-1} z^{q-1} u^{t-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

cannot be 0 independently of the values of the constants $\alpha_{q-1,t-1}$ where $\phi^{(i)}(1/z, u)$ is a specific function of the type $\mathrm{R}^{(i)}_{-i+2}(1/z, u)$. We shall suppose that $\phi^{(i)}(1/z, u)$ actually contains a term $\beta z^{-q}u^{n-t}$ and that u^{n-t} is the highest power of u which appears in the function, while z^{-q} is the highest power of $1/z$ which actually presents itself in the coefficient of this power of u. For the second factor in the product (54) we shall take the single term $\alpha_{q-1,t-1}z^{q-1}u^{t-1}$. The principal residue of the product is then evidently $\beta\alpha_{q-1,t-1}$ and is not 0 independently of the value of $\alpha_{q-1,t-1}$. To equate to 0 the principal residue in a product of a type (54) then imposes a condition on the constants $\alpha_{q-1,t-1}$.

Represent the first factor of the product (53) in the form given in (47) and equate to 0 the principal residue in the product for arbitrary values of the l_∞ constants $\delta_s^{(\infty)}$. We thus subject the constants $\alpha_{q-1,t-1}$ to l_∞ conditions. The individual conditions are obtained on equating to 0 the principal residues in the products

$$\phi_s^{(i)}\left(\frac{1}{z}, u\right) \sum_{t=1}^{n} \sum_{q=-i+2}^{i-1} \alpha_{q-1,t-1}z^{q-1}u^{t-1}; \quad s = 1, 2, \ldots, l_\infty. \quad . \quad . \quad . \quad . \quad (55)$$

That the l_∞ conditions so imposed on the constants $\alpha_{q-1,t-1}$ are linearly independent of one another is readily shown. For suppose that there is a linear equation connecting the principal residues of the l_∞ products (55), regarded as linear expressions in the constants $\alpha_{q-1,t-1}$, and suppose in this equation that the multipliers are $d_1, d_2, \ldots, d_{l_\infty}$ respectively. Constructing the function

$$\phi^{(i)}\left(\frac{1}{z}, u\right) = \sum_{s=1}^{l_\infty} d_s\phi_s^{(i)}\left(\frac{1}{z}, u\right),$$

we see that we should have the principal residue equal to 0 in a product of the type (54) independently of the values of the constants $\alpha_{q-1,t-1}$. This, however, we have seen to be impossible. It follows that the l_∞ conditions to which we subject the constants $\alpha_{q-1,t-1}$ on equating to 0 the principal residues in the products (55) are linearly independent of one another. On equating to 0 the principal residue in the product (53), for arbitrary values of the l_∞ constants $\delta_s^{(\infty)}$ involved in the first factor, we then impose on the constants $\alpha_{q-1,t-1}$ just l_∞ linearly independent conditions. These l_∞ conditions are all necessary in order that the function

$$\Psi(z, u) = \sum_{t=1}^{n} \sum_{q=-i+2}^{i-1} \alpha_{q-1,t-1}z^{q-1}u^{t-1}$$

should have orders of coincidence for the value $z = \infty$ which do not fall short of the numbers $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$ respectively. To prove that these conditions are also sufficient we only have to show that l_∞ is the total number of the conditions to which we must subject the constants $\alpha_{q-1,t-1}$ in order that the function $\Psi(z, u)$ may have the orders of coincidence $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$ for the value $z = \infty$.

For the number of the conditions imposed on the coefficients of the function $\Psi(z, u)$ by the set of orders of coincidence $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$ we derive from (41) the expression

$$n(i-2)+\sum_{s=1}^{r_\infty} \bar{\tau}_r^{(\infty)} \nu_s^{(\infty)}-\tfrac{1}{2} \sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)}-1+\frac{1}{\nu_s^{(\infty)}}\right) \nu_s^{(\infty)} .$$

From the equalities (50) we have

$$\sum_{s=1}^{r_\infty} \tau_s^{(\infty)} \nu_s^{(\infty)}+\sum_{s=1}^{r_\infty} \bar{\tau}_s^{(\infty)} \nu_s^{(\infty)}-2n-\sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)}-1+\frac{1}{\nu_s^{(\infty)}}\right) \nu_s^{(\infty)}=0,$$

and by the aid of this equality the expression preceding can evidently be written in the form

$$ni-\sum_{s=1}^{r_\infty} \tau_s^{(\infty)} \nu_s^{(\infty)}+\tfrac{1}{2} \sum_{s=1}^{r_\infty}\left(\mu_s^{(\infty)}-1+\frac{1}{\nu_s^{(\infty)}}\right) \nu_s^{(\infty)} .$$

This then is an expression for the total number of the conditions to which we must subject the coefficients $\alpha_{q-1, t-1}$ in order that the function $\Psi(z, u)$ may have the orders of coincidence $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$. This is, however, also the expression for l_∞ given in (45). The total number of the conditions which we must impose on the coefficients of the function $\Psi(z, u)$ in order that it may have the orders of coincidence $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$ is therefore l_∞ and the conditions themselves are all obtained on equating to 0 the principal residue in the product (51) for arbitrary values of the constants $\delta_s^{(\infty)}$ involved in the factor $\mathrm{R}^{(i)}(1/z, u)$. The necessary and sufficient conditions then in order that the function $\Psi(z, u)$ may have for the value $z=\infty$ orders of coincidence which are complementary adjoint to the order 2 to the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ are obtained on equating to 0 the principal residue in the product (51), where the function $\mathrm{R}^{(i)}(1/z, u)$ is conditioned by the set of orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$. On taking in particular for the function $\Psi(z, u)$ the integral polynomial form

$$\Psi(z, u)=\sum_{t=1}^{n} \sum_{q=1}^{i-1} \alpha_{q-1, t-1} z^{q-1} u^{t-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

it must evidently still hold true that the necessary and sufficient conditions in order that the function $\Psi(z, u)$ may have for the value $z=\infty$ orders of coincidence which are complementary adjoint to the order 2 to the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ are obtained on equating to 0 the principal residue in the product (51). It is to be borne in mind that throughout the preceding argument we have assumed the integer i to be chosen sufficiently large for our purpose. We assumed, namely, that it was chosen large enough at least to ensure that the coefficient of a term involving z^{-i} or a higher power of $1/z$ was not conditioned by either of the sets of orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$, or $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$, and at the same time we assumed that the possession of either of these sets of orders of coincidence by a function was incompatible with the presence in the function of a term involving z to a higher power than z^{i-2}. If $\Psi(z, u)$ is a polynomial of assigned degree M in z the necessary and sufficient conditions that it may have the orders of coincidence $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$, for the value $z = \infty$ are obtained as above on equating to 0 the principal residue in the product (51), where the integer i is subject to the conditions already specified, but where it is well to bear in mind that the formula (56) implies that i has been taken $\geqq \mathrm{M}+2$.

§ 5. The number of the cycles into which the branches of the equation (1) group themselves for a finite value $z = a_\kappa$ we shall indicate by the symbol r_κ, and the orders of these cycles we shall designate by $\nu_1^{(\kappa)}, \ldots, \nu_{r_\kappa}^{(\kappa)}$ respectively. For the corresponding numbers in connection with the value $z = \infty$ we have already employed the symbols r_∞ and $\nu_1^{(\infty)}, \ldots, \nu_{r_\infty}^{(\infty)}$. So in general, numbers associated with the value $z = a_\kappa$ will be designated by an index or suffix κ, and those associated with the value $z = \infty$ by an index or suffix ∞. For example, adjointness relative to a value $z = a_\kappa$ is defined by the orders of coincidence

$$\mu_1^{(\kappa)} - 1 + \frac{1}{\nu_1^{(\kappa)}}, \ldots, \mu_{r_\kappa}^{(\kappa)} - 1 + \frac{1}{\nu_{r_\kappa}^{(\kappa)}}.$$

When we speak of a set of orders of coincidence for a given value of the variable z it will always be understood, of course, that these are integral multiples of the corresponding numbers $1/\nu_1^{(\kappa)}, \ldots, 1/\nu_{r_\kappa}^{(\kappa)}$.

A set of orders of coincidence corresponding to a value $z = a_\kappa$ we shall designate by the notation $\tau_1^{(\kappa)}, \ldots, \tau_{r_\kappa}^{(\kappa)}$. Assigning a system of sets of orders of coincidence for all values of the variable z, the value $z = \infty$ included, we shall designate such system by the notation (τ). We shall here understand that all but a finite number of the orders of coincidence involved in a system (τ) have the value 0. Such a system (τ) we shall call a *Basis of Coincidences* for the building of a rational function, or, more briefly, we shall simply refer to it as the *basis* (τ). A rational function of (z, u) we shall say is built on the basis (τ) if its orders of coincidence for the different values of z in no case fall short of the corresponding orders of coincidence given by the basis. We shall say of two bases (τ) and $(\bar{\tau})$ that they are *complementary* to each other when for finite values $z = a_\kappa$, the corresponding orders of coincidence furnished by the bases are connected by the relations

$$\tau_s^{(\kappa)} + \bar{\tau}_s^{(\kappa)} = \mu_s^{(\kappa)} - 1 + \frac{1}{\nu_s^{(\kappa)}}; \quad s = 1, 2, \ldots, r_\kappa, \quad \ldots \ldots \quad (57)$$

while for the value $z = \infty$ the orders of coincidence are connected by the relations

$$\tau_s^{(\infty)} + \bar{\tau}_s^{(\infty)} = \mu_s^{(\infty)} + 1 + \frac{1}{\nu_s^{(\infty)}}; \quad s = 1, 2, \ldots, r_\infty. \quad \ldots \ldots \quad (58)$$

By the notation $(\tau)'$ we shall designate that part of the basis (τ) which has reference to finite values of the variable z, and by $(\tau)^{(\infty)}$ we shall mean that part of the basis (τ) which refers to the value $z = \infty$. We shall then speak of a rational function of (z, u) which is conditioned by the partial basis $(\tau)'$ or by the partial basis $(\tau)^{(\infty)}$.

Any rational function of (z, u) can be represented in the form

$$\mathrm{H}(z, u) = \sum_{\kappa} \frac{\phi^{(i_\kappa)}(z, u)}{(z-a_\kappa)^{i_\kappa}} + \mathrm{P}(z, u), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

where $\mathrm{P}(z, u)$ is a polynomial in (z, u), where the summation is extended to a finite number of values $z = a_\kappa$ only, and where any numerator $\phi^{(i_\kappa)}(z, u)$ is a polynomial in (z, u) of degree $i_\kappa - 1$ in z. The polynomials are here, of course, assumed to be reduced in u.

We shall first assume that the basis (τ) involves no positive orders of coincidence for finite values of the variable z, no such restriction, however, being made for the value $z = \infty$. Writing $\tau_s^{(\kappa)} = -\sigma_s^{(\kappa)}$, we may say of a function built on the basis (τ) that, for a finite value $z = a_\kappa$, it becomes infinite to orders which do not exceed the respective numbers of the corresponding set $\sigma_1^{(\kappa)}, \ldots, \sigma_{r_\kappa}^{(\kappa)}$, while for the value $z = \infty$ its orders of coincidence do not fall short of the numbers $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ respectively. Here the numbers $\sigma_s^{(\kappa)}$ are zero or positive, whereas the numbers $\tau_s^{(\infty)}$ may be positive, zero, or negative. The orders of coincidence furnished by the basis $(\bar{\tau})$ for finite values of the variable z are in this case plainly all adjoint.

Suppose $\mathrm{H}(z, u)$ in (59) to be the general rational function of (z, u) conditioned by the partial basis $(\tau)'$ here in question. The polynomial $\mathrm{P}(z, u)$ is evidently arbitrary. Furthermore we may, in the summation on the right-hand side of the formula, take for i_κ the greatest of the integers

$$[\mu_s^{(\kappa)} + \sigma_s^{(\kappa)}]; \; s = 1, 2, \ldots, r_\kappa. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

To show this we note that the orders of coincidence of the numerator $\phi^{(i_\kappa)}(z, u)$ with the branches of the respective cycles corresponding to the value $z = a_\kappa$ must not fall short of the numbers

$$i_\kappa - \sigma_s^{(\kappa)}, \; s = 1, 2, \ldots, r_\kappa. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

These numbers, however, would be simultaneously greater than the corresponding numbers $\mu_s^{(\kappa)}$ if we should give i_κ a value greater than the greatest of the integers in (60), and the numerator $\phi^{(i_\kappa)}(z, u)$ would therefore, by a theorem proved in § 3, be divisible by the factor $z - a_\kappa$.

Choosing then for i_κ the greatest of the integers in (60), we readily see that the orders of coincidence in (61) are not simultaneously greater than the corresponding numbers $\mu_s^{(\kappa)}$, and that therefore the general numerator $\phi^{(i_\kappa)}(z, u)$ is not divisible by the factor $z - a_\kappa$. We see at the same time that the orders of coincidence in (61) are adjoint relatively to the value $z = a_\kappa$. As a consequence, the number of the conditions to which we must subject the otherwise unconditioned constants in the general function of the type $\phi^{(i_\kappa)}(z, u)$ in imposing on it the orders of coincidence given in (61) is obtained on substituting these orders of coincidence for the symbols μ'_s in (25). For the number of the conditions in question we thus obtain

$$ni_\kappa - \sum_{s=1}^{r_\kappa} \sigma_s^{(\kappa)} \nu_s^{(\kappa)} - \tfrac{1}{2} \sum_{s=1}^{r_\kappa} \left(\mu_s^{(\kappa)} - 1 + \frac{1}{\nu_s^{(\kappa)}}\right) \nu_s^{(\kappa)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

Subtracting this number from the total number ni_κ of the arbitrary constant coefficients in the unconditioned function of the form $\phi^{(i_\kappa)}(z, u)$, we obtain the expression

$$l_\kappa = \sum_{s=1}^{r_\kappa} \sigma_s^{(\kappa)} \nu_s^{(\kappa)} + \tfrac{1}{2} \sum_{s=1}^{r_\kappa} \left(\mu_s^{(\kappa)} - 1 + \frac{1}{\nu_s^{(\kappa)}}\right) \nu_s^{(\kappa)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

for the number of the arbitrary constants involved in the numerator $\phi^{(i_\kappa)}(z, u)$ of an element of the summation on the right-hand side of (59). This numerator then we can write in the form

$$\phi^{(i_\kappa)}(z, u) = \sum_{s=1}^{l_\kappa} \delta_s^{(\kappa)} \phi_s^{(i_\kappa)}(z, u), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

where the l_κ coefficients $\delta_s^{(\kappa)}$ are arbitrary constants, while the l_κ functions $\phi_s^{(i_\kappa)}(z, u)$ are linearly independent and possess orders of coincidence for the value $z = a_\kappa$ which do not fall short of the numbers given in (61). It is evident that the summation in (59) is to be extended not only to all those finite values of the variable z to which negative elements in the basis (τ) correspond, but also to all those values $z = a_\kappa$ for which the corresponding numbers $[\mu_1^{(\kappa)}], \ldots, [\mu_{r_\kappa}^{(\kappa)}]$, are not all 0, even if the corresponding elements in the basis (τ) are all 0.

In order that a rational function $\mathrm{H}(z, u)$ should be built on the basis (τ), it is necessary and sufficient that it should be simultaneously representable in the two forms (48) and (59). Identifying the representation of the function $\mathrm{H}(z, u)$ given in (59) with the representation given in (48), we have

$$\sum_\kappa \sum_{s=1}^{l_\kappa} \frac{\delta_s^{(\kappa)} \phi_s^{(i_\kappa)}(z, u)}{(z - a_\kappa)^{i_\kappa}} + \sum_{s=1}^{l_\infty} \delta_s^{(\infty)} \phi_s^{(i)}\left(\frac{1}{z}, u\right) = -\mathrm{P}(z, u) + z^{-i}\left(\left(\frac{1}{z}, u\right)\right). \quad . \quad . \quad (65)$$

Here $\mathrm{P}(z, u)$ evidently identifies itself with that part of the sum $-\sum_{s=1}^{l_\infty} \delta_s^{(\infty)} \phi_s^{(i)}(1/z, u)$ which is integral in (z, u) and the conditions to which the constants δ are subjected, because of the identity (65), are obtained on developing in powers of $1/z$ the coefficients of the several powers of u on the left-hand side of the identity and equating to 0 the aggregate coefficient of $z^{-q}u^{n-t}$ for the values $q = 1, 2, \ldots, i-1$; $t = 1, 2, \ldots, n$, since 0 is the coefficient of the corresponding term on the right-hand side of the identity. If for $q \geqq i$ we equate the coefficient of $z^{-q}u^{n-t}$ on the left-hand side of the identity to the corresponding coefficient on the right-hand side, we so determine an otherwise unconditioned coefficient of the expression $z^{-i}((1/z, u))$ in terms of the constants δ. The coefficient of $z^{-q}u^{n-t}$ on the left-hand side of the identity is an expression linear in the constants δ which we shall represent by the notation $c_{-q,\,n-t}$. The conditions imposed on the constants δ by the identity (65) are then embodied in the identity

$$\sum_{t=1}^{n}\sum_{q=1}^{i-1} c_{-q,n-t}z^{-q}u^{n-t} = 0. \qquad \text{(66)}$$

The $n(i-1)$ conditions imposed on the constants δ by the equations

$$c_{-q,n-t} = 0, \quad q = 1, 2, \ldots, i-1\,; \quad t = 1, 2, \ldots, n \qquad \text{(67)}$$

may or may not be independent of one another.

The general rational function of (z, u) conditioned for the value $z = a_\kappa$ by the orders of coincidence $\tau_1^{(\kappa)}, \ldots, \tau_{r_\kappa}^{(\kappa)}$ can, after the analogy of the function $\Phi(z,u)$ in formula (19), be represented in the form

$$\frac{\phi^{(i_\kappa)}(z, u)}{(z-a_\kappa)^{i_\kappa}} + ((z-a_\kappa, u)). \qquad \text{(68)}$$

Furthermore, the first element in this expression can, after the analogy of formula (27), be represented in the form

$$\frac{\phi^{(i_\kappa)}(z, u)}{(z-a_\kappa)^{i_\kappa}} = \sum_{t=1}^{n}\sum_{q=1}^{j_\kappa-1} \gamma^{(\kappa)}{}_{-q,n-t}z^{-q}u^{n-t} + z^{-j_\kappa}\left(\left(\frac{1}{z}, u\right)\right). \qquad \text{(69)}$$

From (64) we see that the coefficients $\gamma^{(\kappa)}{}_{-q,n-t}$ on the right-hand side of this identity are linear in terms of the l_κ arbitrary constants $\delta_s^{(\kappa)}$.

Taking $\Psi(z, u)$ an integral rational function of (z, u) of arbitrarily assigned degree M in z, and equating too the principal residue relative to the value $z = \infty$ in the product

$$\sum_{t=1}^{n}\sum_{q=1}^{j_\kappa-1} \gamma^{(\kappa)}{}_{-q,n-t}z^{-q}u^{n-t} \,.\, \Psi(z, u), \qquad \text{(70)}$$

we see, on referring to formula (28) and the related text, that we thus obtain the necessary and sufficient conditions in order that $\Psi(z, u)$ may possess for the value $z = a_\kappa$ a set of orders of coincidence which are complementary adjoint to the orders of coincidence $\tau_1^{(\kappa)}, \ldots, \tau_{r_\kappa}^{(\kappa)}$, the integer j_κ being assumed to have been taken sufficiently large. For the degree M of $\Psi(z, u)$ in z we shall find it convenient to choose a definite integer, and for this definite integer it will suit our present purpose to select the greatest degree in z of a rational function of (z, u) which is compatible with the possession by the function of the orders of coincidence $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$ for the value $z = \infty$. We assume, then, that M has been so chosen, and at the same time we assume that the integers j_κ corresponding to the various values $z = a_\kappa$ have all been taken sufficiently large.

In § 4 we saw that the necessary and sufficient conditions in order that an integral rational function $\Psi(z, u)$ should, for the value $z = \infty$, have orders of coincidence which are complementary adjoint to the order 2 to the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ are obtained on equating to 0 the principal residue relative to the value $z = \infty$ in the product

$$\mathrm{R}^{(i)}\left(\frac{1}{z}, u\right) \Psi(z, u) = -\sum_{s=1}^{l_\infty} \delta_s^{(\infty)} \phi_s^{(i)}\left(\frac{1}{z}, u\right) . \Psi(z, u).$$

Here $\mathrm{R}^{(i)}(1/z, u)$ is the general function of the form implied by the index, subject to the condition that it possess the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$. Furthermore, the index i exceeds by 2 at least the degree of $\Psi(z, u)$ in z and is at the same time so large that a term involving z^{-i}, or a higher power of $1/z$, is unconditioned by either of the sets of orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ or $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$.

Writing

$$\sum_{s=1}^{r_\infty} \delta_s^{(\infty)} \phi_s^{(i)}\left(\frac{1}{z}, u\right) = -\mathrm{P}(z, u) + \sum_{t=1}^{n} \sum_{q=1}^{i-1} \gamma^{(\infty)}{}_{-q, n-t} z^{-q} u^{n-t}, \quad . \quad . \quad . \quad . \qquad (71)$$

we see that the necessary and sufficient conditions in order that $\Psi(z, u)$ may have for the value $z = \infty$ orders of coincidence which are complementary adjoint to the order 2 to the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$ are obtained on equating to 0 the principal residue relative to the value $z = \infty$ in the product

$$\sum_{t=1}^{n} \sum_{q=1}^{i-1} \gamma^{(\infty)}{}_{-q, n-t} z^{-q} u^{n-t} . \Psi(z, u). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (72)$$

Here the coefficients $\gamma^{(\infty)}{}_{-q, n-t}$ are linear in the arbitrary constants $\delta_s^{(\infty)}$. Choosing the integer i sufficiently large we shall now take this for the value also of each of the integers j_κ above. For the constants $c_{-q, n-t}$ in (66) we evidently have

$$c_{-q, n-t} = \sum_{\kappa} \gamma^{(\kappa)}{}_{-q, n-t}\,; \quad q = 1, 2, \ldots, i-1\,; \quad t = 1, 2, \ldots, n, \quad . \quad . \quad . \qquad (73)$$

where the summation with regard to κ is supposed to extend not only to the finite values $z = a_\kappa$, which appear in the double summation in (65), but where it is also assumed to contain the term $\gamma^{(\infty)}{}_{-q, n-t}$. The expressions $c_{-q, n-t}$ are linear in terms of the arbitrary constants δ corresponding to the finite values $z = a_\kappa$ and the value $z = \infty$.

On equating to 0 independently of the values of the arbitrary constants δ the principal residue relative to the value $z = \infty$ in the product

$$\sum_{t=1}^{n} \sum_{q=1}^{i-1} c_{-q, n-t} z^{-q} u^{n-t} . \Psi(z, u) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (74)$$

we evidently obtain the necessary and sufficient conditions in order that the integral rational function $\Psi(z, u)$ of degree M in z should be built on the basis $(\bar{\tau})$ complementary to the basis (τ). The conditions so obtained namely coincide with the aggregate of the conditions obtained on equating to 0 the principal residue relative to the value $z = \infty$ in each of the products (70) and in the product (72).

If in the product (74) we take for the function $\Psi(z, u)$ the general integral rational function of degree $i-2$ in z, and if in this product we equate to 0 independently of the values of the arbitrary constants δ the principal residue relative to the value $z = \infty$ we evidently also in this case obtain the necessary and sufficient conditions that the function $\Psi(z, u)$ may be built on the basis $(\bar{\tau})$. For the conditions so arrived at include among them the conditions obtained on equating to 0 the principal residue relative to the value $z = \infty$ in the product (72). These conditions, however, are necessary and sufficient in order that, for the value $z = \infty$, the integral rational function $\Psi(z, u)$ of degree $i-2$ in z should have orders of coincidence which are complementary adjoint to the order 2 to the orders of coincidence $\tau_1^{(\infty)}, \ldots, \tau_{r_\infty}^{(\infty)}$. They therefore involve the reduction of the degree of $\Psi(z, u)$ in z from $i-2$ to M. On taking, then, for $\Psi(z, u)$ in the product (74) the general integral rational function of (z, u) of degree $i-2$ in z and equating to 0 independently of the values of the arbitrary constants δ the principal residue relative to the value $z = \infty$ in the product we impose on the coefficients of the function $\Psi(z, u)$ the necessary and sufficient conditions in order that it may be built on the basis $(\bar{\tau})$.

The general integral rational function $\Psi(z, u)$, of degree $i-2$ in z, conditioned by equating to 0 the principal residue in the product (74), independently of the values of the arbitrary constants δ, is readily seen to be the most general rational function built on the basis $(\bar{\tau})$. For the orders of coincidence furnished by the basis $(\bar{\tau})$ for finite values of the variable z are here all adjoint, and therefore the general rational function of (z, u) built on the basis $(\bar{\tau})$ must be integral. Also i was chosen sufficiently large so that a rational function conditioned for $z = \infty$ by the orders of coincidence $\bar{\tau}_1^{(\infty)}, \ldots, \bar{\tau}_{r_\infty}^{(\infty)}$ could not be of degree in z greater than $i-2$. We might here again recall the limitations imposed on our choice of the integer i in the preceding argument:—It was taken $\geqq \mathrm{M}+2$ and also so large that terms involving z^{-i} and higher powers of $1/z$ in the coefficients were not conditioned by the partial bases $(\tau)^{(\infty)}$ and $(\bar{\tau})^{(\infty)}$. At the same time we required i to be sufficiently large to serve for each of the integers j_κ in the products (70), the least values eligible for these integers being severally dependent on the degree M of $\Psi(z, u)$ in z.

§ 6. The $n(i-1)$ coefficients $c_{-q, n-t}$ regarded as linear expressions in the arbitrary constants δ may or may not be linearly independent of one another. We shall suppose that just λ of them are linearly independent of one another, the remaining $n(i-1)-\lambda$ coefficients being linearly expressible in terms of these. Indicating such λ linearly independent coefficients by the notation $c_1, \ldots, c_\lambda$, we shall assume that the $n(i-1)$ coefficients $c_{-q, n-t}$ are all expressed linearly in terms of these λ coefficients. The principal residue relative to the value $z = \infty$ in the product (74) will then be an expression bilinear in $c_1, \ldots, c_\lambda$ and the coefficients of $\Psi(z, u)$. In this expression equating to 0 the multiplier of each of the quantities $c_1, \ldots, c_\lambda$, we impose on the constant coefficients of $\Psi(z, u)$ conditions not greater in number than λ. The function $\Psi(z, u)$ so conditioned is built on the basis $(\bar{\tau})$, for with $\Psi(z, u)$ so conditioned the principal residue relative to $z = \infty$ in the product (74) is 0 independently of the values of the arbitrary constants δ. The general rational function of (z, u) built on the basis $(\bar{\tau})$ must then involve at least $n(i-1)-\lambda$ arbitrary coefficients, since the general integral rational function $\Psi(z, u)$ of degree $i-2$ in z has $n(i-1)$ arbitrary constant coefficients.

Indicating by $n(i-1)-\lambda'$ the actual number of arbitrary coefficients involved in the general rational function $\Psi(z, u)$ built on the basis $(\bar{\tau})$, we have $n(i-1)-\lambda' \geqq n(i-1)-\lambda$, and therefore $\lambda' \leqq \lambda$. Let us now consider the product

$$\sum_{t=1}^{n} \sum_{q=1}^{i-1} c'_{-q,n-t} z^{-q} u^{n-t} \,.\, \Psi(z, u) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (75)$$

in which the $n(i-1)$ coefficients $c'_{-q,n-t}$ are arbitrary constants, while $\Psi(z, u)$ is a specific function of degree in z not greater than $i-2$. The principal residue in this product cannot be 0 independently of the values of the constants $c'_{-q,n-t}$. For if u^{t-1} be the highest power of u which appears in $\Psi(z, u)$, and if the term $\alpha_{q-1,t-1} z^{q-1} u^{t-1}$ $(\alpha_{q-1,t-1} \neq 0)$ actually presents itself in the function, the principal residue in the product

$$c'_{-q,n-t} z^{-q} u^{n-t} \,.\, \Psi(z, u)$$

is evidently $c'_{-q,n-t} \alpha_{q-1,t-1}$, which can only be 0 for $c'_{-q,n-t} = 0$.

Let $\Psi_1(z, u), \ldots, \Psi_\rho(z, u)$ be ρ linearly independent integral rational functions of degree in z not greater than $i-2$. If in each of the products

$$\sum_{t=1}^{n} \sum_{q=1}^{i-1} c'_{-q,n-t} z^{-q} u^{n-t} \,.\, \Psi(z, u)\,; \; s = 1, 2, \ldots, q, \quad . \quad . \quad . \quad . \quad . \quad (76)$$

we equate the principal residue to 0, we impose ρ independent conditions on the constants $c'_{-q,n-t}$. For suppose the principal residues in the ρ products, regarded as expressions linear in the arbitrary constants $c'_{-q,n-t}$, to be linearly connected, and suppose $d_1, \ldots, d_\rho$ to be the respective multipliers in the relation existing between them. On constructing the function

$$\Psi(z, u) = d_1 \Psi_1(z, u) + \ldots + d_\rho \Psi_\rho(z, u),$$

the principal residue relative to $z = \infty$ in the product (75) would be 0 independently of the values of the constants $c'_{-q,n-t}$, and this we have seen to be impossible. It follows that we impose ρ independent conditions on the arbitrary constants $c'_{-q,n-t}$ when we equate to 0 the principal residue relative to the value $z = \infty$ in each of the ρ products (76). If, then, in the product (75) the integral rational function $\Psi(z, u)$, of degree $i-2$ in z, involves a certain number of arbitrary coefficients, we impose just this number of conditions on the constants $c'_{-q,n-t}$ on equating to 0 the principal residue relative to $z = \infty$ in the product (75). This means that we connect the constants $c'_{-q,n-t}$ by this number of independent linear equations.

Suppose the function $\Psi(z, u)$ to be the general rational function built on the basis $(\bar{\tau})$. It then involves just $n(i-1)-\lambda'$ arbitrary coefficients. Equating to 0 the principal residue relative to the value $z=\infty$ in the product (75) independently of the values of the $n(i-1)-\lambda'$ arbitrary coefficients in $\Psi(z, u)$, we force the constants $c'_{-q,n-t}$ to satisfy this many independent linear equations. These $n(i-1)-\lambda'$ linear equations must then be satisfied by the coefficients $c_{-q,n-t}$ in the first factor of the product (74) independently of the values of the constants δ. For independently of the values of the arbitrary constants δ involved in the coefficients $c_{-q,n-t}$ in (74) the principal residue relative to the value $z=\infty$ in the product is 0 when $\Psi(z, u)$ is the general rational function built on the basis $(\bar{\tau})$. Regarded as linear expressions in the constants δ, then $n(i-1)-\lambda'$ of the $n(i-1)$ coefficients $c_{-q,n-t}$ in (74) are linearly expressible in terms of the remaining λ' coefficients. It follows that the number of the coefficients $c_{-q,n-t}$ which are linearly independent of one another is $\leqq \lambda'$. The number of these coefficients which are actually independent of one another is, however, λ. We therefore have $\lambda \leqq \lambda'$. We have, however, already found $\lambda' \leqq \lambda$. We derive $\lambda=\lambda'$. The number of the arbitrary coefficients involved in the general rational function built on the basis $(\bar{\tau})$ is then $n(i-1)-\lambda$, and this is also precisely the number of the coefficients $c_{-q,n-t}$ which are linearly expressible in terms of the remaining λ coefficients.

Employing the notation $\mathrm{N}_{\bar{\tau}}$ to designate the number of the arbitrary coefficients involved in the expression of the general rational function built on the basis $(\bar{\tau})$, the number of the coefficients $c_{-q,n-t}$ which are linearly independent of one another is just $n(i-1)-\mathrm{N}_{\bar{\tau}}$. This, then, is precisely the number of the conditions which we impose on the arbitrary constants δ when we equate to 0 the $n(i-1)$ coefficients $c_{-q,n-t}$ in the identity (66). The subsistence of the identity (65) therefore imposes $n(i-1)-\mathrm{N}_{\bar{\tau}}$ conditions on the constants δ, these being the conditions which are necessary and sufficient in order that a rational function representable in either of the forms (48) or (59) should at the same time be representable in the other form also, it being understood that the functions $\phi^{(i_\kappa)}(z, u)$ which appear in the summation in (59) have the special forms given by formula (64).

Referring to formulæ (45) and (63) we obtain for the total number of the constants δ here in question the expression

$$\sum_{\kappa} l_\kappa = ni-\sum_{\kappa}\sum_{s=1}^{r_\kappa} \tau_s^{(\kappa)}\nu_s^{(\kappa)}+\tfrac{1}{2}\sum_{\kappa}\sum_{s=1}^{r_\kappa}\left(\mu_s^{(\kappa)}-1+\frac{1}{\nu_s^{(\kappa)}}\right)\nu_s^{(\kappa)}, \quad . \quad . \quad . \quad . \quad . \quad (77)$$

since $\sigma_s^{(\kappa)}=-\tau_s^{(\kappa)}$. Subtracting $n(i-1)-\mathrm{N}_{\bar{\tau}}$ from this expression, we obtain

$$\mathrm{N}_{\bar{\tau}}+n-\sum_{\kappa}\sum_{s=1}^{r_\kappa} \tau_s^{(\kappa)}\nu_s^{(\kappa)}+\tfrac{1}{2}\sum_{\kappa}\sum_{s=1}^{r_\kappa}\left(\mu_s^{(\kappa)}-1+\frac{1}{\nu_s^{(\kappa)}}\right)\nu_s^{(\kappa)} \quad . \quad . \quad . \quad . \quad . \quad (78)$$

for the number of the constants δ which remain arbitrary after the forms (48) and (59) have been identified. For the moment we shall indicate the expression (78) by the letter s. In the case where $s = 0$ the constants δ must all have the value 0. In this case, then, on referring to the representation given in (59), we see that the general rational function $H(z, u)$ built on the basis (τ) must reduce to the polynomial $P(z, u)$, and on referring also to the identity (65), we furthermore see that the polynomial $P(z, u)$ must be 0 identically since its coefficients are linear in terms of the constants $\delta_s^{(\infty)}$. Where $s = 0$ then the only rational function built on the basis (τ) is the constant 0.

Where s is >0 we can select among the constants δ a set of s arbitrary constants $\delta_1, \ldots, \delta_s$, in terms of which we can express all the other constants δ linearly. The representation of the general rational function of (z, u) built on the basis (τ) will be obtained in the form (59) on replacing in the functions $\phi^{(i_\kappa)}(z, u)$ each of the constants $\delta^{(\kappa)}$ by its linear expression in terms of the arbitrary constants $\delta_1, \ldots, \delta_s$, and on doing the same for each of the constants $\delta^{(\infty)}$ which presents itself in the coefficients of $P(z, u)$. The general rational function built on the basis (τ) can then be represented in the form

$$\delta_1 U_1 + \ldots + \delta_s U_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (79)$$

where $U_1, \ldots, U_s$ are specific rational functions of (z, u).

That the functions $U_1, \ldots, U_s$ here in question are linearly independent of one another we can readily show. For suppose, if possible, that these functions are connected by a linear relation

$$d_1 U_1 + \ldots + d_s U_s = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (80)$$

We have seen that the constants δ must all be equal to 0 if the function represented by the forms (48) and (59) is to be 0 identically. Now the form (79) is obtained from the form (59) on expressing each of the remaining constants δ in terms of the s constants $\delta_1, \ldots, \delta_s$, and the left-hand side of (80) is thereafter obtained from the form (79) by giving to the constants $\delta_1, \ldots, \delta_s$ the values $d_1, \ldots, d_s$, respectively. The left-hand side of (80) is then obtained from the form (59) on attributing to the constants δ in this form certain values, including the values $d_1, \ldots, d_s$ for the constants $\delta_1, \ldots, \delta_s$, respectively. The resulting function, however, is identically 0, and consequently $d_1, \ldots, d_s$ must all be 0. The functions $U_1, \ldots, U_s$, then, are not connected by a linear relation involving multipliers which are different from 0. The general rational function built on the basis (τ) then involves effectively s arbitrary constants as we see from its representation in the form (79). Employing the notation N_τ to designate the number of the arbitrary constants involved in the expression of the general rational function built on the basis (τ), we have from (78)

$$N_\tau = N_{\bar{\tau}} + n - \sum_\kappa \sum_{s=1}^{r_\kappa} \tau_s^{(\kappa)} \nu_s^{(\kappa)} + \tfrac{1}{2} \sum_\kappa \sum_{s=1}^{r_\kappa} \left(\mu_s^{(\kappa)} - 1 + \frac{1}{\nu_s^{(\kappa)}} \right) \nu_s^{(\kappa)}. \quad . \quad . \quad . \quad . \quad (81)$$

In deriving this formula the sole limitation on the basis (τ) was that all of its numbers corresponding to finite values of the variable z were zero or negative.

Dropping this restriction, we shall now suppose (τ) to be any basis whatever. The complementary basis, as before, we indicate by $(\bar{\tau})$. The most general rational functions built on these bases we shall designate by $\mathrm{H}(z, u)$ and $\overline{\mathrm{H}}(z, u)$ respectively. On properly choosing a definite polynomial $g(z)$ it is readily seen that $\mathrm{H}(z, u)/g(z)$, and $g(z)\overline{\mathrm{H}}(z, u)$ are the most general rational functions built on bases (t) and $(\bar{t})$ which are complementary, the former basis at the same time offering no positive orders of coincidence for finite values of the variable z. We therefore have for the bases (t) and $(\bar{t})$ the formula

$$\mathrm{N}_t = \mathrm{N}_{\bar{t}}+n-\sum_\kappa \sum_{s=1}^{r_\kappa} t_s^{(\kappa)}\nu_s^{(\kappa)}+\tfrac{1}{2}\sum_\kappa \sum_{s=1}^{r_\kappa}\left(\mu_s^{(\kappa)}-1+\frac{1}{\nu_s^{(\kappa)}}\right)\nu_s^{(\kappa)}.$$

Here, however, we evidently have $\mathrm{N}_t = \mathrm{N}_\tau$, $\mathrm{N}_{\bar{t}} = \mathrm{N}_{\bar{\tau}}$, and

$$\sum_\kappa \sum_{s=1}^{r_\kappa} t_s^{(\kappa)}\nu_s^{(\kappa)} = \sum_\kappa \sum_{s=1}^{r_\kappa} \tau_s^{(\kappa)}\nu_s^{(\kappa)},$$

so that we immediately verify the formula (81) for the more general complementary bases (τ) and $(\bar{\tau})$ here in question.

From (57) and (58) we derive

$$\sum_\kappa \sum_{s=1}^{r_\kappa} \tau_s^{(\kappa)}\nu_s^{(\kappa)}+\sum_\kappa \sum_{s=1}^{r_\kappa} \bar{\tau}_s^{(\kappa)}\nu_s^{(\kappa)} = 2n+\sum_\kappa \sum_{s=1}^{r_\kappa}\left(\mu_s^{(\kappa)}-1+\frac{1}{\nu_s^{(\kappa)}}\right)\nu_s^{(\kappa)}. \quad . \quad . \quad . \quad (82)$$

Combining this with (81) we obtain

$$\mathrm{N}_\tau+\tfrac{1}{2}\sum_\kappa \sum_{s=1}^{r_\kappa} \tau_s^{(\kappa)}\nu_s^{(\kappa)} = \mathrm{N}_{\bar{\tau}}+\tfrac{1}{2}\sum_\kappa \sum_{s=1}^{r_\kappa} \bar{\tau}_s^{(\kappa)}\nu_s^{(\kappa)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (83)$$

This is the *Complementary Theorem.* The complementary theorem then states that the number of arbitrary constants involved in the expression of the general function built on a basis (τ) plus half the sum of all the orders of coincidence required by the basis is equal to the like number constructed with reference to the complementary basis $(\bar{\tau})$, that is, with reference to the basis whose numbers are connected with those of the basis (τ) by the relations (57) and (58).

The formula (83) continues to hold good when we replace (57) and (58) by the somewhat more general relations

$$\tau_s^{(\kappa)} + \bar{\tau}_s^{(\kappa)} = m_s^{(\kappa)} -1+\frac{1}{\nu_s^{(\kappa)}}; \; s = 1, \ldots, r_\kappa, \quad . \quad . \quad . \quad . \quad . \quad . \quad (84)$$

and

$$\tau_s^{(\infty)}+\bar{\tau}_s^{(\infty)} = m_s^{(\infty)}+1+\frac{1}{\nu_s^{(\infty)}}; \; s = 1, \ldots, r_\infty, \quad . \quad . \quad . \quad . \quad . \quad . \quad (85)$$

where $m_1^{(\kappa)}, \ldots, m_{r_\kappa}^{(\kappa)}$ represent the actual orders of coincidence of an arbitrarily chosen rational function $\mathrm{R}(z, u)$ with the branches of the several cycles corresponding to the value $z = a_\kappa$. To see this it is only necessary to remember that the aggregate sum of all the orders of coincidence of any rational function is equal to 0 and to note that the general rational function built on the basis $(\bar{\tau})$ defined with reference to the basis (τ) by the relations (84) and (85) is obtained on multiplying by $\mathrm{R}(z, u)/f_u'(z, u)$, the general rational function built on the basis *originally* defined as complementary to the basis (τ).

While the complementary theorem has here been deduced on the hypothesis that the fundamental equation is an integral algebraic equation, it is easy to verify that the generalized theorem holds also when the fundamental equation is not integral. For more detail in connection with the theorem, and for some of its consequences, the reader is referred to Chapter XII. and the following chapters of the book already cited. In the present paper it has been the object of the writer to present a more simple and elegant treatment of the theory leading up to the complementary theorem.

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ON THE SCATTERING AND ABSORPTION OF LIGHT IN GASEOUS MEDIA, WITH APPLICATIONS TO THE INTENSITY OF SKY RADIATION.

BY

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XII. *On the Scattering and Absorption of Light in Gaseous Media, with Applications to the Intensity of Sky Radiation.*

By Louis Vessot King, *B.A.* (*Cantab.*), *late Scholar of Christ's College, Cambridge; Lecturer in Physics, McGill University, Montreal.*

Communicated by Sir Joseph Larmor, *Sec. R.S.*

Received June 7,—Read November 7, 1912.

Contents.

Part I.

§ 1. *On the Scattering of Parallel Radiation by Molecules and Small Particles.*

The effect of small particles in scattering incident radiation was first worked out by Lord Rayleigh.[*] When a stream of parallel radiation falls on a particle whose dimensions are small compared with the wave-length the resulting secondary disturbance travels in all directions at the expense of the intensity in the original direction. In a later paper Lord Rayleigh[†] gave reasons for believing that the molecules of a gas are themselves able to scatter radiation in this way. In a gaseous medium it is legitimate to sum up the intensities of the scattered radiation due to each molecule in an element of volume without a consideration of phase-difference in consequence of the continuous change in the relative positions of a molecule in a gas.

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[*] Rayleigh, 'Phil. Mag.,' XLI., pp. 107, 274, 447 (1871); XII., p. 81 (1881); 'Collected Works,' vol. I., pp. 87, 104, 518.

[†] Rayleigh, 'Phil. Mag.,' XLVII., pp. 375–384 (1899); 'Collected Works,' vol. IV., pp. 397–405.

Published separately, February 8, 1913.

The same remark applies to the case where the scattering is due to small particles of dust since these partake, to some extent at least, of the molecular agitation of the gas in which they are held in suspension.

The intensity of radiation at any point is measured by the amount of energy crossing unit area of a surface normal to the direction of the radiation in unit time. Unpolarized radiation of intensity E falls on an element δv of a gas of density ρ and containing N molecules per unit volume. The intensity of the scattered radiation in a direction θ with the incident radiation and at a distance r from δv we denote by $r^{-2}\mathrm{I}(r, \theta)\,\delta v$, so that $\mathrm{I}(r, \theta)\,\delta v\,\delta\omega$ is the energy contained in a small solid angle $\delta\omega$ crossing a spherical surface at distance r in unit time.

The expression for $\mathrm{I}(0, \theta)$ is of the form

$$\mathrm{I}(0, \theta) = \mu(\theta)\,\mathrm{E} \quad \ldots\ldots\ldots\ldots \quad (1)$$

where $\mu(\theta)$ depends on the direction θ and is proportional to the number N of molecules per unit volume, *i.e.*, $\mu(\theta)$ is also proportional to the density ρ.

If $\mu_0(\theta)$, N_0, ρ_0 refer to values of $\mu(\theta)$, N, ρ under determinate conditions of pressure and temperature we have

$$\mu(\theta)/\mu_0(\theta) = \mathrm{N}/\mathrm{N}_0 = \rho/\rho_0 \quad \ldots\ldots\ldots\ldots \quad (2)$$

$\mu(\theta)$ may be expressed in terms of the optical properties of the medium: the results of RAYLEIGH,[*] and KELVIN[†] worked out on various hypotheses of the molecule and of the æther agree in giving rise to the expression,

$$\mu(\theta) = \tfrac{1}{2}\pi^2(n^2-1)^2\lambda^{-4}(1+\cos^2\theta)/\mathrm{N} \quad \ldots\ldots\ldots \quad (3)$$

where n is the refractive index of the gas and λ the wave-length of the incident radiation.

SCHUSTER[‡] has recently obtained this result from general considerations independently of any particular theory.

Since $n-1$ and N are both proportional to the density of the gas we notice that $\mu(\theta)$ is also proportional to the density, as already stated.

Formula (3) shows that the intensity of the scattered radiation is twice as great in the direction of the incident radiation as it is in a direction at right angles. Considerable simplification in the analysis is obtained by employing the mean value of $\mu(\theta)$ over a spherical surface. Thus, writing

$$4\pi\bar{\mu} = \int \mu(\theta)\,d\omega \quad \ldots\ldots\ldots\ldots \quad (4)$$

(3) gives

$$\bar{\mu} = \tfrac{2}{3}\pi^2(n^2-1)^2\lambda^{-4}/\mathrm{N} \quad \ldots\ldots\ldots\ldots \quad (5)$$

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[*] RAYLEIGH, 'Phil. Mag.,' XLI., p. 107; 'Collected Works,' vol. I., p. 87.

[†] KELVIN, 'Baltimore Lectures' (1904), p. 311.

[‡] SCHUSTER, 'Theory of Optics,' 2nd ed. (1909), p. 325.

and under standard conditions of pressure and temperature,

$$\bar{\mu}_0 = \tfrac{2}{3}\pi^2(n_0^2-1)^2\lambda^{-4}/\mathrm{N}_0 \quad \ldots\ldots\ldots\ldots \quad (6)$$

We denote by κ_0 the expression

$$\kappa_0 = 4\pi\bar{\mu}_0 = \tfrac{8}{3}\pi^3(n_0^2-1)^2\lambda^{-4}/\mathrm{N}_0. \quad \ldots\ldots\ldots\ldots \quad (7)$$

The effect of scattering is to diminish the intensity of the incident radiation, giving rise to the phenomenon of attenuation especially noticeable in the diminution of intensity of solar radiation in its passage through the earth's atmosphere. The consideration of attenuation as due to scattering alone involves the assumption that energy is nowhere accumulating in the gas. In order to give greater generality to the application of the analysis we introduce a term expressing the fact that the temperature at any point is increasing.

If E be the intensity of radiation crossing unit area of a plane at a point x in unit time, the loss to E in a distance dx in unit time due to the conversion of radiant energy into molecular agitation represented by a rise of temperature is of the form

$$d\mathrm{E} = -\alpha\mathrm{E}\,dx. \quad \ldots\ldots\ldots\ldots \quad (8)$$

when α is proportional to the number of molecules per unit volume, *i.e.*, if α_0 and ρ_0 refer to standard conditions of pressure and temperature, $\alpha/\alpha_0 = \rho/\rho_0$.

In the case of a pure gas α is a quantity depending on the distribution of energy between vibrating systems within the molecules and the motions of the molecules themselves which define the temperature of a gas on the kinetic theory scale as proportional to the mean squares of molecular velocities.

If ρ be the density of the gas, s its specific heat at constant pressure and $d\Theta$ the increment of temperature in time dt due to the conversion of radiant energy $\alpha\mathrm{E}\,dx\,dt$ into heat, we have

$$\alpha\mathrm{E} = \rho s\frac{d\Theta}{dt}, \quad \ldots\ldots\ldots\ldots \quad (9)$$

E being measured in calories per unit area normal to the direction of E per second.

In the case of a gas exposed continuously to external radiation we may suppose the temperature to attain to a steady state when $d\Theta/dt = 0$ and therefore $\alpha = 0$ in which case no energy accumulates in the medium. In the problem of the earth's atmosphere, however, the term α will give rise to a small diurnal variation of temperature throughout the atmosphere. The term α may also be taken to include the effect of dust in absorbing solar radiation without scattering as well as effects of selective absorption if we regard α as a function of the wave-length. The existence and magnitude of this quantity can be determined by a comparison of theoretical results with the results of observation. Actual numerical values for air are obtained in Part III. of the present paper.

§ 2. *On the General Integral Equation for the Scattered Radiation.*

Suppose a mass of gas to be completely enclosed by a boundary Σ and illuminated by a distribution of radiation whose intensity at a point (x, y, z) is E, and whose direction is defined at that point. Each element of volume will scatter a certain proportion of the radiation incident upon it, so that each element besides being illuminated by the incident radiation is also subject to the aggregate radiation from all the other elements within the surface Σ, *i.e.*, to the effect of *self-illumination*. This constitutes what SCHUSTER[*] has called the problem of "Radiation through a Foggy Atmosphere." The problem does not lend itself easily to a complete formulation in terms of differential equations, but can be expressed in terms of an *integral equation.*

At an element of volume δv at (x, y, z) the incident radiation is E. At a distance r from δv in a direction θ with the incident radiation the scattered radiation crossing unit area in unit time is denoted by $\mathrm{I}(r, \theta)\,\delta v\, r^{-2}$. If we wish to express the dependence of $\mathrm{I}(r, \theta)\,\delta v\, r^{-2}$ on the position of δv in the surface Σ we write it in the form $\mathrm{I}(x, y, z, r, \theta)\,\delta v\, r^{-2}$.

Our first problem will be to express the scattered radiation $\mathrm{I}(r, \theta)$ in terms of the scattered radiation $\mathrm{I}(0, \theta)$ per unit solid angle in the neighbourhood δv.

Consider the radiation $\mathrm{I}(r, \theta)\,\delta v\,\delta\omega$ coming from an element of volume δv and contained in a small solid angle $\delta\omega$ in a direction θ with the incident radiation. The intensity of the radiation crossing a spherical surface of radius r is $\mathrm{I}(r, \theta)\,\delta v\,\delta\omega$; that cutting the surface $r+\delta r$ is

$$\left\{\mathrm{I}(r, \theta)+\frac{\delta}{\delta r}\,\mathrm{I}(r, \theta)\,\delta r\right\}\delta v\,\delta\omega.$$

We thus obtain the equation

$$-\frac{\delta}{\delta r}\mathrm{I}(r, \theta)\,\delta v\,\delta\omega = \alpha\mathrm{I}(r, \theta)\,r^{-2}\,\delta v\,r^{2}\,\delta\omega\,\delta r+4\pi\bar{\mu}\mathrm{I}(r, \theta)\,r^{-2}\,\delta v\,r^{2}\,\delta\omega\,\delta r. \quad . \quad . \qquad (10)$$

The first term on the right-hand side represents by (8) the energy lost to the element of volume $r^2\,\delta\omega\,\delta r$ by the conversion of radiant energy into a rise of temperature or into long-wave heat radiation, which transformation we assume to go on at a constant rate.

The second term accounts for the energy lost to the element of volume $r^2\,\delta\omega\,\delta r$ by scattering. We neglect the effect of self-illumination within the small solid angle $\delta\omega$ since this only enters into the equation to the second order of small quantities.

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[*] SCHUSTER, "Radiation through a Foggy Atmosphere," 'Astrophysical Journal,' XXI, January, 1905, p. 1. A somewhat similar problem had been previously considered by the same writer in a paper "The Influence of Radiation on the Transmission of Heat," 'Phil. Mag.,' February, 1903. Recently it has been shown by JACKSON, W. H. ('Bull. Am. Soc. Math.,' XVI, June, 1910, p. 473), that the generalized differential equation obtained in SCHUSTER'S paper can be transformed into an *integral equation* of the Fredholm type.

Writing $\kappa = 4\pi\bar{\mu}$ the above equation gives

$$-\frac{\delta}{\delta r}\mathrm{I}(r, \theta) = (\alpha+\kappa)\,\mathrm{I}(r, \theta). \quad \ldots \quad (11)$$

If we write

$$\mathrm{K} = \alpha+\kappa, \quad \ldots \quad (12)$$

the solution of (11) is

$$\mathrm{I}(r, \theta) = \mathrm{I}(0, \theta)\, e^{-\int_0^r \mathrm{K}\, dr}, \quad \ldots \quad (13)$$

which puts into evidence the variation of α and κ with the density of the gas.

Consider now the radiation incident on an element of volume δv at (x, y, z):—

(i) The external illumination E which contributes to the scattered radiation from δv an amount

$$\mu(\theta)\,\mathrm{E}(x, y, z)\,\delta v\,\delta\omega;$$

(ii) An element of volume $\delta v'$ at (x', y', z') gives rise to an intensity $\mathrm{I}(x', y', z', r', \theta')\,\delta v'\, r'^{-2}$ at the point (x, y, z): this contributes to the scattered radiation from δv the amount

$$\mu(\widehat{rr'})\,\mathrm{I}(x', y', z', r', \theta')\,\delta v'\,\delta\omega\,\delta v\, r'^{-2},$$

$\widehat{rr'}$ denoting the angle between r and r'. The total contribution to the scattered radiation from δv due to self-illumination by the entire volume Σ is

$$\delta\omega\,\delta v \int_{\Sigma} \mu(\widehat{rr'})\,\mathrm{I}(x', y', z', r', \theta')\, r'^{-2}\, dv',$$

the integral being taken throughout the entire volume enclosed by the surface Σ.

By definition the sum of contributions (i) and (ii) is $\mathrm{I}(x, y, z, 0, \theta)$, so that we obtain the following *integral equation* for the scattered radiation at and from any point,

$$\mathrm{I}(x, y, z, 0, \theta) = \mu(\theta)\,\mathrm{E}(x, y, z) + \int_{\Sigma} \mu(\widehat{rr'})\,\mathrm{I}(x', y', z', 0, \theta')\, r'^{-2} e^{-\int_0^{r'} \mathrm{K}\, dr'}\, dv', \quad . \quad (14)$$

$\mathrm{I}(x', y', z', r', \theta')$ being expressed in terms of $\mathrm{I}(x', y', z', 0, \theta')$ by means of (13).

A differential equation involving $\mathrm{E}(x, y, z)$ is obtained by considering the rate of accumulation of energy in an element of volume.

As soon as $\mathrm{I}(x, y, z, 0, \theta)$ is known as a function of the position of the point O, (x, y, z), in the volume bounded by the surface Σ, the radiation scattered to any point P within the boundary Σ contained in a small solid angle ω is given by the formula

$$\mathrm{T}\omega = \omega \int_0^{r_0} \mathrm{I}(x, y, z, 0, \theta)\, e^{-\int_0^r \mathrm{K}\, dr}\, dr, \quad \ldots \quad (15)$$

where $r = \mathrm{PO}$, $r_0 = \mathrm{PQ}$, the radius vector to the boundary, and T is the intensity at

P for unit solid angle. The formula (15) is easily modified to include the case where P is without the surface Σ.

It is interesting to point out the analogy which the method of the present section bears to the ordinary procedure of potential theory. The function $I(x, y, z)$ corresponds to a potential function and is expressed in terms of an external effect $E(x, y, z)$ by means of an *integral equation.* The *total intensity* in a small solid angle, the effect which is physically measurable, is derived by *integrating* between definite limits along a given direction.

Further progress towards a solution of (14) is impossible without a number of simplifying assumptions which are best considered in dealing with a particular problem, such, for instance, as that presented by the effect of the earth's atmosphere in absorbing and scattering the sun's radiation.

PART II.

§ 3. *Application to Radiation and Absorption in the Earth's Atmosphere.*

In the following sections we shall assume as an approximation that the surface of the earth is a plane and that the density is a function of the height above the earth's surface only. We also neglect effects due to reflection from the earth's surface and to refraction by the earth's atmosphere.

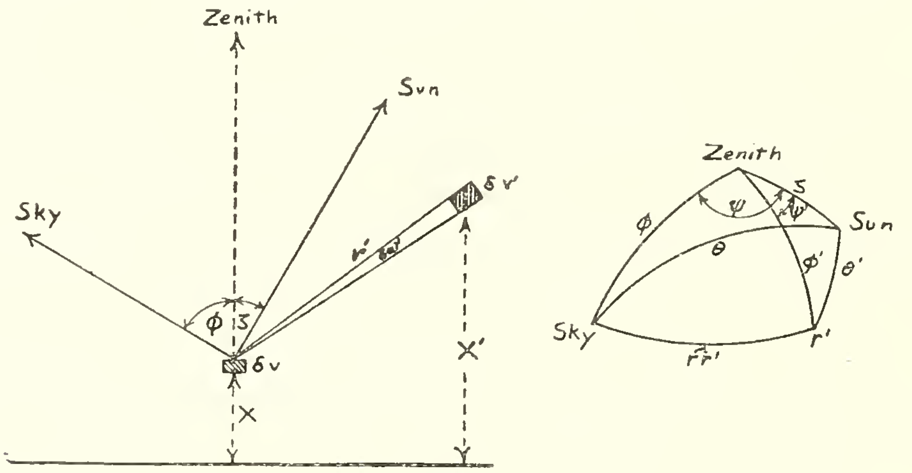

Fig. 1.

The integral equation (14) for the scattered radiation in a direction θ (fig. 1) with the direction of the sun and coming from an element δv of the atmosphere at a height x above the earth's surface, takes the form

$$I(x, 0, \theta) = \mu(\theta) E(x) + \int_{\Sigma} \mu(\widehat{rr'}) \frac{I(x', 0, \theta')}{r'^2} e^{-\int_0^{r'} \kappa \, dr'} dv, \quad . \quad . \quad . \quad . \quad (16)$$

where the integral is taken throughout the entire atmosphere.

In order to simplify the solution of (16) we assume that the scattered radiation from a molecule can to a first approximation be taken equal in all directions, *i.e.*, the equation can be reduced to one with a single variable by writing

$$\mu(\theta) = \mu(\widehat{rr'}) = \bar{\mu}.$$

Equation (16) may now be written, since $dv' = r'^2\,d\omega'\,dr'$,

$$\mathrm{I}(x) = \bar{\mu}\mathrm{E}(x) + \bar{\mu}\int_{\Sigma} \mathrm{I}(x')\,e^{-\int_0^{r'}\mathrm{K}\,dr'}\,d\omega'\,dr'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Remembering that $\bar{\mu}/\bar{\mu}_0 = \kappa/\kappa_0 = \alpha/\alpha_0 = \mathrm{K}/\mathrm{K}_0 = \rho/\rho_0$, we now employ the transformations

$$\mathrm{R} = \int_0^r \frac{\rho}{\rho_0}\,dr, \quad \mathrm{X} = \int_0^x \frac{\rho}{\rho_0}\,dx, \quad \mathrm{H} = \int_0^\infty \frac{\rho}{\rho_0}\,dx, \quad \mathrm{J}(\mathrm{X}) = \frac{\rho_0}{\rho}\mathrm{I}(x), \quad . \quad . \quad (18)$$

and (17) now takes the form

$$\mathrm{J}(\mathrm{X}) = \bar{\mu}_0\mathrm{E}(\mathrm{X}) + \bar{\mu}_0\int \mathrm{J}(\mathrm{X}')\,e^{-\mathrm{K}_0\mathrm{R}'}\,d\omega'\,d\mathrm{R}', \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

while (15) transforms into

$$\mathrm{T}\omega = \omega\int_0^{\mathrm{R}_0} \mathrm{J}(\mathrm{X})\,e^{-\mathrm{K}_0\mathrm{R}}\,d\mathrm{R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The integral on the right-hand side of (19) must now be taken throughout a *homogeneous* atmosphere of density ρ_0 included between the planes $\mathrm{X} = 0$ and $\mathrm{X} = \mathrm{H}$.

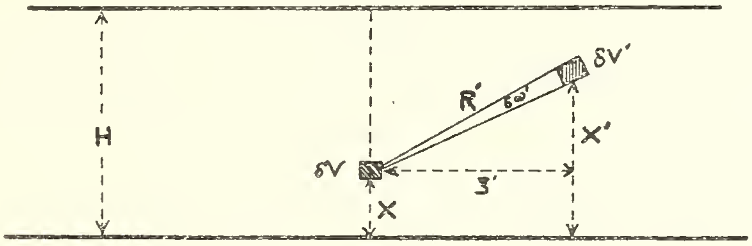

Fig. 2.

Expressing the integral in (18) in cylindrical co-ordinates (ξ', ψ') (fig. 2), we have

$$d\omega'\,d\mathrm{R}' = \frac{d\mathrm{V}'}{\mathrm{R}'^2} = \frac{d\mathrm{X}'\,\xi'\,d\xi'\,d\psi'}{\xi'^2+(\mathrm{X}'-\mathrm{X})^2},$$

where ψ' is the azimuth of the element of volume $d\mathrm{V}'$ referred to some fixed direction of reference. The integral then becomes

$$\int_{\mathrm{X}'} \mathrm{J}(\mathrm{X}')\,d\mathrm{X}' \int_0^{2\pi} d\psi' \int_0^\infty e^{-\mathrm{K}_0[\xi'^2+(\mathrm{X}'-\mathrm{X})^2]^{1/2}} \frac{\xi'\,d\xi'}{\xi'^2+(\mathrm{X}'-\mathrm{X})^2}.$$

The last integral when integrated with respect to ξ' gives

$$\int_0^\infty e^{-\mathrm{K}_0[\xi'^2+(\mathrm{X}'-\mathrm{X})^2]^{1/2}} \frac{\xi'\,d\xi'}{\xi'^2+(\mathrm{X}'-\mathrm{X})^2} = -Ei\,\{-\mathrm{K}_0(\mathrm{X}'-\mathrm{X})\} \quad \text{when} \quad \mathrm{X}<\mathrm{X}'<\mathrm{H}$$

$$\text{and} \quad = -Ei\,\{-\mathrm{K}_0(\mathrm{X}-\mathrm{X}')\} \quad \text{when} \quad 0<\mathrm{X}'<\mathrm{X},$$

where $Ei(-x)$ is GLAISHER'S* *Exponential Integral* denoted by

$$Ei(-x) = -\int_x^\infty u^{-1}e^{-u}\,du. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The integral equation (19) now takes the form

$$J(X) = \bar{\mu}_0 E(X) - 2\pi\bar{\mu}_0\left[\int_0^X J(X')Ei\{-K_0(X-X')\}dX' + \int_X^H J(X')Ei\{-K_0(X'-X)\}dX'\right]. \quad (22)$$

[The differential equation by means of which E may be expressed as a function of X can be obtained by a consideration of the rate of accumulation of energy of the direct solar radiation between the planes x and $x+dx$. An analysis similar to that by means of which equation (13) was obtained, together with the transformations of equation (18), lead to the expression

$$E(X) = Se^{K_0(X-H)\sec\zeta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where S is the intensity of solar radiation outside the earth's atmosphere corresponding to a given wave-length and ζ is the zenith distance of the sun.

If we consider the rate of accumulation of the total energy (including both direct and scattered radiation) between the planes x and $x+dx$, it can be shown by making use of the integral equation connecting the direct with the scattered radiation that the exponential law of transmission expressed in (23) is valid.†]

It is well to state clearly the assumptions involved in obtaining (13), (19), and (23):—

(i) In obtaining the differential equation leading to (13) the direct radiation is considered independently of the scattered radiation within the small solid angle ω.

(ii) The integral equation (22) assumes as an approximation that the radiation scattered by an element of volume is distributed equally in all directions.

(iii) With these two conditions it can be shown from a consideration of attenuation of total radiation in a thin layer dx that the ordinary exponential law of transmission (23) follows; *i.e.*, that the transmission of direct radiation may be considered independently of the scattered radiation.

(iv) By means of the transformation (18) it is shown that the problem of scattered

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* GLAISHER, 'Phil. Trans.,' 1870, p. 367.

[† *Note added September 20, 1912.*—The calculation referred to was given at length in the paper as originally communicated; the analysis is, however, somewhat tedious and hardly necessary in view of the fact that (13) is obtained according to the assumption that the direct radiation is considered independently of the scattered radiation within the small solid angle ω. It is to be expected, therefore, that the attenuation of direct radiation in a parallel beam of solar radiation may be considered independently of the scattered radiation consistently with the above assumption leading immediately to (23); the consideration of the attenuation of the total radiation confirms this point and leads to the same result. The writer is indebted to the referees for the above suggestion.]

radiation in the earth's atmosphere reduces to the case of an atmosphere of uniform density contained between two parallel planes $X = 0$ and $X = H$. This transformation is independent of any law of density with height, provided the planes of equal density are parallel to the earth's surface.

§ 4. *On the Approximate Solution of Integral Equations.*

The integral equation (21) is of the Fredholm type,*

$$u(x) = f(x) + \int_{x_1}^{x_2} u(\xi)\, K(x, \xi)\, d\xi. \quad \ldots \ldots \quad (24)$$

Except for special forms of the *kernel* $K(x, \xi)$ the formal solutions of (24) do not lend themselves easily to numerical evaluation: we therefore develop a method of approximation which applies with sufficient accuracy to the problem in hand.

Suppose for all values of x between x_1 and x_2 that $f(x)$ lies between A and a $(A > a)$. Then to a first approximation

$$u(x) \text{ lies between } A + A\int_{x_1}^{x_2} K(x, \xi)\, d\xi \quad \text{and} \quad a + a\int_{x_1}^{x_2} K(x, \xi)\, d\xi,$$

provided $K(x, \xi)$ is everywhere positive.

We write

$$\phi(x) = \int_{x_1}^{x_2} K(x, \xi)\, d\xi, \quad \ldots \ldots \quad (25)$$

then if for all values of x, $\phi(x)$ lies between B and b $(B > b)$ we have to a second approximation

$$a + (a + ab)\, b < u(x) < A + (A + AB)\, B,$$

or

$$a(1 + b + b^2) < u(x) < A(1 + B + B^2).$$

A repetition of the process shows that

$$a(1 + b + b^2 + b^3 + \ldots) < u(x) < A(1 + B + B^2 + B^3 + \ldots).$$

If $|B| < 1$ both series are convergent and

$$\epsilon_1 < u(x) < \epsilon_2 \quad \text{where} \quad \epsilon_1 = a/1 - b \quad \text{and} \quad \epsilon_2 = A/1 - B. \quad \ldots \quad (26)$$

Substituting in (24) we see that the solution $u(x)$ lies between the limits

$$u_1(x) = f(x) + \epsilon_1 \phi(x), \quad \text{and} \quad u_2(x) = f(x) + \epsilon_2 \phi(x). \quad \ldots \quad (27)$$

$u_1(x)$ and $u_2(x)$ may be called the *extreme solutions.*

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* *Cf.* BÔCHER, M., 'An Introduction to the Study of Integral Equations,' Cambridge, 1909, p. 14; also BATEMAN, H., "Report on the History and Present State of the Theory of Integral Equations," 'Brit. Assoc. Report,' 1910, p. 25.

If now a represent the mean value of $f(x)$ between x_1 and x_2, *i.e.*,

$$a = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} f(x)\, dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

and β stand for the mean value of $\phi(x)$ between x_1 and x_2, *i.e.*,

$$\beta = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} \phi(x)\, dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

while $\epsilon = a/(1-\beta)$, the solution $\bar{u}(x) = f(x) + \epsilon\phi(x)$ may be called the *mean solution*, while the three solutions may be expressed in a single formula by the notation

$$u(x) = f(x) + \begin{pmatrix} \epsilon_1 \\ \epsilon \\ \epsilon_2 \end{pmatrix} \phi(x). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

We notice that $u_1(x) < u(x) < u_2(x)$. In the applications to be considered, $u_1(x)$ and $u_2(x)$ are sufficiently close to warrant the use of the mean solution $\bar{u}(x)$. As long as $\bar{u}(x)$ does not depart far from the arithmetical mean of the extreme solutions, $\frac{1}{2}\{u_1(x) + u_2(x)\}$, we may take the value of $\bar{u}(x)$ to represent an approximation not far removed from the exact solution of the integral equation (24).

It is perhaps worth noting here that to a higher degree of approximation the approximate solution of the integral equation may be written

$$u(x) = f(x) + \int_{x_1}^{x_2} f(\xi)\, K(x, \xi)\, d\xi + \begin{pmatrix} b\epsilon_1 \\ \beta\epsilon \\ B\epsilon_2 \end{pmatrix} \phi(x). \quad . \quad . \quad . \quad . \quad . \quad (31)$$

In the following sections the solutions (31) involve the evaluation of troublesome integrals, so that the simpler but somewhat less accurate approximations given in (30) will be employed.

§ 5. *On the Solution of the Integral Equation for Sky Radiation.*

In the integral equation (22) we may express to a first approximation the dependence of the scattered radiation in any direction on the angle which that direction makes with the incident radiation by retaining the term $\mu_0(\theta)$ instead of $\bar{\mu}_0$ in the first term of the right-hand side of the equation which may be written, on making use of (23),

$$J(X) = \mu_0(\theta)\, S e^{-K_0(H-X)\sec\zeta} - \tfrac{1}{2}\kappa_0 \left[\int_0^X J(X')\, Ei\{-K_0(X-X')\}\, dX' + \int_X^H J(X')\, Ei\{-K_0(X'-X)\}\, dX' \right]. \quad . \quad . \quad (32)$$

In the notation of the preceding section we have to solve the above integral equation for

$$u(\mathrm{X}) = \mathrm{J}(\mathrm{X})/\mathrm{S}\mu_0(\theta).$$

We have

$$\mathrm{A} = 1 \quad \text{and} \quad a = e^{-\mathrm{K}_0 \mathrm{H} \sec \zeta}, \quad \ldots \ldots \quad (33)$$

while

$$\phi(\mathrm{X}) = -\tfrac{1}{2}\kappa_0 \left[\int_0^{\mathrm{X}} Ei\{-\mathrm{K}_0(\mathrm{X}-\mathrm{X}')\}\, d\mathrm{X}' + \int_{\mathrm{X}}^{\mathrm{H}} Ei\{-\mathrm{K}_0(\mathrm{X}'-\mathrm{X})\}\, d\mathrm{X}'\right].$$

If we notice that

$$\int_c^{\infty} -Ei(-ax)\, dx = f(ac)/a, \quad \ldots \ldots \quad (34)$$

where

$$f(x)\text{[*]} = e^{-x} + xEi(-x) = x\int_x^{\infty} e^{-u}u^{-2}\, du, \quad \ldots \ldots \quad (35)$$

we find

$$\phi(\mathrm{X}) = \tfrac{1}{2}[2 - f(\mathrm{K}_0\mathrm{X}) - f\{\mathrm{K}_0(\mathrm{H}-\mathrm{X})\}]\,\kappa_0/\mathrm{K}_0. \quad \ldots \ldots \quad (36)$$

This expression is symmetrical with respect to the plane $\mathrm{X} = \frac{1}{2}\mathrm{H}$, where it has its maximum value. The minimum value of the expression occurs at $\mathrm{X} = 0$ and $\mathrm{X} = \mathrm{H}$.

We write for brevity

$$\mathrm{C} = \mathrm{K}_0\mathrm{H}, \qquad c = \kappa_0\mathrm{H}, \qquad \gamma = \alpha_0\mathrm{H}, \qquad \mathrm{C} = c + \gamma. \quad \ldots \ldots \quad (37)$$

We then find

$$\mathrm{B} = \{1 - f(\tfrac{1}{2}\mathrm{C})\}\, c/\mathrm{C} \quad \text{and} \quad b = \tfrac{1}{2}\{1 - f(\mathrm{C})\}\, c/\mathrm{C}. \quad \ldots \ldots \quad (38)$$

We also have

$$\alpha = \mathrm{H}^{-1}\int_0^{\mathrm{H}} e^{-\mathrm{K}_0(\mathrm{H}-\mathrm{X})\sec\zeta}\, d\mathrm{X} = (1 - e^{-\mathrm{C}\sec\zeta})/\mathrm{C}\sec\zeta, \quad \ldots \quad (39)$$

or, introducing the notation

$$\mathrm{G}(x) = (1 - e^{-x})/x, \quad \ldots \ldots \quad (40)$$

we have

$$\alpha = \mathrm{G}(\mathrm{C}\sec\zeta). \quad \ldots \ldots \quad (41)$$

Further, we find

$$\beta = \mathrm{H}^{-1}\int_0^{\mathrm{H}} \phi(\mathrm{X})\, d\mathrm{X},$$

or

$$\beta = \tfrac{1}{2}\mathrm{H}^{-1}\left[\int_0^{\mathrm{H}} \{1 - f(\mathrm{K}_0\mathrm{X})\}\, d\mathrm{X} + \int_0^{\mathrm{H}} [1 - f\{\mathrm{K}_0(\mathrm{H}-\mathrm{X})\}]\, d\mathrm{X}\right] c/\mathrm{C},$$

$$\beta = \mathrm{C}^{-1}\left[\int_0^{\mathrm{C}} \{1 - f(u)\}\, du\right] c/\mathrm{C}.$$

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[*] The function $f(x)$, as defined above, occurs in a number of absorption problems. Its properties are described in a paper by the writer (KING, L. V., 'Phil. Mag.,' February, 1912, p. 245), where a short numerical table of the function is given.

It can easily be shown by integrating by parts that

$$\int_0^{\mathrm{C}} f(u)\,du = \tfrac{1}{2}(1-e^{-\mathrm{C}}) + \tfrac{1}{2}\mathrm{C}f(\mathrm{C}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (42)$$

so that

$$\beta = \{1-\tfrac{1}{2}f(\mathrm{C}) - \tfrac{1}{2}\mathrm{G}(\mathrm{C})\}\, c/\mathrm{C}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (43)$$

Finally we obtain for ϵ_2, ϵ, ϵ_1 the expressions

$$\left.\begin{aligned} \epsilon_2 &= \frac{1}{\gamma/\mathrm{C}+f(\frac{1}{2}\mathrm{C})\,c/\mathrm{C}} \\ \epsilon &= \frac{\mathrm{G}(\mathrm{C}\sec\zeta)}{\gamma/\mathrm{C}+\frac{1}{2}\{f(\mathrm{C})+\mathrm{G}(\mathrm{C})\}\,c/\mathrm{C}}, \\ \epsilon_1 &= \frac{e^{-\mathrm{C}\sec\zeta}}{\gamma/\mathrm{C}+\frac{1}{2}\{1+f(\mathrm{C})\}\,c/\mathrm{C}}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (44)$$

The approximate solution of (32) may now be written

$$\frac{\mathrm{J}(\mathrm{X})}{\mu_0(\theta)\,\mathrm{S}} = e^{-\mathrm{K}_0(\mathrm{H}-\mathrm{X})\sec\zeta} + \begin{pmatrix}\epsilon_1\\ \epsilon\\ \epsilon_2\end{pmatrix}\phi(\mathrm{X}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (45)$$

where $\phi(\mathrm{X})$ is defined by (36) and the values ϵ_1, ϵ, ϵ_2 are given by (44) and are employed in (45) according as we wish to make use of the extreme or mean solutions.

From (20) the radiation scattered to a point on the earth's surface, contained in a small solid angle ω in a direction ϕ with the vertical, is given by

$$\omega\mathrm{T} = \omega\int_0^{\mathrm{R}_0}\mathrm{J}(\mathrm{X})\,e^{-\mathrm{K}_0\mathrm{R}}\,d\mathrm{R}.$$

Since $\mathrm{R} = \mathrm{X}\sec\phi$ this equation becomes

$$\mathrm{T}(\phi,\zeta) = \sec\phi\int_0^{\mathrm{H}} e^{-\mathrm{K}_0\mathrm{X}\sec\phi}\,\mathrm{J}(\mathrm{X})\,d\mathrm{X}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (46)$$

where the dependence of the sky radiation per unit solid angle on the direction ϕ and on the zenith distance of the sun ζ is denoted by $\mathrm{T}(\phi,\zeta)$.

If we denote by $\omega\mathrm{R}(\phi,\zeta)$ the radiation to a point at $\mathrm{X}=\mathrm{H}$ contained in a small solid angle ω pointing earthwards in a direction ϕ with the vertical, we have

$$\mathrm{R}(\phi,\zeta) = \sec\phi\int_0^{\mathrm{H}} e^{-\mathrm{K}_0(\mathrm{H}-\mathrm{X})\sec\phi}\,\mathrm{J}(\mathrm{X})\,d\mathrm{X}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (47)$$

Substituting for $\mathrm{J}(\mathrm{X})$ from (45) we obtain from (46)

$$\mathrm{T}(\phi,\zeta) = \mu_0(\theta)\,\mathrm{S}\sec\phi\left\{e^{-\mathrm{K}_0\mathrm{H}\sec\zeta}\int_0^{\mathrm{H}} e^{-\mathrm{K}_0\mathrm{X}(\sec\phi-\sec\zeta)}\,d\mathrm{X} + \begin{pmatrix}\epsilon_1\\ \epsilon\\ \epsilon_2\end{pmatrix}\int_0^{\mathrm{H}} e^{-\mathrm{K}_0\mathrm{X}\sec\phi}\,\phi(\mathrm{X})\,d\mathrm{X}\right\}.$$

The first term in the brackets may be written

$$\left.\begin{array}{l} e^{-\mathrm{C}\sec\phi}\,\mathrm{G}\,\{(\sec\zeta-\sec\phi)\,\mathrm{C}\}\,\mathrm{C}/\mathrm{K}_0 \ \text{ if } \zeta>\phi \\ \text{or} \\ e^{-\mathrm{C}\sec\zeta}\,\mathrm{G}\,\{(\sec\phi-\sec\zeta)\,\mathrm{C}\}\,\mathrm{C}/\mathrm{K}_0 \ \text{ if } \phi>\zeta \end{array}\right\} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (48)$$

The evaluation of the second integral is more difficult; we have

$$\int_0^{\mathrm{H}} e^{-\mathrm{K}_0\mathrm{X}\sec\phi}\phi\,(\mathrm{X})\,d\mathrm{X} = \tfrac{1}{2}\frac{c}{\mathrm{C}}\int_0^{\mathrm{H}} e^{-\mathrm{K}_0\mathrm{X}\sec\phi}\,[2-f(\mathrm{K}_0\mathrm{X})-f\{\mathrm{K}_0(\mathrm{H}-\mathrm{X})\}]\,d\mathrm{X}. \quad . \qquad (49)$$

Writing $\mathrm{K}_0\mathrm{X} = u$, the above integral takes the form

$$\frac{1}{2\mathrm{K}_0}\frac{c}{\mathrm{C}}\left[\frac{2\,(1-e^{-\mathrm{C}\sec\phi})}{\sec\phi} - \int_0^{\mathrm{C}} e^{-u\sec\phi}f(u)\,du - e^{-\mathrm{C}\sec\phi}\int_0^{\mathrm{C}} e^{u\sec\phi}f(u)\,du\right]. \quad . \qquad (50)$$

We denote by $\mathrm{B}(x)$ and $\mathrm{B}(-x)$ the functions

$$\mathrm{B}(x) = Ei\,(-x)-\log x, \qquad \mathrm{B}(-x) = Ei\,(x)-\log x. \quad . \quad . \quad . \quad . \qquad (51)$$

The expansion when x is small of the exponential integral is

$$Ei\,(x) = \gamma+\tfrac{1}{4}\log x^4+x+\frac{x^2}{2\,.\,2\,!}+\frac{x^3}{3\,.\,3\,!}+\frac{x^4}{4\,.\,4\,!}+\ldots, \quad . \quad . \quad . \quad . \qquad (52)$$

where γ is EULER's constant, $\gamma = 5572$ and the expansion holds for both positive and negative values of x.

Thus when x is small the expansions for $\mathrm{B}(x)$ and $\mathrm{B}(-x)$ are

$$\left.\begin{array}{l} \mathrm{B}(x) = \gamma-x+\dfrac{x^2}{2\,.\,2\,!}-\dfrac{x^3}{3\,.\,3\,!}+\ldots \\ \text{and} \\ \mathrm{B}(-x) = \gamma+x+\dfrac{x^2}{2\,.\,2\,!}+\dfrac{x^3}{3\,.\,3\,!}+\ldots \end{array}\right\} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (53)$$

It can be shown that the integral

$$\int_0^c f(ax)\,e^{-bx}\,dx = \frac{1}{b}\{1-e^{-bc}f(ac)\}$$
$$+\frac{a}{b}\left[\frac{1}{b}\log\left|\frac{a}{a+b}\right|-\frac{1}{b}e^{-bc}Ei\,(-ac)+\frac{1}{b}Ei\,\{-(a+b)\,c\}\right]. \quad . \quad . \qquad (54)$$

The result holds for positive as well as negative values of b provided the argument of $(a+b)\,c$ in the logarithm and in $Ei\,\{-(a+b)\,c\}$ is the same.

By means of this result and in the notation defined in (51) it can be shown that (50) reduces to

$$\tfrac{1}{2}\frac{c}{\mathrm{C}}\,\frac{1}{\mathrm{K}_0}\,\frac{1}{\sec\phi}\,\Phi\,(\mathrm{C},\phi) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (55)$$

where

$$\Phi(\mathrm{C}, \phi) = (1-e^{-\mathrm{C}\sec\phi})\{1-f(\mathrm{C})\} + \cos\phi[\mathrm{B}(\mathrm{C})-\mathrm{B}\{\mathrm{C}(1+\sec\phi)\}+e^{-\mathrm{C}\sec\phi}\{\mathrm{B}(\mathrm{C})-\mathrm{B}[-\mathrm{C}(\sec\phi-1)]\}] \quad . . \quad (56)$$

We notice that for $\phi = 0$, $\sec\phi = 1$,

$$\Phi(\mathrm{C}, 0) = (1-e^{-\mathrm{C}})\{1-f(\mathrm{C})\}+\mathrm{B}(\mathrm{C})-\mathrm{B}(2\mathrm{C})+e^{-\mathrm{C}}\{\mathrm{B}(\mathrm{C})-\gamma\}, \quad . \quad . \quad . \quad (57)$$

where γ here stands for EULER's constant.

For $\phi = \frac{1}{2}\pi$, $\sec\phi = \infty$ (56) reduces to

$$\Phi(\mathrm{C}, \tfrac{1}{2}\pi) = 1-f(\mathrm{C}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

From (48) and (55) the expression for the intensity at the earth's surface of radiation from that portion of sky which is in any direction ϕ with the vertical and azimuth ψ measured from a vertical plane through the sun is, for $\zeta > \phi$.

$$\mathrm{T}(\phi, \zeta) = \frac{\mu_0(\theta)}{\mathrm{K}_0}\mathrm{S}\left[\mathrm{C}\sec\phi e^{-\mathrm{C}\sec\phi}\,\mathrm{G}\{\mathrm{C}(\sec\zeta-\sec\phi)\}+\tfrac{1}{2}\frac{c}{\mathrm{C}}\begin{pmatrix}\epsilon_1\\ \epsilon\\ \epsilon_2\end{pmatrix}\Phi(\mathrm{C}, \phi)\right], \quad (59)$$

while for $\zeta < \phi$ we have

$$\mathrm{T}(\phi, \zeta) = \frac{\mu_0(\theta)}{\mathrm{K}_0}\mathrm{S}\left[\mathrm{C}\sec\phi e^{-\mathrm{C}\sec\zeta}\,\mathrm{G}\{\mathrm{C}(\sec\phi-\sec\zeta)\}+\tfrac{1}{2}\frac{c}{\mathrm{C}}\begin{pmatrix}\epsilon_1\\ \epsilon\\ \epsilon_2\end{pmatrix}\Phi(\mathrm{C}, \phi)\right]. \quad (60)$$

From equations (3) and (7) we notice that

$$\mu_0(\theta) = \tfrac{3}{4}(1+\cos^2\theta)\,\bar{\mu}_0 = \tfrac{3}{4}(1+\cos^2\theta)\,\kappa_0/4\pi,$$

so that the factor

$$\mathrm{S}\mu_0(\theta)/\mathrm{K}_0 = \mathrm{S}\,(4\pi)^{-1}\tfrac{3}{4}(1+\cos^2\theta)\,c/\mathrm{C}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

From the polar diagram fig. 1 we see that

$$\cos\theta = \cos\phi\cos\zeta + \sin\phi\sin\zeta\cos\psi. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

The first terms in equations (59) and (60) give the contribution to the intensity of sky light due to the sun's radiation which has been once scattered by the atmosphere.

If C is small and if the attenuation is due to scattering only, ($c = \mathrm{C}$), the first term of (60) gives for the scattered radiation coming from a direction ϕ the value

$$(4\pi)^{-1}\mathrm{S}\,\tfrac{3}{4}(1+\cos^2\theta)\,c\sec\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

which agrees with the value obtained by KELVIN.*

The first terms in (59) and (60) taken as they stand with $\mathrm{C} = c$ take into account the fact that both the incident and scattered radiations suffer attenuation: this effect

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* KELVIN, *loc. cit.* equation (19), p. 313.

is considered in a formula obtained by RAYLEIGH.* The term γ in $C = c+\gamma$ allows for attenuation by absorption alone (*i.e.*, without scattering). The second terms in (59) and (60) represent the contribution of self-illumination to the scattered radiation coming from any particular direction. An evaluation of this effect has not, so far as the writer is aware, been submitted to calculation although the importance of the effect is realized both by KELVIN† and RAYLEIGH,* and in an analogous problem by LOMMEL.‡

The expressions (59) and (60) for the scattered radiation from any direction besides depending on the coefficients of absorption for the radiation of wave-length under consideration, depend also on the angular co-ordinates of direction ϕ and ψ as well as on ζ the zenith distance of the sun. If we consider the intensity from zenith sky the expressions are greatly simplified. Writing $\phi = 0$ and $\theta = \zeta$, (59) gives,

$$\mathrm{T}(0, \zeta) = \frac{\mu_0(\zeta)}{\mathrm{K}_0} \mathrm{S} \left[\mathrm{C}e^{-\mathrm{C}} \mathrm{G}\{\mathrm{C}(\sec \zeta - 1)\} + \tfrac{1}{2} \frac{c}{\mathrm{C}} \begin{pmatrix} \epsilon_1 \\ \epsilon \\ \epsilon_2 \end{pmatrix} \Phi(\mathrm{C}, 0) \right], \quad . \quad . \quad (64)$$

where $\Phi(\mathrm{C}, 0)$ is given by (57) and is tabulated in Table V.

It is not difficult to construct a double-entry table in terms of C and ζ giving the values for the functions which occur in (64) so that observations on zenith sky are most appropriate for comparison with the results of calculation from the attenuation coefficients determined by observations at the *same* time.

The intensity of sky radiation from the direction of the horizon $\left(\phi = \frac{\pi}{2}\right)$ is given by

$$\mathrm{T}\left(\frac{\pi}{2}, \zeta\right) = \frac{\mu_0(\theta)\,\mathrm{S}}{\mathrm{K}_0} \left\{ e^{-\mathrm{C}\sec\zeta} + \tfrac{1}{2} \frac{c}{\mathrm{C}} \begin{pmatrix} \epsilon_1 \\ \epsilon \\ \epsilon_2 \end{pmatrix} \Phi(\mathrm{C}, \tfrac{1}{2}\pi) \right\}, \quad . \quad . \quad . \quad . \quad (65)$$

where by (62) θ is given by $\cos\theta = \sin\zeta\cos\phi$ and $\Phi(\mathrm{C}, \frac{1}{2}\pi)$ is defined by (58). It will be noticed that this formula unlike the approximate one (63), obtained by KELVIN,

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* RAYLEIGH, 'Phil. Mag.,' XLI., p. 116.

† KELVIN, *loc. cit.*, p. 302, sect. 54.

‡ LOMMEL, E., 'Sitzungb. der math.-phys. Classe der K. Bayer. Akad. der Wiss.,' Bd. 17 (1887), p. 95; (the analysis is reproduced by MÜLLER, 'Photometrie der Gestirne,' Leipzig, 1897, pp. 47–52). In working out the scattering of radiation by opaque, diffusely reflecting surfaces on an absorption theory, LOMMEL obtains a first order approximation to the effect of self-illumination in giving rise to deviations from LAMBERT'S Law of diffuse reflection, the modified formula being referred to as the Lommel-Seeliger Law of Illumination. This problem is included as a particular case of the investigation of the present paper. LOMMEL'S formula for diffuse reflection is represented in the present instance by equation (69), which is the solution of an integral equation expressing exactly the effect of self-illumination. MÜLLER points out that even LOMMEL'S modification of LAMBERT'S Law does not represent exactly the results of observation on diffuse reflection; it may happen that the more complete solution represented by (69), adapted to the case of intense absorption, gives a better representation of fact. This point must, however, be left over for further investigation.

remains finite, although its application to the case of the earth's atmosphere is somewhat invalidated by the curvature of the earth.

On examining (59) it will be noticed that as long as C is not too large we may write

$$\mathrm{T}(\phi, \zeta) = \frac{\mu_0(\theta)}{\mu_0(\zeta)} \sec\phi \mathrm{T}(0, \zeta) = \frac{1+\cos^2\theta}{1+\cos^2\zeta} \sec\phi \mathrm{T}(0, \zeta), \quad . \quad . \quad . \quad . \quad (66)$$

which may be taken as a rough approximation for the intensity of sky-radiation from any direction not too close to the horizon where (65) must be used. When C is large the wave-length corresponding is small, and the intensity in the normal solar spectrum outside the atmosphere also becomes small. Hence the formula (66) is sufficiently accurate when the total intensity on a horizontal plane is required. Denoting by H (ζ) the intensity of scattered radiation of wave-length λ received per unit time on unit area of horizontal surface, we have

$$\mathrm{H}(\zeta) = \int \mathrm{T}(\phi, \zeta) \cos\phi \, d\omega,$$

the integral being taken over the entire sky.

Since $d\omega = \sin\phi \, d\phi \, d\psi$, we have

$$\mathrm{H}(\zeta) = \int_0^{2\pi} d\psi \int_0^{\frac{1}{2}\pi} \mathrm{T}(\phi, \zeta) \cos\phi \sin\phi \, d\phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

and making use of the approximation in (66) we have

$$\mathrm{H}(\zeta) = \frac{\mathrm{T}(0, \zeta)}{1+\cos^2\zeta} \int_0^{2\pi} d\psi \int_0^{\frac{1}{2}\pi} (1+\cos^2\theta) \sin\phi \, d\phi.$$

The total intensity for all wave-lengths per unit area of a horizontal surface is given by

$$\int_0^\infty \mathrm{H}(\zeta) \, d\lambda = \frac{2\pi}{\frac{3}{4}(1+\cos^2\zeta)} \int_0^\infty \mathrm{T}(0, \zeta) \, d\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

Of some interest is the intensity of the radiation which is scattered from the atmosphere back into interplanetary space. If we write (H−X) for X in (47) we notice that

$$\mathrm{R}(\phi, \zeta) = \sec\phi \int_0^{\mathrm{H}} e^{-\mathrm{K}_0 \mathrm{X} \sec\phi} \mathrm{J}(\mathrm{H}-\mathrm{X}) \, d\mathrm{X};$$

we also notice from (36) that $\phi(\mathrm{H}-\mathrm{X}) = \phi(\mathrm{X})$.

We thus obtain from (45)

$$\mathrm{R}(\phi, \zeta) = \mu_0(\theta) \mathrm{S} \sec\phi \left[\int_0^{\mathrm{H}} e^{-\mathrm{K}_0 \mathrm{X} (\sec\phi + \sec\zeta)} d\mathrm{X} + \begin{pmatrix}\epsilon_1 \\ \epsilon \\ \epsilon_2\end{pmatrix} \int_0^{\mathrm{H}} e^{-\mathrm{K}_0 \mathrm{X} \sec\phi} \phi(\mathrm{X}) \, d\mathrm{X} \right],$$

which reduces to

$$\mathrm{R}(\phi, \zeta) = \frac{\mu_0(\theta) \mathrm{S}}{\mathrm{K}_0} \left[\mathrm{C} \sec\phi \mathrm{G} \{ \mathrm{C}(\sec\phi + \sec\zeta) \} + \frac{1}{2} \frac{c}{\mathrm{C}} \begin{pmatrix}\epsilon_1 \\ \epsilon \\ \epsilon_2\end{pmatrix} \Phi(\mathrm{C}, \phi) \right]. \quad . \quad . \quad (69)$$

We notice that $R(\phi, \zeta)$ is only approximately equal to $T(\phi, \zeta)$ when C is small, *i.e.*, that the usual assumption that as much radiation is scattered in the direction of incidence as in the opposite direction only holds approximately when the coefficient of attenuation is small.

§ 6. *Note on the Polarization of Sky Radiation.*

It is well known that sky radiation is partly polarized in a vertical plane passing through the position of the sun (the principal plane): in so far as the radiation to be scattered is direct solar radiation, the polarization ought to be complete. That portion of the sky radiation due to self-illumination is largely unpolarized and may to a large extent account for this deficiency from complete polarization: this point is mentioned by RAYLEIGH in his 1871 paper and the analysis of the present paper enables the magnitude of this factor to be roughly estimated. The complete solution of the problem from this aspect would require us to split up the incident radiation into two components, one of which is polarized in the principal plane, the other at right angles to it: the effect of self-illumination would lead to two simultaneous integral equations in three variables, the solution of which would be much too complicated to be useful.

If, however, we refer to equations (59) and (60) it will be noticed that the expression for the intensity of sky radiation may be written in the form

$$T(\phi, \zeta) = \mu_0(\theta)\, S\,\{P(\phi, \zeta)+Q(\phi, \zeta)\}/K_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

where $P(\phi, \zeta)$ stands for the first term in the brackets of (59) or (60) and

$$Q(\phi, \zeta) = \tfrac{1}{2}\frac{c}{C}\begin{pmatrix}\epsilon_1\\ \epsilon\\ \epsilon_2\end{pmatrix}\Phi(C, \phi)$$

represents the effect of self-illumination.

In default of a rigorous solution it is not unreasonable to suppose that the portion of the scattered radiation due to self-illumination is independent of the angle of polarization of the incident radiation. As far as the primary scattered radiation alone is concerned, the intensities polarized in the principal plane and in a plane at right angles to it are in the proportion 1 to $\cos^2\theta$. Thus from (70) the ratio of the sky intensities polarized in the principal plane and in the plane at right angles to it are given by the ratio

$$\frac{T_1(\phi, \zeta)}{T_2(\phi, \zeta)} = \frac{P(\phi, \zeta)+Q(\phi, \zeta)}{\cos^2\theta P(\phi, \zeta)+Q(\phi, \zeta)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (71)$$

If we make use of the approximations of equation (66),

$$P(\phi, \zeta) = \sec\phi\, P(0, \zeta)\, \mu_0(\theta)/\mu_0(\zeta), \qquad Q(\phi, \zeta) = \sec\phi\, Q(0, \zeta)\, \mu_0(\theta)/\mu_0(\zeta)$$

(71) may be written

$$\frac{T_2(\phi, \zeta)}{T_1(\phi, \zeta)} = \frac{\cos^2\theta + Q(0, \zeta)/P(0, \zeta)}{1 + Q(0, \zeta)/P(0, \zeta)} \quad \ldots \ldots \quad (72)$$

From this formula we see that sky polarization is most complete for $\theta = \frac{1}{2}\pi$, *i.e.*, over a great circle an angular distance $\frac{1}{2}\pi$ from the sun polarization would be complete in light from this direction if $Q(0, \zeta)$ were zero, *i.e.*, if the effects of self-illumination were negligible.

For the sake of comparison with observation the ratio $T_1(\phi, \zeta)/T_2(\phi, \zeta)$ is calculated for zenith sky, $(\phi = 0)$, in the form

$$\frac{T_1(0, \zeta)}{T_2(0, \zeta)} = \frac{1 + Q(0, \zeta)/P(0, \zeta)}{\cos^2\zeta + Q(0, \zeta)/P(0, \zeta)} \quad \ldots \ldots \quad (73)$$

Part III.

§ 7. *Analysis of Observations on the Attenuation of Solar Radiation by the Earth's Atmosphere.*

The intensity of solar radiation transmitted to a station at a height x above sea-level is given by equation (23) in the form

$$E(X) = Se^{-K_0(H-X)\sec\zeta},$$

where

$$X = \int_0^x \frac{\rho}{\rho_0}\,dx, \quad \text{and} \quad H = \int_0^\infty \frac{\rho}{\rho_0}\,dx$$

represents the height of the "homogeneous atmosphere."

Thus

$$H - X = \int_x^\infty \frac{\rho}{\rho_0}\,dx, \quad \text{so that} \quad \frac{H-X}{H} = \frac{\int_x^\infty \rho\,dx}{\int_0^\infty \rho\,dx} = \frac{p}{p_0},$$

where p and p_0 are the pressures of the atmosphere at the station and at the sea-level respectively. We thus have, writing $C_x = Cp/p_0$, the expression

$$E(x) = Se^{-C_x\sec\zeta} \quad \ldots \ldots \quad (74)$$

If the heights of the barometer at the station and at sea-level are known at the time of observation, the comparison of absorption coefficients is independent of the law of variation of atmospheric pressure-gradient with height.

We notice from (37), writing $C = c+\gamma = \kappa_0 H + \alpha_0 H_0$, that

$$\left.\begin{aligned} C &= \tfrac{32}{3}\pi^3 (n_0-1)^2 \lambda^{-4} H/N_0 + \alpha_0 H, \\ {}^{*}C &= \beta\lambda^{-4}+\gamma, \quad \text{where} \quad \beta = \tfrac{32}{3}\pi^3 (n_0-1)^2 H/N_0, \end{aligned}\right\} \quad \text{i.e.,} \qquad (75)$$

which gives

$$C_x p_0/p = \beta\lambda^{-4}+\gamma. \qquad (76)$$

Extensive observations on the determination of the coefficient of attenuation C_x for different wave-lengths have been carried out at various stations by the work of the Smithsonian Astrophysical Observatory.[†] The mean coefficients of atmospheric transmission for Washington, Mount Wilson, and Mount Whitney have recently been given by ABBOT.[‡] These are quoted in Table I., while for the sake of independent comparison, the results of MÜLLER[§] for Potsdam are also added.

In order to study the correctness of formula (76) the coefficients of transmission for the different stations are plotted on a base λ^{-4}, λ being measured in microns (10^{-4} cm.). The results are shown in Diagram I., and give rise to a number of straight lines. If the absorption were due to air-molecules alone, (76) shows that we should obtain a family of straight lines all passing through the same point ($\lambda^{-4} = -\gamma/\beta$). The straight lines actually obtained show that some variable factor in the atmosphere other than the molecules themselves is effective in attenuation, especially for stations below the level of Mount Wilson. This factor is generally referred to as atmospheric "dust." A slight generalization of the analysis by which (76) was obtained enables us to interpret the results shown graphically in Diagram I.

Let N' be the number of "dust" particles per unit volume at a height x above the earth's surface. The coefficient of attenuation, which includes the effects of scattering and absorption both by air molecules and by "dust," may be written in the form

$$C_x = (\beta\lambda^{-4}+\gamma)p/p_0 + K'_0(\lambda)\int_x^\infty \frac{N'}{N'_0}\,dx, \qquad (77)$$

where N'_0 is a constant representing the number of dust particles per unit volume at the earth's surface, and $K'_0(\lambda)$ depends on the nature of absorption and scattering by the dust particles. The distribution of "dust" N' in the atmosphere may be regarded

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[*] The representation of the coefficient of attenuation as the sum of two terms, one constant and the other varying inversely as the fourth power of the wave-length, seems to have been first recognized by BECKER (see KELVIN, 'Baltimore Lectures,' p. 321, equation 33) from an analysis of MÜLLER's observations.

[†] 'Annals of the Smithsonian Astrophysical Observatory,' vol. II., by C. G. ABBOT and F. E. FOWLE, Washington, 1908. Referred to subsequently as 'Annals,' vol. II.

[‡] ABBOT, C. G., "The Sun's Energy-Spectrum and Temperature," 'Astrophysical Journal,' XXXIV., October, 1911.

[§] MÜLLER, G., "Photometrie der Gestirne," Leipzig, 1897, p. 140.

as an unknown and variable quantity. Diagram I. shows that for Mount Wilson and for Mount Whitney the effect of "dust" is small, *i.e.*, we may take $N' = 0$ for x greater than 1780 metres. In this case (77) reduces to (76) and the attenuation may be taken to be due almost entirely to the effect of air-molecules, while the existence of a small term, γ, indicates that even in the comparatively dust-free air above Mount Whitney there is a small amount of attenuation by absorption, *i.e.*, a direct conversion of solar radiation into thermal agitation of atmospheric molecules.

We notice from Table II. that for the comparatively dust-free air above the level of Mount Wilson the value of γ under standard conditions of pressure is $\gamma = \alpha_0 H = \cdot 032$, or, since $H = 7\cdot 988 \times 10^5$ cm. at 0° C., the value of α_0 is

$$\alpha_0 = 4\cdot 0 \times 10^{-8} \text{ cm.}^{-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (78)$$

On referring to (8) we notice that α_0 is the fraction of radiant energy converted per centimetre of path into thermal molecular agitation. This fraction is greatly increased by the presence of small solid particles such as "dust," &c. From (9) we can estimate the rate of increase of temperature in a gas under atmospheric pressure due to solar radiation passing through it.

We have $\dfrac{d\Theta}{dt} = \dfrac{\alpha_0 E}{\rho_0 s}$ from equation (9).

Taking the value of α_0 for dust-free air from (78) and writing $E = 1\cdot 92$ calories per minute, $\rho_0 = \cdot 001293$, $s = \cdot 237$, we find

$$\left.\begin{aligned} \frac{d\Theta}{dt} &= 2\cdot 5 \times 10^{-4} \text{ degrees C. per minute} \\ &= 1\cdot 5 \times 10^{-2} \text{ degrees C. per hour} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (79)$$

In the case of ordinary air at sea-level, the Washington observations from Table II. show that the rate of increase of temperature calculated in (79) must be increased to about six times this value.

With regard to sea-level stations, Diagram I. seems to indicate, both for the Washington and Potsdam observations, a marked change in the nature of the absorption due to "dust" in the neighbourhood of $\cdot 610\mu$. We therefore discuss separately the case of long-wave radiation ($\lambda > \cdot 610\mu$) and short-wave radiation ($\lambda < \cdot 610\mu$).

(i) *Long-wave Radiation* ($\lambda > \cdot 610\mu$).

For long waves the straight lines of Diagram I. show that the term $K'_0(\lambda)$ of (77) must be of the form

$$K'_0(\lambda) = \beta''\lambda^{-4} + \gamma'',$$

where β'' and γ'' are constants for the range of wave-lengths greater than $\cdot 610\mu$. This indicates that the presence of "dust" gives rise to both absorption and scattering; (77) may then be written

$$C_x = \frac{1}{\lambda^4}\left\{\frac{p}{p_0}\beta + \beta''\int_0^\infty \frac{N'}{N'_0}\,dx\right\} + \Gamma''\frac{p}{p_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (80)$$

where

$$\Gamma'' = \gamma + \frac{p_0}{p}\gamma''\int_x^\infty \frac{N'}{N'_0}\,dx.$$

Diagram I. shows clearly that for long waves the straight lines both for Potsdam and Washington intersect in the same point, $\lambda^{-4} = -\gamma/\beta$, as do the lines for Mount Wilson and Mount Whitney.

From (80) this result requires that

$$\beta/\gamma = \beta''/\gamma'', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (81)$$

a condition which is independent of the law of distribution of the "dust" particles.

The ratio $\frac{\beta}{\gamma}$ is proportional to the ratio

$$\frac{\text{energy of incident wave scattered by small particles}}{\text{energy of incident wave converted into molecular agitation}},$$

and (81) indicates from the results of observation that for long-wave radiation this ratio is independent of the nature of the scattering particles, whether "dust" or air-molecules. This result throws some light on the question raised at the end of §1 as to the mechanism by which the molecules of a gas can convert a portion of the radiant energy incident upon them into thermal molecular agitation. The same mechanism which is effective in scattering radiation is also capable of effecting molecular velocities, and therefore the rate of increase of temperature in such a way that the ratio β/γ is independent of the nature of the molecule or even of the small "dust" particle giving rise to the absorption and scattering.

(ii) *Short-wave Radiation* ($\lambda < \cdot 610\mu$).

For short waves we may suppose that the incident radiation is not scattered by the dust-particles but is absorbed and converted into heat. On this supposition $K'_0(\lambda)$ in (77) is of the form γ', where γ' is a constant independent of the wave-length. Equation (77) then takes the form

$$C_x = \lambda^{-4}\beta p/p_0 + \gamma p/p_0 + \gamma'\int_x^\infty \frac{N'}{N'_0}\,dx = \lambda^{-4}\beta p/p_0 + \Gamma' p/p_0. \quad . \quad . \quad . \quad (82)$$

The slope of this line in the graphical representation of Diagram I. is given by

$$\tan\theta' = \beta p/p_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (83)$$

and is independent of the distribution of "dust" in the atmosphere. This conclusion is justified by calculating β for the various stations from the slope of the lines in

Diagram I. and a knowledge of the mean barometric pressures at these stations. The results are tabulated and described in Table II. From these values of β we may by (75) calculate N_0 the number of molecules in a gas under standard conditions of pressure and temperature. We take $n_0 - 1 = {\cdot}000293$, $H = 7{\cdot}988 \times 10^5$ cm. at 0° C. and (71) then gives

$$N_0 = 2{\cdot}269 \times 10^{17}/\beta. \qquad (84)$$

The results for each set of observations are given in Table II. The values of N_0 agree remarkably well among themselves, and give for a mean value*

$$N_0 = 2{\cdot}32 \times 10^{19}. \qquad (85)$$

This result is in substantial agreement with the value of N_0 obtained by RUTHERFORD and GEIGER†

$$N_0 = 2{\cdot}72 \times 10^{19},$$

and with the value obtained by MILLIKAN‡ from a recent determination of the elementary electrical charge, $e = 4{\cdot}891 \times 10^{-10}$ E.S.U., which gives

$$N_0 = 2{\cdot}644 \times 10^{19},$$

taking the Faraday constant to be 9·655 absolute E.M. units. This agreement indicates that for short-wave radiation the scattering is almost entirely due to air-molecules, while the effect of "dust" is to produce a genuine absorption effect, *i.e.* a direct conversion of radiant energy into heat.

The term

$$\Gamma' = \gamma + \frac{p_0}{p}\gamma' \int_x^\infty \frac{N'}{N'_0}\,dx \qquad (86)$$

involves the distribution of atmospheric "dust" and may therefore be expected to be an extremely variable factor with respect both to place and time. The method of analysis of the present section offers a convenient method of studying the variations in the distribution of atmospheric "dust" and their connection with other meteorological phenomena.

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* The close agreement of coefficients of attenuation calculated from the formula $e = \beta/\lambda^{-4}$, using RUTHERFORD and GEIGER's value of N_0, with coefficients calculated from observations on *selected clear days* at Washington and Mount Wilson, was pointed out by SCHUSTER ("Molecular Scattering and Atmospheric Absorption," 'Nature,' July 22, 1909; 'Optics,' 2nd ed., 1909, p. 329).

† RUTHERFORD, E., and GEIGER, H., "Charge and Nature of the α-Particle," 'Roy. Soc. Proc.,' A, vol. 81, 1908, p. 171.

‡ MILLIKAN, R. A., "The Isolation of an Ion, a Precision Measurement of its Charge, and the Correction of STOKES' Law," 'Phys. Rev.,' XXXII., April, 1911. A summary of the various physical measurements which lead to the value of N_0 is given by PERRIN, J. ('Annales de Chimie et de Physique,' 8^me^ sér., September, 1909, translated by SODDY, F.; 'Brownian Movement and Molecular Reality,' Taylor and Francis, 1910, p. 90).

§ 8. *On the Intensity of Sky Radiation as Calculated from the Mean Coefficients of Attenuation at Mount Wilson and Washington.*

It will be noticed from (64) that the intensity from zenith sky for different wave-lengths can be expressed in terms of the zenith distance of the sun and the coefficients of attenuation C, c, and γ which are determined for a given station by an analysis of atmospheric transmission observations according to the method of the preceding section. In order to simplify the calculations from (64) the various functions of C and ζ which occur in this formula are tabulated in Tables III., IV., and V.

The intensity from zenith sky is then worked out for the two stations Mount Wilson and Washington from the mean coefficients of attenuation at these two places. In the first case the numerical values corresponding to the extreme and mean solutions of the integral equation are carried throughout all the calculations and in this way give the limit of errors due to an approximate solution. In the second case, which is taken as typical of a sea-level station, numerical values corresponding to the mean solution of the integral equation are alone given, the reason being that the absorption at sea-level is an extremely variable quantity which would give rise to fluctuations in sky radiation probably exceeding the difference of the extreme solutions.

Zenith intensities of sky radiation for different wave-lengths and for various zenith distances of the sun are given in Table VI. for Mount Wilson and in Table VIII. for Washington. The unit of intensities is arbitrary and is that employed in Table I. for the normal solar spectrum outside the earth's atmosphere. The results are shown graphically in Diagrams II. to VII. for Mount Wilson and in Diagram XII. for Washington. From these curves it is possible to obtain by double interpolation the intensity from zenith sky corresponding to any wave-length and zenith distance of the sun. In this way a comparison was made of the quality of sky radiation obtained by calculation with that obtained experimentally at Mount Wilson.* The results are given numerically in Table X. and are compared graphically in Diagram XIII.

By integrating the curves for the zenith intensity and making use of the approximate formula (66) we are able to obtain a rough approximation to the total intensity of sky radiation from any direction. On comparing (66) with (65), for which $\phi = \frac{1}{2}\pi$, it must be noted that the first of these formulæ can only be used for zenith distances which are not too great. It will also be noticed that $T(\frac{1}{2}\pi, \zeta)$ does not vary as rapidly with the wave-length as $T(0, \zeta)$. The nature of the scattered radiation from a portion of the sky near the horizon is governed principally by the term $Se^{-C\sec\zeta}$, *i.e.*, it is of nearly the same quality as the direct sunlight except for the contribution to the intensity due to the second term in $T(\frac{1}{2}\pi, \zeta)$ which represents the effect of self-illumination. This feature is not shown by

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[*] 'Annals,' vol. II., Table 32, p. 155.

expressions for sky radiation hitherto obtained; in fact the whitish colour of the sky near the horizon was considered by KELVIN* to be an objection to the theory of scattering.

By calculating the values of the intensities of solar radiation which reaches the earth's surface for various zenith distances of the sun and for various wave-lengths, and by integrating the curves so obtained, we obtain the values of the total intensity of solar radiation reaching the two stations Mount Wilson and Washington. Taking the value of the solar constant to be 1·922 calories per square centimetre per minute,† the results are given in the same units and are calculated for solar radiation incident on a plane normal to the sun's rays as well as for the solar radiation incident on a horizontal plane. The results are given in Tables VII. and IX., and are shown graphically in Diagrams IX. and X.

These results enable the value of the total sky intensity in any direction to be compared with the intensity of direct solar radiation at the station in the form *sky/sun* for equal solid angles (semi-diameter of sun taken as 16′ of arc). The results are given in Tables VII. and IX., both for Mount Wilson and Washington, and are shown graphically in Diagram XI.

By interpolation from the diagram just mentioned the values of *sky/sun* for various directions of sky and for various zenith distances of the sun are compared with the values observed at Mount Wilson.‡ The comparison is made in Tables XI. and XIII.; the results of calculation are in fair agreement with observation except for regions of sky near the sun and near the horizon. The first of these discrepancies is probably brought about by the simplifying assumption made in equation (17) by writing $\bar{\mu}$ for $\mu(\theta)$ and $\mu(\widehat{rr'})$. The existence of such a term depending on an angular co-ordinate complicates the integral equation beyond hope of solution; it can be seen, however, that its existence gives rise to a bright region of sky in the neighbourhood of the sun not represented by the approximate solution considered in the present paper. The discrepancy which exists in the case of directions of sky near the horizon is due to the failure of the approximate formula (66) for large values of ϕ. In such cases the complete formula (60) should be employed. The use of this formula would require the tabulation of functions of two and three variables, which might be undertaken when more numerous and more accurate observations on sky radiation are available. It must be remembered in making these comparisons that the result of sky observations on certain specified days are compared with values based on mean coefficients of attenuation. The only satisfactory method of making the comparison is to obtain sky radiation observations on the same day as observations are made for the coefficients of attenuation of solar

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[*] KELVIN, *loc. cit.*, p. 307.

[†] ABBOT, C. G., and FOWLE, F. E., "The Value of the Solar Constant of Radiation," 'Astrophysical Journal,' XXXIII., April, 1911, p. 191.

[‡] 'Annals,' vol. II., Table 32, p. 151.

radiation.* In the present paper no account is taken of the reflecting power of the earth's surface. The tolerable agreement between the results of observation and those of a theory based on a non-reflecting surface shows that for an ordinary landscape the effect of reflection from field and foliage need not be as great as is sometimes supposed.† The effect of snow on the polarization of sky radiation is well-known‡: on this point Lord RAYLEIGH mentions in his 1871 paper the interest which would be attached to sky radiation observations taken over a landscape covered with snow or over the sea, reflection from these surfaces being in both cases especially determinate.§

For meteorological purposes it is important to know the total solar radiation incident on a horizontal plane as well as the contribution due to sky radiation. The results are given in calories per square centimetre per minute for Mount Wilson and Washington in Tables VII. and IX., and are shown graphically in Diagrams IX. and X. It will be noticed that for large zenith distances of the sun the contribution of sky radiation to the total radiation on a horizontal plane is a very considerable fraction of that due to direct solar radiation. The factor of sky radiation is thus of considerable importance in the meteorology of northern latitudes.

The agreement between the results of calculations and such observations as are available gives rise to a hope that the present communication may serve as a guide towards systematic observations of the type dealt with, and to their interpretation in terms of a theory of scattering and absorption; by this means one may hope to obtain absorption constants and methods of using them which will be of some service to meteorology and astrophysics.

Summary.

The analysis of the present paper seems to support the view that at levels above Mount Wilson molecular scattering is sufficient to account completely both for

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* In the "Report on the Astrophysical Observatory" (C. G. ABBOT, 'Annual Report of the Smithsonian Institution,' 1911, p. 65), the Director announces that sky radiation observations have been successfully taken at Mount Whitney (August, 1910). Since the transmission coefficients at the time of observation are also determined, the results will enable an accurate comparison of sky radiation results to be made with the values obtained by calculation in terms of the coefficients of attenuation.

† NICOLS, "Theories of the Colour of the Sky," 'Phys. Rev.,' XXVI., June, 1908, p. 507.

‡ Observations have been made by MCCONNEL, J. C., on the effect of the nature of the ground on the degree of polarization of the sky at 90 degrees from the sun; the effect of a covering of snow is to diminish the degree of polarization. (PERNTNER, 'Meteorological Optics,' Part IV., 1910, p. 643. The above reference is taken from 'A History of the Cavendish Laboratory,' Longmans, Green & Co., 1910, p. 129.)

§ The analysis of the present paper could be extended without difficulty to take into account the effect of reflection from the earth's surface on the intensity and polarization of sky radiation, provided the landscape were covered by a layer of uniform substance such as snow, or observations were taken over the sea, which presents a determinate reflecting surface.

attenuation of solar radiation and for the intensity and quality of sky radiation. Even at sea-level the effect of "atmospheric dust" can be taken into account in a simple manner in the formulæ for absorption and scattering. Should future observations support the validity of the simple law expressed by equation (2) connecting the coefficient of attenuation with the wave-length, we may with considerable assurance make use of the law to obtain the coefficients for very short or very long wave-lengths when the direct method of calculation from high and low sun observations leaves room for considerable uncertainty owing to the small intensities in the solar spectrum at these wave-lengths and owing to other experimental difficulties.

SCHUSTER[*] points out in this connection the extreme importance of determining accurately the form of the solar intensity curve outside the earth's atmosphere for short wave-lengths, since the effect of a solar atmosphere in absorbing and scattering radiation is to give rise to an intensity-curve which does not agree with that given by PLANCK's formula especially for short wave-lengths.

Absorption and scattering of radiation by the sun's atmosphere, taken in conjunction with effects of self-illumination, constitutes a problem analogous to that just considered for the earth's atmosphere. By making a comparison between the calculated variation of intensity of radiation of different wave-lengths over the solar disc and the results of observation it will be possible to determine from the intensity curve of the normal solar spectrum outside the earth's atmosphere the intensity-curve at the radiating layer of the sun. This corrected curve may then be compared with that given by PLANCK's formula and a closer approximation made to the temperature of the sun than the values now given. This investigation the writer hopes to be able to deal with in a future communication

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[*] SCHUSTER, *loc. cit.*

Numerical Tables and Comparison of Theory with Observation.

Discussion of Results.

TABLE I.—*Coefficients of Attenuation for Washington, Mount Wilson, Mount Whitney, and Potsdam.*

The table of constants of solar intensities and coefficients of attenuation for Washington, Mount Wilson, and Mount Whitney is taken from the revised reductions based on the most recent observations of the Smithsonian Astrophysical Observatory.[*] The unit expressing the relative intensities of solar radiation between wave-lengths λ and $\lambda+d\lambda$ is arbitrary, and can be reduced to calories per square centimetre per minute by multiplying by a factor η such that

$$\eta\int_0^\infty \mathrm{S}\,d\lambda = 1\cdot 922 \text{ calories per square centimetre per minute.}\dagger$$

In terms of the unit of intensity given in the table, and taking $d\lambda = \cdot 1\mu$, we find by graphical integration $\int_0^\infty \mathrm{S}\,d\lambda = 3321\cdot 0$, so that $\eta = \cdot 000578$.

No account is taken of the water-vapour bands which occur mainly in the infra-red, where the intensity of solar radiation is comparatively small. The position and extent of these bands is shown in the curve of the intensities in the normal solar spectrum given in Vol. II. of the 'Annals.'[‡]

The transmission coefficients for Potsdam are those given by MÜLLER.[§]

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[*] ABBOT, C. G., "The Sun's Energy-Spectrum and Temperature," 'Astrophysical Journal,' XXXIV., October, 1911, p. 197.

[†] ABBOT, C. G., and FOWLE, F. E., "The Value of the Solar Constant of Radiation," 'Astrophysical Journal,' XXXIII., April, 1911, p. 191.

[‡] 'Annals,' vol. II., p. 104.

[§] MÜLLER, G., 'Die Photometrie der Gestirne,' Leipzig, 1897, p. 138

TABLE I.

Wave-length in microns, λ.	Mean solar intensity, S.	Per-centage probable error.	Mean coefficients of atmospheric transmission, e^{-C_x}.					
			Washington, 1902–07.		Mount Wilson, 1909–10.		Mount Whitney, 1909–10.	
			e^{-C_x}.	C_x.	e^{-C_x}.	C_x.	e^{-C_x}.	C_x.
0·30 μ	(440)	—	—	—	—	—	(0·510)	(·691)
0·325	1285	30·	—	—	0·(550)	(·598)	0·584	·538
0·35	2700	7·3	—	—	0·612	·491	0·660	·416
0·375	3464	2·7	—	—	0·662	·412	0·738	·304
0·39	3620	1·7	0·445	·810	0·694	·365	0·763	·270
0·42	5261	1·3	0·586	·534	0·764	·269	0·806	·216
0·43	5340	1·7	0·600	·511	0·778	·251	0·822	·196
0·45	6047	1·4	0·640	·446	0·800	·223	0·851	·161
0·47	6253	1·8	0·671	·399	0·827	·190	0·880	·128
0·50	6064	1·9	0·705	·350	0·858	·153	0·900	·105
0·55	5627	2·1	0·739	·302	0·876	·132	0·918	·0866
0·60	5047	2·1	0·760	·274	0·890	·117	0·934	·0683
0·70	3650	0·4	0·839	·176	0·942	·0597	0·956	·0450
0·80	2672	1·2	0·865	·145	0·964	·0367	0·972	·0284
1·00	1664	0·7	0·901	·104	0·973	·0274	0·980	·0202
1·30	897	0·7	0·916	·0876	0·972	·0284	0·980	·0202
1·60	526	1·4	0·930	·0726	0·975	·0253	0·978	·0222
2·00	245	2·4	0·909	·0943	0·957	·0439	0·940	·0619
2·50	43	4·8	0·870	·139	0·(900)	(·105)	0·930	·0726
3·00	(12)	45·	—	—	—	—	0·910	·0943

Mean transmission coefficients for Potsdam.					
λ.	e^{-C_x}.	C_x.	λ.	e^{-C_x}.	C_x.
·44μ	0·706	·348	·58μ	0·830	·186
·46	0·740	·301	·60	0·840	·174
·48	0·764	·269	·62	0·850	·162
·50	0·781	·247	·64	0·861	·150
·52	0·795	·229	·66	0·871	·138
·54	0·808	·213	·68	0·881	·127
·56	0·819	·200			

Coefficients of Attenuation for Washington, Mount Wilson, Mount Whitney, and Potsdam.

TABLE II.—*Constants of Atmospheric Scattering and Absorption.*

The coefficients of attenuation given in Table I. for various stations were plotted on a large scale diagram against λ^{-4} as abscissæ. The results are shown in Diagram I. From the large-scale drawing the slopes of the straight lines passing through the mean position of the observed points were obtained and the values of $\tan\theta'$ and $\tan\theta''$ corresponding to short- and long-wave radiation were calculated.* From a knowledge of the mean barometric pressures at these stations the values of β as defined in (75) were calculated for short-wave radiation, leading by (84) to an estimate of N_0, the number of molecules per cubic centimetre of a gas at 0° C. and 760 mm. pressure. The values of the absorption constants Γ' and Γ'' of (80) and (82), which include the effect of "dust" especially noticeable at low-level stations, are also given in the table. At levels higher than Mount Wilson the atmosphere is comparatively dust-free and $\Gamma' = \Gamma'' = \gamma$. This value of γ can then be employed in (78) to give a numerical estimate of molecular absorption.

[* If greater accuracy is required the lines of closest fit to the system of observed points can be drawn by calculating in each case the position of the major axis of inertia of the corresponding system of material points of equal weight. Formulæ for the determination of this line are given by KARL PEARSON ('Phil. Mag.,' vol. II., 6th series, November, 1901, p. 559), and also by SNOW, E. C. ('Phil. Mag.,' March, 1911).—*Note added December* 31, 1912.]

TABLE III.—*Tabulation of the Function*, $Ce^{-C}G\{C(\sec\zeta-1)\}$.

The function $G(x) = (1-e^{-x})/x$ is tabulated by W. LASH MILLER and T. R. ROSEBRUGH* in a set of extensive tables of the integrals

$$\int_x^\infty u^{-2}e^{-u}\,du,\qquad \int_x^\infty u^{-1}e^{-u}\,du = Ei(-x),\qquad \int_x^\infty ue^{-u}\,du,\qquad \int_x^\infty u^2e^{-u}\,du.$$

Values are given to 9 significant figures at intervals of ·001 between $x = 0$ and $x = 1$, and at intervals of ·01 between $x = 1$ and $x = 2$. From these tables the double-entry Table III. was easily constructed. The calculations of the present table, as well as those of the other tables, were performed on a slide-rule, so that their limit of accuracy is about one or two parts in a thousand.

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* W. LASH MILLER and T. R. ROSEBRUGH, 'Trans. Roy. Soc. of Canada,' 2nd series, vol. IX., 1903, sect. iii., pp. 73-107.

TABLE II.

Station.	Height above sea-level.	Mean barometric pressure, p.	Short-wave radiation, $\lambda < \cdot 610\mu$.				Long-wave radiation, $\lambda > \cdot 610\mu$.		
			$\tan\theta'$.	β.	N_0.	Γ'.	$\tan\theta''$.	Γ''.	$\beta/\gamma = \beta''/\gamma''$.
	metres.	mm.							
Potsdam	100	*752	·00893	·00904	$2 \cdot 51 \times 10^{19}$	·105	·0170	·054	·32
Washington . .	10	†763·7	·01016	·01011	$2 \cdot 24 \times 10^{19}$	·192	·0277	·088	·32
Mount Wilson .	1780	‡617	·00806	·00994	$2 \cdot 28 \times 10^{19}$	·032	·00806	·032	·32
Mount Whitney	4420	§446·7	·00592	·01003	$2 \cdot 26 \times 10^{19}$	·032	·00592	·032	·32

Constants of Atmospheric Scattering and Absorption.

Authorities :—

* The mean barometric pressure at Potsdam is given by MÜLLER, *loc. cit.*, p. 138.

† The mean annual barometric pressure at Washington is taken from BARTHOLOMEW'S 'Atlas of Meteorology,' 1899.

‡ The mean barometric pressure at Mount Wilson is not given explicitly in the 'Annals.' The value given in the above table is obtained by finding the reduction of pressure to sea-level corresponding to an elevation of 5886 feet (the air-temperature being taken at 60° F.) from HAZEN'S Tables. ('Professional Papers of the Signal Service,' No. VI., Washington, 1882.)

§ The barometric pressure at Mount Whitney is obtained from observations given by LANGLEY, September 2–6, 1881 (LANGLEY, "Researches on Solar Heat: A Report of the Mount Whitney Expedition," 'Professional Papers of the Signal Service,' No. XV., 1884.)

TABLE III.

C. \ ζ.	0°.	20°.	40°.	60°.	70°.	80°.
0·00	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000
·05	·0476	·0475	·0472	·0464	·0443	·0424
·10	·0905	·0902	·0891	·0861	·0813	·0720
·14	·1217	·1212	·1191	·1133	·1072	·0889
·18	·1502	·1492	·1461	·1377	·1270	·1009
·22	·1766	·1753	·1708	·1583	·1439	·1093
·26	·2002	·1985	·1927	·1761	·1575	·1150
·30	·2220	·2200	·2136	·1953	·1749	·1174
·34	·2420	·2395	·2298	·2052	·1776	·1198
·38	·2600	·2568	·2450	·2163	·1844	·1206
·50	·303	·298	·280	·238	·1964	·1154
·60	·329	·323	·301	·248	·1950	·1090
·70	·348	·340	·313	·250	·1930	·1006
·80	·359	·350	·318	·247	·1850	·0923
·90	·366	·356	·320	·241	·1740	·0856

Table of the Function $Ce^{-C}G\{C(\sec\zeta - 1)\}$.

TABLE IV.—*Tabulation of the Function* G (C sec ζ).

This function occurs in calculating the mean coefficient, ϵ, in the solution of the integral equation (44). It is easily tabulated from LASH MILLER'S tables.

TABLE V.—*Tabulation of the Auxiliary Functions* Φ (C, 0), G (C), f (C).

The function $f(x)$ defined by the relation

$$f(x) = x\int_x^\infty u^{-2}e^{-v}\,du = e^{-x}+xEi\,(-x)$$

occurs in the theory of absorption in a flat plate which itself absorbs radiation from a uniform distribution of radiating elements throughout its own volume. A short table of the function $f(x)$ has been given by the writer in a previous paper.*

We write as in (51),

$$\mathrm{B}\,(x) = Ei\,(-x)-\log x, \qquad \mathrm{B}\,(-x) = Ei\,(x)-\log x.$$

The function B (x) is given in LASH MILLER'S Tables.† The function B $(-x)$ was calculated by making use of the tables of the exponential integral $Ei\,(x)$.‡

From these a table of the function

$$\Phi\,(\mathrm{C},0) = (1-e^{-\mathrm{C}})\,\{1-f\,(\mathrm{C})\}+\mathrm{B}\,(\mathrm{C})-\mathrm{B}\,(2\mathrm{C})+e^{-\mathrm{C}}\,\{\mathrm{B}\,(\mathrm{C})-\gamma\}$$

was constructed.

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[*] KING, L. V., "Absorption Problems in Radioactivity," 'Phil. Mag.,' February, 1912, p. 245.

[†] W. LASH MILLER and T. R. ROSEBRUGH, *loc. cit.*, p. 81.

[‡] *Cf.* DALE, 'Five-Figure Tables of Mathematical Functions,' Arnolds, London, 1908.

Table IV.

ζ. C.	0°.	20°.	40°.	60°.	70°.	80°.
0·00	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
·05	·975	·974	·968	·952	·929	·873
·10	·952	·948	·940	·906	·868	·770
·14	·933	·929	·913	·872	·820	·688
·18	·916	·910	·891	·840	·778	·623
·22	·897	·892	·869	·809	·737	·567
·26	·880	·874	·848	·780	·700	·536
·30	·864	·856	·828	·752	·666	·476
·34	·848	·839	·808	·726	·633	·438
·38	·832	·822	·788	·701	·603	·406
·50	·788	·777	·735	·632	·526	·328
·60	·751	·740	·694	·583	·472	·281
·70	·718	·704	·656	·538	·428	·243
·80	·688	·672	·622	·499	·386	·215
·90	·658	·642	·588	·464	·357	·192

Table of the Function G (C sec ζ).

Table V.

C.	Φ (C, 0).	G (C).	f (C).	$\frac{1}{2}\{G(C)+f(C)\}$.	$\frac{1}{2}\{1+f(C)\}$.	$f\left(\frac{C}{2}\right)$.
0·00	0·0000	1·0000	1·0000	1·000	1·000	1·000
·05	·0095	·9754	·828	·902	·914	·897
·10	·0311	·9516	·722	·837	·861	·828
·14	·0536	·933	·656	·794	·828	·782
·18	·0801	·916	·600	·758	·800	·741
·22	·1081	·897	·550	·724	·775	·705
·26	·1403	·880	·508	·694	·754	·672
·30	·1723	·864	·469	·667	·735	·641
·34	·2065	·848	·435	·642	·718	·613
·38	·2414	·832	·404	·618	·702	·587
·50	·349	·787	·327	·557	·664	·518
·60	·438	·752	·276	·514	·638	·469
·70	·525	·719	·235	·477	·618	·427
·80	·612	·688	·201	·445	·601	·389
·90	·686	·659	·172	·416	·586	·356

Table of Auxiliary Functions Φ (C, 0), G (C), f (C).

TABLE VI.—*Relative Intensities from Zenith Sky Calculated from Mount Wilson Observations in Terms of Mean Attenuation Coefficients.*

The wave-lengths at Mount Wilson level corresponding to the tabulated values of the attenuation coefficients C were determined from the formula (76), $C = \beta\lambda^{-4}+\gamma$, making use of the constants β and γ given in Table II., which themselves are derived from observations on the transmission of solar-radiation.

A large scale chart of the intensities in the normal solar spectrum outside the atmosphere was prepared from the data reproduced in Table I. The values of S corresponding to various values of λ were then estimated from this curve of solar intensities. Auxiliary tables of the coefficients ϵ_2, ϵ, ϵ_1 were calculated from (44), making use of Table V. In this way a table of the function

$$\tfrac{1}{2}\frac{c}{C}\begin{pmatrix}\epsilon_2\\ \epsilon\\ \epsilon_1\end{pmatrix}\Phi(C, 0)$$

was prepared. This table, with Table III., enabled the term in square brackets in the expression for $T(0, \zeta)$ to be calculated. Finally, making use of the values of S just determined, the present table of the intensity from zenith sky, $T(0, \zeta)$, was calculated. The extreme and mean solutions of the integral equation are retained throughout. It will be noticed that the extreme solutions diverge rapidly for large values of C and ζ; it must be remembered that for large values of C the value of S decreases with extreme rapidity, no appreciable intensity having been measured for a wave-length less than $\cdot 3\mu$. Consequently, in calculating the total intensity of sky radiation on a horizontal surface, the divergence of the extreme solutions does not lead to a very great divergence in the final results. The results given in the present table are shown graphically in Diagrams II.–VII.

TABLE VI.

C.	λ.	S.	0°.	20°.	40°.	60°.	70°.	80°.
·05	·741μ	3140	*9·8* 9·8 **9·8**	*9·2* 9·2 **9·2**	*7·7* 7·7 **7·7**	*6·0* 6·0 **6·0**	*5·1* 5·1 **5·1**	*4·6* 4·6 **4·6**
·10	·571	5380	*50·9* 50·6 **50·2**	*47·7* 47·4 **47·0**	*39·8* 39·5 **39·0**	*30·4* 30·1 **29·6**	*25·9* 25·4 **24·8**	*21·6* 20·8 **20·0**
·14	·510	6000	*88·5* 87·2 **85·9**	*83·0* 81·7 **80·3**	*69·0* 67·7 **66·4**	*52·2* 50·7 **49·4**	*44·6* 42·8 **41·3**	*35·6* 32·9 **31·2**
·18	·474	6260	*124·3* 121·7 **118·3**	*116·7* 113·8 **110·2**	*96·5* 93·7 **90·7**	*72·8* 69·8 **66·1**	*61·2* 57·5 **54·0**	*48·0* 42·3 **38·1**
·22	·446	5910	*146·0* 141·5 **136·8**	*137·0* 132·5 **127·8**	*113·0* 108·4 **104·0**	*84·5* 79·8 **75·1**	*70·1* 64·5 **59·6**	*53·9* 45·4 **40·0**
·26	·427	5320	*166·9* 159·0 **151·0**	*156·0* 148·5 **140·8**	*128·5* 121·2 **114·1**	*95·5* 87·7 **80·6**	*79·4* 70·1 **62·5**	*60·7* 48·0 **39·4**
·30	·410	4480	*168·0* 158·4 **148·5**	*157·1* 147·9 **137·9**	*130·0* 120·6 **108·2**	*97·0* 86·6 **78·0**	*80·5* 69·0 **60·3**	*60·0* 43·7 **34·6**
·34	·397	4000	*173·2* 161·0 **148·1**	*162·0* 150·0 **137·1**	*133·1* 121·3 **110·0**	*98·4* 85·6 **75·1**	*80·8* 66·5 **55·8**	*61·5* 41·6 **31·5**
·38	·385	3720	*184·1* 168·0 **152·0**	*171·9* 156·0 **140·9**	*141·0* 126·1 **111·6**	*103·8* 87·9 **75·2**	*85·1* 67·1 **54·6**	*65·1* 41·0 **29·5**
·50	·357	2960	*205·0* 178·0 **151·7**	*191·5* 165·0 **140·0**	*156·4* 131·0 **108·8**	*115·3* 89·6 **69·5**	*94·5* 65·2 **47·6**	*73·1* 36·4 **22·5**
·60	·341	2140	*185·5* 153·0 **123·8**	*173·1* 141·4 **113·7**	*141·8* 111·3 **87·0**	*103·4* 73·0 **52·8**	*84·0* 52·1 **34·3**	*68·0* 26·5 **15·1**

Relative Intensities from Zenith Sky Calculated from Mount Wilson Observations in Terms of Mean Attenuation Coefficients.

$$\mathrm{T}(0, \zeta) = \frac{1}{4\pi}\left\{\tfrac{3}{4}(1+\cos^2\zeta)\right\}\frac{c}{\mathrm{C}}\,\mathrm{S}\left[\mathrm{C}e^{-\mathrm{C}}\mathrm{G}\left\{\mathrm{C}(\sec\zeta-1)\right\}+\tfrac{1}{2}\frac{c}{\mathrm{C}}\left(\epsilon\right)_{\epsilon_1}^{\epsilon_2}\Phi(\mathrm{C}, 0)\right]$$

TABLE VII.—*Total Solar and Sky Radiation Calculated at Mount Wilson Level from Mean Attenuation Coefficients.*

In order to obtain the total solar intensity reaching the earth's surface for different zenith distances of the sun, a table of the values of $Se^{-C\sec\zeta}$ was drawn up for the various values of C, λ, S, and ζ given in Table VI. From these curves were drawn on a large scale, which, when integrated, gave the values of

$$\int_0^\infty E(\zeta)\, d\lambda = \int_0^\infty Se^{-C\sec\zeta}\, d\lambda,$$

the units of intensity being those given for S in Table I., and the unit of wave-length being taken as 1μ, and $d\lambda = \cdot 1\mu$. As a check on the calculations it is interesting to see how far the total intensity can be represented by a formula of the type

$$\int_0^\infty E(\zeta)\, d\lambda = e^{-\bar{C}\sec\zeta} \int_0^\infty S\, d\lambda.$$

The values of the "apparent" coefficient of attenuation $\bar{C}$ calculated from the integrated area of each of the curves of solar intensity corresponding to different values of ζ are given below :—

ζ.	0°.	20°.	40°.	60°.	70°.	80°.	Mean values $\bar{C}$ between 0° and 60°.
$\bar{C}$	·1023	·1140	·1293	·1079	·0953	·0817	$\bar{C} = \cdot 1134$, $e^{-\bar{C}} = \cdot 893$.

The value of the apparent transmission of total radiation given for Mount Wilson* is $e^{-\bar{C}} = \cdot 895$, $\bar{C} = \cdot 111$, in good agreement with the above values. It will be noticed that an exponential formula for the total intensity fails for greater zenith distances than 60°.

From the intensities from zenith sky given in Table VI., and drawn in Diagrams II.–VII., the integrals $\int_0^\infty T(0, \zeta)\, d\lambda$ were calculated for various values of ζ. From these the total sky radiation on a horizontal plane, H (ζ), was calculated from the approximate formula (68), and is plotted against values of ζ in Diagram IX. It will be noticed that the value of the ratio

$$\int_0^\infty H(\zeta)\, d\lambda \Big/ \int_0^\infty E(\zeta)\, d\lambda$$

is very nearly constant for all zenith distances and has the mean value ·050. This value is in fair agreement with the value ·052 (August 18, 1905) but is considerably smaller than the value ·077 (September 8, 1906, October 19, 1906) determined at Mount Wilson.† It will be noticed under Table XII. that the attenuation coefficients for August 18, 1905, are in much better agreement with the mean values employed in these calculations than those for October 19, 1906.

The entries in the last row of the present table give the ratio *sky/sun* for equal solid angles, the semi-diameter of the sun being taken as 16′ of arc. These values are those most often measured in observations on sky radiation ; the results are shown graphically in Diagram XI.

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* 'Annals,' vol. II., p. 96.

† 'Annals,' vol. II., Table 35, p. 153.

TABLE VII.

	Units.	0°.	20°.	40°.	60°.	70°.	80°.
Total Solar Radiation per unit area normal to sun's rays reaching earth's surface. Values of $\int_0^\infty \mathrm{E}(\zeta)\,d\lambda$ $\int_0^\infty \mathrm{S}\,d\lambda = 3321\,(\mathrm{S},\lambda)$ units $= 1\cdot922$ calories per sq. cm. per minute.	(S, λ) units $d\lambda = \cdot1\mu$.	3000·5	2944·5	2782·5	2673·0	2512·0	2018·5
	Calories per square centimetre per minute.	1·740	1·706	1·623	1·550	1·457	1·169
Total Solar Radiation per unit area of horizontal plane reaching earth's surface. Values of $\cos\zeta\int_0^\infty \mathrm{E}(\zeta)\,d\lambda$.	(S, λ) units $d\lambda = \cdot1\mu$.	3000·5	2770	2130	1337	858	350
	Calories per square centimetre per minute.	1·740	1·602	1·242	·775	·498	·203
Total Radiation per unit area of horizontal surface from unit solid angle of zenith sky. Values of $\int_0^\infty \mathrm{T}(0,\zeta)\,d\lambda$.	(S, λ) units $d\lambda = \cdot1\mu$.	*33·85* 36·15 **38·05**	*32·2* 34·4 **36·6**	*25·5* 27·8 **30·0**	*18·3* 20·3 **22·6**	*13·4* 15·9 **18·6**	*9·8* 11·4 **14·9**
	Calories per square centimetre per minute.	*·0196* ·0209 **·0220**	*·0186* ·0199 **·0212**	*·0147* ·0161 **·0173**	*·0106* ·0117 **·0131**	*·0077* ·0092 **·0107**	*·0057* ·0066 **·0086**
Total Sky Radiation per unit area of horizontal surface. Values of $\int_0^\infty \mathrm{H}(\zeta)\,d\lambda = \frac{2\pi}{\frac{3}{4}(1+\cos^2\zeta)}\int_0^\infty \mathrm{T}(0,\zeta)\,d\lambda$.	(S, λ) units $d\lambda = \cdot1\mu$.	*141·9* 151·2 **159·3**	*143·2* 153·1 **163·0**	*134·8* 147·0 **158·6**	*122·2* 135·9 **151·1**	*100·6* 119·2 **139·6**	*79·4* 92·5 **120·9**
	Calories per square centimetre per minute.	*·0824* ·0877 **·0925**	*·0832* ·0888 **·0945**	*·0782* ·0853 **·0920**	*·0710* ·0788 **·0876**	*·0584* ·0692 **·0809**	*·0461* ·0537 **·0701**
Total Radiation on horizontal surface $\int_0^\infty \{\cos\zeta\,\mathrm{E}(\zeta)+\mathrm{H}(\zeta)\}\,d\lambda$.	Calories per square centimetre per minute.	*1·822* 1·828 **1·833**	*1·685* 1·691 **1·697**	*1·320* 1·327 **1·334**	*·846* ·854 **·863**	*·556* ·567 **·597**	*·249* ·257 **·273**
Ratio $\frac{\int_0^\infty \mathrm{H}(\zeta)\,d\lambda}{\cos\zeta\int_0^\infty \mathrm{E}(\zeta)\,d\lambda}$.	—	*·0473* ·0504 **·0531**	*·0517* ·0553 **·0588**	*·0633* ·0690 **·0744**	*·0915* ·1018 **·1131**	*·1171* ·1390 **·1623**	*·227* ·264 **·346**
Ratio $\frac{\int_0^\infty \mathrm{H}(\zeta)\,d\lambda}{\int_0^\infty \mathrm{E}(\zeta)\,d\lambda}$.	—	*·0473* ·0504 **·0531**	*·0487* ·0520 **·0553**	*·0485* ·0529 **·0570**	*·0453* ·0508 **·0565**	*·0400* ·0475 **·0555**	*·0394* ·0458 **·0597**
Ratio $\omega\,\frac{\int_0^\infty \mathrm{T}(0,\zeta)\,d\lambda}{\int_0^\infty \mathrm{E}(\zeta)\,d\lambda}$. $\omega = 2\pi(1-\cos 16') = 6\cdot80\times10^{-5}$	—	*76·6 × 10⁻⁸* 82·0 **86·2**	*74·3 × 10⁻⁸* 79·5 **84·5**	*62·2 × 10⁻⁸* 67·9 **73·2**	*46·6 × 10⁻⁸* 51·7 **57·5**	*36·3 × 10⁻⁸* 43·1 **50·3**	*33·0 × 10⁻⁸* 38·4 **50·2**

Total Solar and Sky Radiation Calculated at Mount Wilson Level from Mean Attenuation Coefficients.

TABLE VIII.—*Relative Intensities from Zenith Sky Calculated from Washington Observations in Terms of Mean Attenuation Coefficients.*

This table is constructed on the same plan as Table VI. for Mount Wilson, making use of the attenuation constants given in Table II. for Washington. The effect of "dust" requires us to make use of different constants for long- and for short-wave radiation in calculating wave-lengths corresponding to the tabulated values of C from the formula $C = \beta\lambda^{-4} + \gamma$. The result is a discontinuity in the sky radiation curve in the neighbourhood of $\cdot 610\mu$, shown in the curves of Diagram XII. The mean value of the solution of the integral equation is alone given, since the values of the absorption coefficients vary so rapidly from day to day that the intensities of sky radiation calculated from them probably differ by more than the difference between the extreme solutions.

Table VIII.

C.	λ.	S.	0°.	20°.	40°.	60°.	70°.	80°.
·10	1·08 μ	1360	3·04	2·85	2·37	1·81	1·54	1·25
·14	·824	2470	16·2	15·2	12·5	9·44	7·85	6·11
·18	·725	3350	38·5	36·1	29·9	22·15	18·23	13·4
·22	·654	4240	69·0	64·9	52·8	38·70	31·40	22·1
·26	·625	4640	97·5	91·1	74·4	53·8	42·9	29·3
·30	·556	5460	58·5	54·5	44·5	32·1	25·6	16·0
·34	·509	6020	88·0	83·0	67·1	47·3	36·4	22·8
·38	·482	6230	127·1	109·0	88·0	61·1	46·5	28·4
·50	·426	5320	163·1	150·9	119·4	80·5	59·4	32·8
·60	·398	4320	173·0	160·0	126·0	82·4	57·3	30·8
·70	·376	3460	169·8	156·0	121·8	77·5	53·9	27·0
·80	·360	2900	166·9	153·1	118·2	73·6	49·7	22·8
·90	·346	2240	146·0	133·8	102·6	62·0	41·3	19·5

Relative Intensities from Zenith Sky Calculated from Washington Observations in Terms of Mean Attenuation Coefficients.

$$\mathrm{T}(0, \zeta) = \frac{1}{4\pi}\{\tfrac{3}{4}(1+\cos^2\zeta)\}\frac{c}{\mathrm{C}}\mathrm{S}\left[\mathrm{C}e^{-\mathrm{C}}\mathrm{G}\{\mathrm{C}(\sec\zeta-1)\}+\tfrac{1}{2}\frac{c}{\mathrm{C}}\epsilon\Phi(\mathrm{C}, 0)\right].$$

TABLE IX.—*Total Solar and Sky Radiation Calculated at Washington Level from Mean Attenuation Coefficients.*

This table is drawn up on the same plan as Table VII., making use of the Washington data given in Table II. The values of the "apparent" coefficients of attenuation, $\bar{C}$, derived from the integrated solar radiation curves corresponding to different zenith distances of the sun are given below :—

ζ.	0°.	20°.	40°.	60°.	70°.	80°.	Mean value $\bar{C}$ between 0° and 60°.
$\bar{C}$	·247	·247	·252	·246	·235	·210	$\bar{C} = \cdot 248$, $e^{-\bar{C}} = \cdot 780$

The value of the apparent transmission of total radiation given for Washington* is $e^{-\bar{C}} = \cdot 787$, $\bar{C} = \cdot 240$ in substantial agreement with the above mean value between 0° and 60°.

The ratio

$$\int_0^\infty \mathrm{H}(\zeta)\, d\lambda \bigg/ \int_0^\infty \mathrm{E}(\zeta)\, d\lambda$$

is approximately constant for all zenith distances to 70° and has the mean value ·078. The value of this ratio for $\zeta = 80°$ seems to indicate the existence of a rapidly increasing value of the ratio beyond that angle: the analysis by which sky radiation is calculated ceases to hold even approximately for greater zenith distances on account of the curvature of the earth.

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* 'Annals,' vol. II., p. 96.

TABLE IX.

	Units.	0°.	20°.	40°.	60°.	70°.	80°.
Total Solar Radiation per unit area normal to sun's rays reaching earth's surface. Values of $\int_0^\infty E(\zeta)\,d\lambda$ $\int_0^\infty S\,d\lambda = 3321$ (S, λ) units = 1·922 calories per sq. cm. per minute.	(S, λ) units $d\lambda = \cdot 1\mu$.	2597·5	2553·0	2389·0	2032·5	1670·0	991·0
	Calories per square centimetre per minute.	1·502	1·478	1·382	1·177	·967	·574
Total Solar Radiation per unit area of horizontal plane reaching earth's surface. Values of $\cos\zeta \int_0^\infty E(\zeta)\,d\lambda$.	(S, λ) units $d\lambda = \cdot 1\mu$.	2597·5	2400	1830	1016	571	172
	Calories per square centimetre per minute.	1·502	1·390	1·060	·589	·331	·100
Total Radiation per unit area of horizontal surface from unit solid angle of zenith sky. Values of $\int_0^\infty T(0,\zeta)\,d\lambda$.	(S, λ) units $d\lambda = \cdot 1\mu$.	47·5	44·1	34·9	24·1	17·4	10·6
	Calories per square centimetre per minute.	·0275	·0255	·0202	·0140	·0101	·0062
Total Sky Radiation per unit area of horizontal surface. Values of $\int_0^\infty H(\zeta)\,d\lambda = \frac{2\pi}{\frac{3}{4}(1+\cos^2\zeta)} \int_0^\infty T(0,\zeta)\,d\lambda$.	(S, λ) units $d\lambda = \cdot 1\mu$.	199	197	184	161	130	86
	Calories per square centimetre per minute.	·115	·114	·1065	·0931	·0753	·0497
Total Radiation on horizontal surface $\int_0^\infty \{\cos\zeta\, E(\zeta) + H(\zeta)\}\,d\lambda$.	Calories per square centimetre per minute	1·617	1·504	1·166	·682	·406	·150
Ratio $\frac{\int_0^\infty H(\zeta)\,d\lambda}{\cos\zeta \int_0^\infty E(\zeta)\,d\lambda}$.	—	·0778	·0821	·1005	·1588	·228	·506
Ratio $\frac{\int_0^\infty H(\zeta)\,d\lambda}{\int_0^\infty E(\zeta)\,d\lambda}$.	—	·0778	·0773	·0766	·0793	·0779	·0865
Ratio $\omega \frac{\int_0^\infty T(0,\zeta)\,d\lambda}{\int_0^\infty E(\zeta)\,d\lambda}$. $\omega = 2\pi(1 - \cos 16') = 6\cdot80 \times 10^{-5}$.	—	$124\cdot3 \times 10^{-8}$	$117\cdot6 \times 10^{-8}$	$99\cdot4 \times 10^{-8}$	$80\cdot7 \times 10^{-8}$	$70\cdot8 \times 10^{-8}$	$72\cdot7 \times 10^{-8}$

Total Solar and Sky Radiation Calculated at Sea-Level from Mean Attenuation Coefficients at Washington.

TABLE X.—*Quality of Sky Radiation at Mount Wilson, October 17, 1906.*

Observations on the quality of sky-radiation have been made at Mount Wilson.* The values given in the present table are calculated in terms of the *mean* coefficients of attenuation at that station. The units of intensity in the calculated and observed values are both arbitrary. The calculated intensities are reduced to the same units as the observed intensities by multiplying the former by the mean value of the ratios of the intensities corresponding to the different wave-lengths. The results are compared graphically in Diagram XIII. The agreement is seen to be fairly satisfactory, in spite of the fact that the *mean* values of the coefficients of attenuation are used in calculating intensities on a particular day.

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* 'Annals,' vol. II., p. 155.

TABLE X.

		·422μ.	·457μ.	·491μ.	·556μ.	·614μ.	·660μ.
(i.) *Quality of Sky Radiation.* Comparison of Calculated Values with Mount Wilson Observations, October 17, 1906. ζ = 43°. ϕ = 23°. ψ = 79°.	Solar intensity, ζ = 43°.	3430	4700	4960	4630	4080	3600
	Zenith sky, ζ = 43°.	*124* 116 **109**	*102* 97 **92**	*83* 80 **78**	*44* 43 **42**	*26* 26 **26**	*18* 18 **18**
	Sky/sun, ζ = 43°.	361×10^{-4} 339 **318**	218×10^{-4} 206 **196**	167×10^{-4} 161 **157**	$95 \cdot 0 \times 10^{-4}$ 92·5 **90·5**	$63 \cdot 5 \times 10^{-4}$ 63·5 **63·5**	50×10^{-4} 50 **50**
	Observed *sky/sun*.	655	521	294	188	106	100
	Calculated *sky/sun*.	*722* 678 **636**	*436* 412 **392**	*334* 321 **314**	*190* 185 **181**	*127* 127 **127**	*100* 100 **100**
(ii.) *Quality of Sky Radiation.* Comparison of Calculated Values with Mount Wilson Observations. ζ = 58°. ϕ = 17°. ψ = 146°.	Solar intensity, ζ = 58°.	3050	4210	4570	4360	3850	3420
	Zenith sky, ζ = 58°.	*99·0* 91·0 **82·5**	*81·0* 77·5 **73·5**	*65* 62 **60**	*37* 36 **35**	*20·5* 20·5 **20·5**	*13·5* 13·5 **13·5**
	Sky/sun, ζ = 58°.	325×10^{-4} 295 **271**	193×10^{-4} 184 **175**	142×10^{-4} 136 **131**	$85 \cdot 0 \times 10^{-4}$ 82·5 **80·0**	$53 \cdot 3 \times 10^{-4}$ 53·3 **53·3**	$39 \cdot 5 \times 10^{-4}$ 39·5 **39·5**
	Observed *sky/sun*.	574	425	317	191	124	104
	Calculated *sky/sun*.	*750* 680 **625**	*445* 424 **403**	*327* 314 **302**	*196* 190 **185**	*123* 123 **123**	*91* 91 **91**
(iii.) *Quality of Sky Radiation.* Comparison of Calculated Values of Zenith Sky with Mean Absolute Intensity of Sky Radiation. Mean, ζ = 50°.	Zenith sky.	*112·6* 104·5 **97·0**	*92·0* 88·0 **83·6**	*73·5* 71·5 **69·0**	*40·5* 40·0 **39·5**	*22·2* 22·2 **22·2**	*15·7* 15·7 **15·7**
	Observed mean sky.	1194	986	701	395	231	174
	Calculated zenith sky.	*1192* 1109 **1030**	*975* 933 **885**	*780* 758 **731**	*429* 424 **418**	*235* 235 **235**	*166* 166 **166**

Quality of Sky Radiation at Mount Wilson, October 17, 1906.

TABLE XI.—*Total Sky Radiation at Mount Wilson, October 19, 1906.*

Observations on the total intensity of sky-radiation are given for Mount Wilson* under the date October 19, 1906. Attenuation coefficients for this day are not given, so that the observations are compared with values calculated from the mean coefficients at Mount Wilson. If ω is the solid angle subtended by the sun, the value of

$$\omega \int_0^\infty \mathrm{T}(\phi, \zeta)\, d\lambda$$

is calculated from the approximate formula (66),

$$\omega \int_0^\infty \mathrm{T}(\phi, \zeta)\, d\lambda = \omega \frac{1+\cos^2\theta}{1+\cos^2\zeta} \sec\phi \int_0^\infty \mathrm{T}(0, \zeta)\, d\lambda.$$

Making use of the values of

$$\omega \int_0^\infty \mathrm{T}(0, \zeta)\, d\lambda \Big/ \int_0^\infty \mathrm{E}(\zeta)\, d\lambda$$

from Table VII., and interpolating for intermediate values of ζ from the curves given in Diagram XI., the ratio

$$\omega \int_0^\infty \mathrm{T}(\phi, \zeta)\, d\lambda \Big/ \int_0^\infty \mathrm{E}(\zeta)\, d\lambda$$

was calculated.

The angle θ between sun and sky was calculated from the formula

$$\cos\theta = \cos\phi\cos\zeta + \sin\phi\sin\zeta\cos\psi,$$

the azimuth ψ being measured from a vertical plane through the sun in the direction N.–E.–S.–W.

The comparison of the calculated ratios with those observed is fairly satisfactory; the greatest discrepancies occur when θ is small and when ζ is large. The probable reasons for this lack of agreement are given at the end of Section 8.

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* 'Annals,' vol. II., Table 32, p. 151.

TABLE XI.

ζ.	ϕ.	ψ.	θ.	$\frac{1+\cos^2\theta}{1+\cos^2\zeta}$.	sec ϕ.	$\frac{\text{Zenith sky}}{\text{Sun}}\times 10^{-8}$.	$\frac{\text{Sky}}{\text{Sun}}\times 10^{-8}$.	Observed Sky/Sun × 10^{-8}.
55°·8	79°·2	− 43°·5	46°·1	1·127	5·34	*60·2* 55·0 49·0	*361* 330 294	295
55·5	67·4	− 41·2	37·9	1·228	2·60	*60·6* 55·1 50·0	*193* 176 160	219
54·0	54·5	− 35·5	28·7	1·316	1·72	*61·8* 56·3 50·5	*140* 127 114	165
53·6	44·6	− 21·3	18·6	1·402	1·40	*62·0* 57·0 51·0	*122* 112 100	190
50·4	40·5	− 6·7	11·5	1·392	1·31	*64·6* 59·3 53·2	*118* 108 97	285
49·8	31·1	12·9	20·6	1·327	1·17	*65·0* 60·0 54·0	*101* 93 84	350
49·2	49·7	− 149·6	94·4	·696	1·55	*65·5* 60·4 54·5	*70·7* 65·2 58·8	98
48·9	50·4	− 113·3	79·1	·707	1·57	*65·8* 60·6 54·8	*73·0* 67·2 60·8	108
47·4	79·2	− 63·4	63·2	·826	5·34	*67·0* 61·8 56·0	*296* 273 247	222
47·0	77·9	− 84·5	77·7	·714	4·77	*67·2* 62·0 56·2	*229* 211 191	171
46·5	29·2	− 79·6	48·5	·977	1·15	*67·8* 62·5 57·0	*76·1* 70·2 64·0	98
46·2	27·8	144·8	70·3	·752	1·13	*68·0* 63·0 57·1	*57·7* 53·5 48·5	68

Total Sky Radiation at Mount Wilson, October 19, 1906.

Comparison of ratio *sky/sun* for equal solid angles with results of calculation from the formula

$$\omega\int_0^\infty \mathrm{T}(\phi,\zeta)\,d\lambda\Big/\int_0^\infty \mathrm{E}(\zeta)\,d\lambda.$$

TABLE XII.—*Average Intensities of Sky Radiation, Mount Wilson.*

Observations are given at Mount Wilson* for the average total intensity of sky radiation taken for different azimuths. The theoretical formula corresponding to average sky intensity is by (66),

$$\frac{1}{2\pi}\int_0^{2\pi} d\psi \int_0^{\infty} \mathrm{T}\,(\phi,\,\zeta)\,d\lambda = \left[\frac{1}{2\pi}\int_0^{2\pi} \frac{1+\cos^2\theta}{1+\cos^2\zeta}\,d\psi\right] \sec\phi \int_0^{\infty} \mathrm{T}\,(0,\,\zeta)\,d\lambda.$$

The term in square brackets denoted by

$$\left[\frac{1+\cos^2\theta}{1+\cos^2\zeta}\right]_{\text{av.}} = 1-\tfrac{1}{2}\sin^2\phi\,.\,\frac{3\cos^2\zeta-1}{1+\cos^2\zeta}\,.$$

In calculating *average sky/sun* for equal solid angles, the value of

$$\omega\int_0^{\infty} \mathrm{T}\,(0,\,\zeta)\,d\lambda \Big/ \int_0^{\infty} \mathrm{E}\,(\zeta)\,d\lambda$$

is derived by interpolation from Diagram XI.

In order to compare the attenuation coefficients on the dates of the above sky observations, these values taken from the Mount Wilson observations† are compared in a table with the mean values employed in the calculation. It will be noticed that the absorption constants on August 18, 1905, are in much better agreement with the mean values than those of September 8, 1906. The result is that as we should expect the sky observations on the former date agree more closely with the calculated values than those on the latter.

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* 'Annals,' vol. II., Table 32, p. 151.

† 'Annals,' vol. II., pp. 96–97.

TABLE XII.

ζ.	ϕ.	$\left[\frac{1+\cos^2\theta}{1+\cos^2\zeta}\right]_{\text{av.}}$	sec ϕ.	$\frac{\text{Zenith sky}}{\text{Sun}} \times 10^{-8}$.	$\frac{\text{Av. sky}}{\text{Sun}} \times 10^{-8}$.	Observed Av. sky/Sun × 10^{-8}.
47°·3	29°·4	·969	1·15	*67·0* 62·0 **56·1**	*74·8* 69·2 **62·6**	122
51·2	47·9	·945	1·49	*64·0* 59·0 **53·1**	*90·0* 83·0 **74·7**	129
54·7	64·5	·999	2·24	*61·1* 56·0 **50·0**	*137* 125 **112**	185
50·0	78·8	·918	5·15	*65·0* 60·0 **53·8**	*308* 284 **255**	214
54·5	85·5	·995	12·75	*60·6* 56·0 **50·0**	*770* 710 **635**	500 ?

Sky Radiation, Mount Wilson, September 8, and October 19, 1906.

ζ.	ϕ.	$\left[\frac{1+\cos^2\theta}{1+\cos^2\zeta}\right]_{\text{av.}}$	sec ϕ.	$\frac{\text{Zenith sky}}{\text{Sun}} \times 10^{-8}$.	$\frac{\text{Av. sky}}{\text{Sun}} \times 10^{-8}$.	Observed Av. sky/Sun × 10^{-8}.
27°	20°	·953	1·064	*82·0* 77·0 **71·8**	*83·2* 78·0 **73·0**	78
22	30	·894	1·155	*84·0* 79·0 **74·0**	*87·0* 81·8 **76·6**	82
23	45	·791	1·414	*83·9* 78·8 **73·4**	*94·0* 88·4 **82·2**	67
32	55	·781	1·743	*79·0* 74·4 **69·0**	*108* 102 **94**	81
23	65	·658	2·366	*83·9* 78·8 **73·4**	*131* 123 **114**	93
29	80	·642	5·76	*81·5* 76·0 **70·9**	*301* 281 **262**	116

Sky Radiation, Mount Wilson, August 18, 1905.

Average Intensities of Sky Radiation.

λ.	C, Aug. 18, 1905.	C, Sept. 8, 1906.	C, average.	Date.	$\frac{p}{p_0}\beta$.	$\frac{p}{p_0}\gamma$.
·40μ	·342	·263	·356	Aug. 18, 1905	·0087	·050
·45	·265	·180	·230			
·50	·202	·129	·148	Sept. 8, 1906	·0059	·033
·60	·139	·065	·085			
·70	·081	·036	·070	Mean at Mount Wilson	·0081	·026
·80	·051	·024	·043			
·90	·046	·020	·036			
1·00	·048	·016	·032			
1·20	·045	·014	·028			
1·60	·046	·010	·025			

Attenuation Coefficients on Dates of Sky Observations.

TABLE XIII.—*Polarization of Sky Radiation Calculated from Mount Wilson and Washington Observations.*

Numerical results on the polarization of sky radiation are calculated from the approximate formulæ given in Section 6. In order to save space numerical values corresponding to the formulæ given at the foot of the table are entered in the same order under each value of λ and ζ.

The values of

$$P(0, \zeta) = Ce^{-C}G\{C(\sec\zeta - 1)\}$$

and

$$Q(0, \zeta) = \tfrac{1}{2}c/C \, . \, \epsilon\Phi(C, 0)$$

are obtained from Tables VI. and VIII.

The ratios of the intensities of zenith sky polarized in the principal plane and in a plane at right angles to it are calculated in the form

$$\frac{T_1(0, \zeta)}{T_2(0, \zeta)} = \frac{1 + Q(0, \zeta)/P(0, \zeta)}{\cos^2\zeta + Q(0, \zeta)/P(0, \zeta)} \, .$$

The results are shown graphically in Diagram XIV.

The ratios $Q(0, \zeta)/P(0, \zeta)$ given in the present table compare the contribution of self-illumination to the sky intensity of different wave-lengths with the effect of direct sunlight on sky radiation.

The ratios

$$\frac{Q(0, \zeta)/P(0, \zeta)}{1 + Q(0, \zeta)/P(0, \zeta)}$$

compare the *residual intensity* of sky radiation over the great circle of most complete polarization 90° from the sun to the intensity polarized in a plane at right angles. It will be noticed that this ratio remains nearly the same for all zenith distances, and is very small for long wave-lengths when the effect of self-illumination is small.

TABLE XIII.

C.	Mount Wilson.				Washington.			
	λ.	20°.	60°.	80°.	λ.	20°.	60°.	80°.
·05	·741μ	*1·19* ·055 **·052**	*3·47* ·054 **·051**	*18·42* ·054 **·051**	∞	—	—	—
·10	·571	*1·17* ·142 **·124**	*2·91* ·142 **·124**	*6·55* ·145 **·127**	1·08μ	*1·14* ·033 **·032**	*3·64* ·035 **·034**	*15·98* ·035 **·034**
·14	·510	*1·16* ·204 **·170**	*2·63* ·208 **·172**	*5·10* ·207 **·172**	·824	*1·12* ·097 **·088**	*3·16* ·097 **·089**	*8·60* ·098 **·089**
·18	·474	*1·15* ·268 **·212**	*2·44* ·268 **·212**	*4·23* ·271 **·213**	·725	*1·11* ·157 **·136**	*2·84* ·157 **·136**	*6·14* ·159 **·137**
·22	·446	*1·15* ·291 **·225**	*2·39* ·292 **·220**	*3·98* ·296 **·228**	·654	*1·11* ·212 **·175**	*2·62* ·214 **·176**	*4·95* ·217 **·178**
·26	·427	*1·13* ·388 **·280**	*2·18* ·384 **·277**	*3·20* ·411 **·291**	·625	*1·10* ·271 **·213**	*2·44* ·273 **·214**	*4·06* ·287 **·224**
·30	·416	*1·13* ·446 **·308**	*2·09* ·440 **·306**	*2·96* ·464 **·317**	·556	*1·11* ·135 **·119**	*2·95* ·134 **·118**	*6·70* ·140 **·123**
·34	·397	*1·13* ·504 **·335**	*1·99* ·510 **·338**	*2·71* ·526 **·345**	·509	*1·11* ·184 **·155**	*2·75* ·178 **·151**	*5·35* ·193 **·162**
·38	·385	*1·12* ·566 **·362**	*1·91* ·570 **·363**	*2·56* ·594 **·373**	·482	*1·11* ·234 **·190**	*2·54* ·237 **·192**	*4·48* ·249 **·199**
·50	·357	*1·10* ·749 **·429**	*1·74* ·763 **·438**	*2·15* ·814 **·449**	·426	*1·09* ·380 **·275**	*2·18* ·387 **·279**	*3·20* ·413 **·292**
·60	·341	*1·10* ·902 **·474**	*1·63* ·920 **·480**	*1·93* 1·012 **·507**	·398	*1·09* ·504 **·335**	*1·98* ·518 **·341**	*2·62* ·570 **·363**
·70	*Polarization of zenith sky* $\left.\right\}\frac{T_1(0,\zeta)}{T_2(0,\zeta)} = \frac{1+Q(0,\zeta)/P(0,\zeta)}{\cos^2\zeta + Q(0,\zeta)/P(0,\zeta)}$.				·376	*1·08* ·633 **·387**	*1·82* ·660 **·398**	*2·26* ·740 **·425**
·80	Ratio $Q(0,\zeta)/P(0,\zeta)$.				·360	*1·07* ·768 **·435**	*1·70* ·814 **·450**	*2·00* ·945 **·486**
·90	**Polarization of sky 90° from sun** } **Ratio** $\frac{Q(0,\zeta)/P(0,\zeta)}{1+Q(0,\zeta)/P(0,\zeta)}$.				·346	*1·07* ·901 **·474**	*1·62* ·961 **·490**	*1·90* 1·11 **·527**

Polarization of Sky Radiation Calculated from Mount Wilson and Washington Observations.

DIAGRAM I.—*Variation of Coefficients of Atmospheric Attenuation with Wave-Length.*

The curves of Diagram I. are drawn from the data given in Table I. The coefficients of attenuation C_x at the various stations are plotted against the inverse fourth power of the wave-lengths, the wave-lengths λ being expressed in microns. The observations give rise to a law of the form

$$C_x = \beta\lambda^{-4}+\gamma.$$

The stations to which the various lines refer are as follows:—

Curve I.	Mount Whitney.	*Curve III.*	Potsdam.
Curve II.	Mount Wilson.	*Curve IV.*	Washington.

The conclusions derived from these observations are described in Section 7, and the constants of atmospheric scattering and absorption derived from similar curves plotted on a large scale are given in Table II.

The discontinuity in the curves in the neighbourhood of $\cdot 610\mu$ at low-level stations is clearly marked, and the observations show that the curves may be represented by broken straight lines. We cannot suppose, however, that the discontinuity at $\lambda = \cdot 610\mu$ will in reality be as sharp as the intersection of two straight lines would require. The precise cause of this well-marked point of discontinuity furnishes a point which must be left to further investigation.

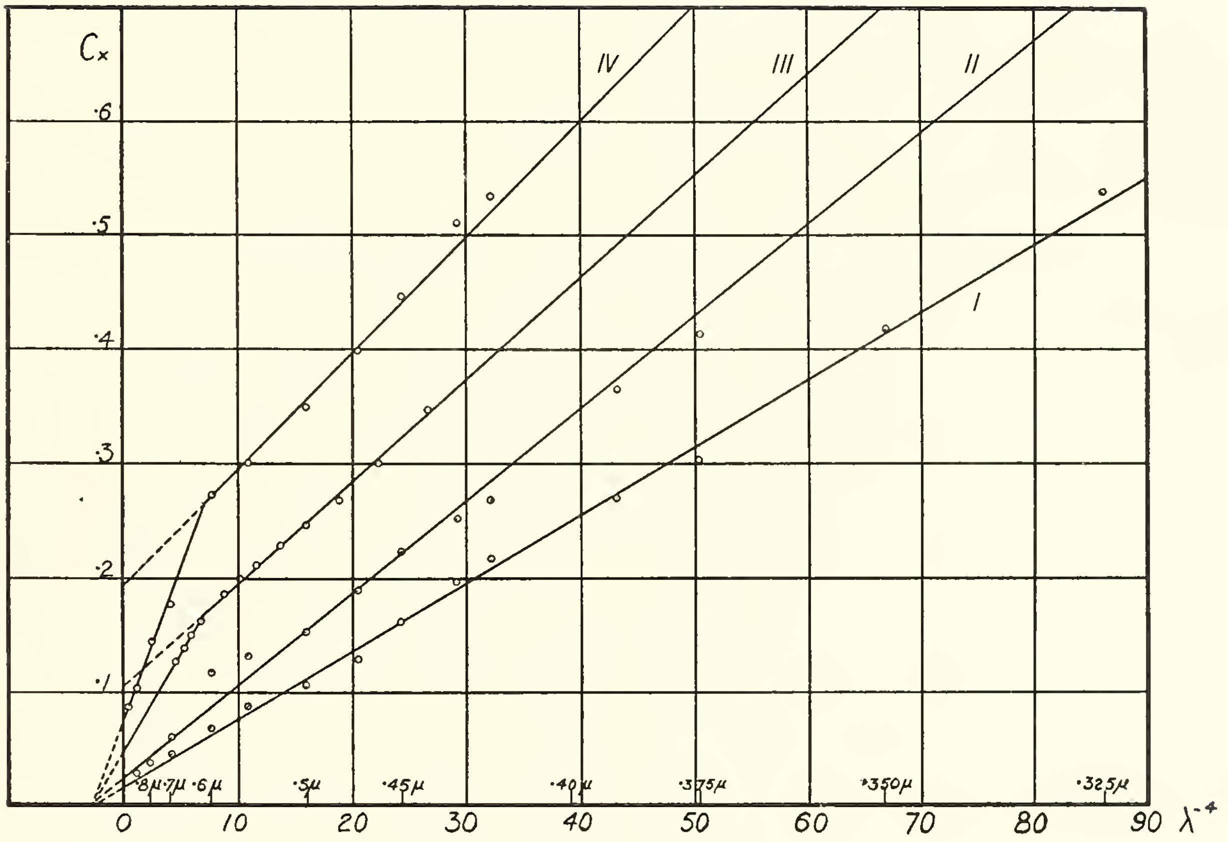


Diagram I. Variation of coefficients of atmospheric attenuation with wave-length.

DIAGRAMS II.–VII.—*Relative Intensities from Zenith Sky Calculated for Different Wave-Lengths at Mount Wilson from Mean Coefficients of Attenuation.*

The curves given on Diagrams II.–VII. are calculated for various wave-lengths from formula (64) in terms of the mean coefficients of attenuation for Mount Wilson given in Table II. The numerical values from which these curves are drawn are given in Table VI. The three outer curves of each set represent the extreme and mean solutions of the integral equation (64),

$$\mathrm{T}(0, \zeta) = (4\pi)^{-1}\left[\tfrac{3}{4}(1+\cos^2\zeta)\right]\mathrm{S}\left[\mathrm{P}(0, \zeta)+\mathrm{Q}(0, \zeta)\right].c/\mathrm{C},$$

where

$$\mathrm{P}(0, \zeta) = \mathrm{C}e^{-\mathrm{C}}\,\mathrm{G}\left[\mathrm{C}(\sec\zeta - 1)\right]$$

and

$$\mathrm{Q}(0, \zeta) = \tfrac{1}{2}\frac{c}{\mathrm{C}}\begin{pmatrix}\epsilon_2\\ \epsilon\\ \epsilon_1\end{pmatrix}\Phi(\mathrm{C}, 0).$$

The inmost curve of each set gives the intensity from zenith sky neglecting self-illumination, *i.e.*, it represents the value of

$$(4\pi)^{-1}\left[\tfrac{3}{4}(1+\cos^2\zeta)\right]\mathrm{SP}(0, \zeta).c/\mathrm{C}.$$

In this way the contribution of self-illumination to the intensity of sky radiation is made clear. We notice the divergence of the extreme solutions for large values of the sun's zenith distance.

The curves just described resemble the curves obtained by NICOLS* in his observations on the intensities in the spectrum of zenith sky compared with corresponding intensities in the spectrum of an acetylene flame. The results given by NICOLS were taken at various times of the day (July 18, 1907) at Sterzing in the Tyrol (lat. 46° 54′ N., long. 11° 25′ E., elevation 3110 feet above sea-level). Numerous observations have been taken by CROVA,† ZETTWUCH‡, MAJORANA,§ and others.‖ The results are not strictly comparable with theory since the attenuation coefficients at the time of observation are not given. The forthcoming observations of the Smithsonian Astrophysical Observatory on sky radiation at Mount Whitney¶ (August, 1910) will enable an accurate comparison to be made with the results calculated from the attenuation coefficients measured on the same day.

---

* NICOLS, E. L., "Theories of the Colour of the Sky," 'Physical Review,' XXVI., June, 1908, p. 497. An extensive bibliography on sky observations is given in this paper.

† CROVA, C. R., 'Comptes Rendus,' CIX., p. 493; CXII., p. 1178; also 'Annales de Chimie et de Physique,' (6), XX., p. 480.

‡ ZETTWUCH, G., "Ricerche sul Bleu del Cielo," translated in the 'Phil. Mag.,' (6), IV., August, 1902, p. 199.

§ MAJORANA, Q., "On the Relative Luminous Intensities of Sun and Sky," 'Phil. Mag.,' (6), I., May, 1901, p. 555.

[‖ The writer is indebted to Dr. OTTO KLOTZ, of the Dominion Observatory, Ottawa, for calling his attention to the work of EXNER along these lines. EXNER, 'Sitzungsbericht d. K. Akad. d. Wissen., Wien, M. N. Klasse,' 1909, vol. 118, IIA. A summary of EXNER's work and of the observations of WIESNER and SCHRAMM, W., is given by ABBOT, C. G., in his recent book, 'The Sun,' p. 299 (Appleton and Co., 1911). A problem of somewhat the same nature as the present one is considered by GOLD, E., "The Isothermal Layer of the Atmosphere and Atmospheric Radiation," 'Roy. Soc. Proc.,' A, vol. 82, 1909.—*Note added December* 31, 1912.]

¶ ABBOT, C. G., "Report on the Astrophysical Observatory," 'Annual Report of the Smithsonian Institution,' 1911, p. 65.

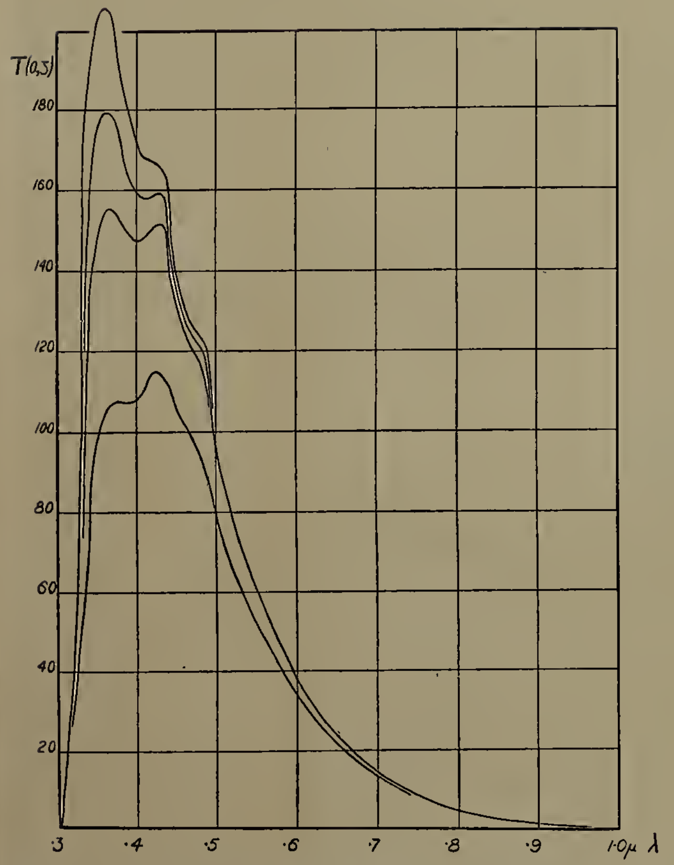


Diagram II. Relative intensities from zenith sky calculated from Mount Wilson observations. ζ = 0°.

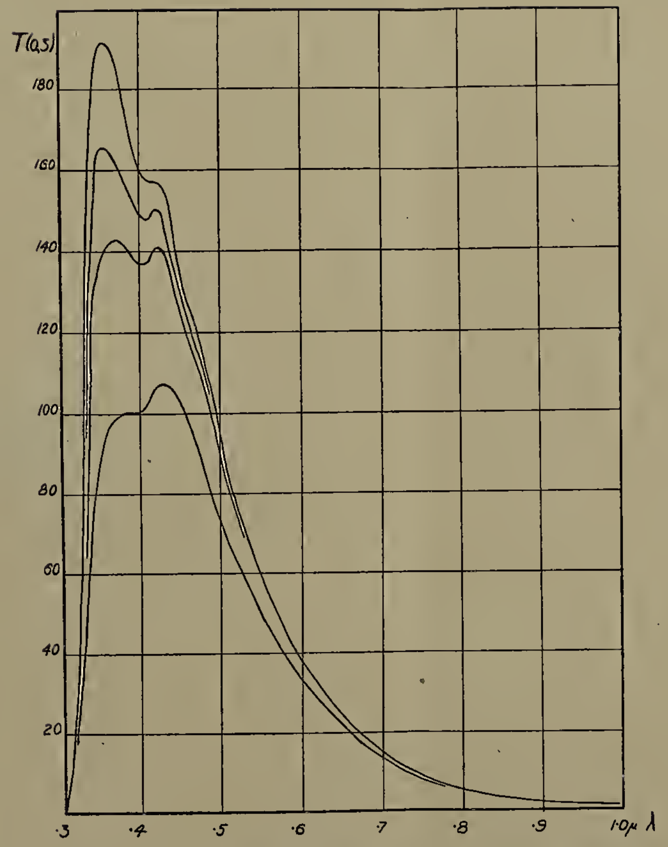


Diagram III. Relative intensities from zenith sky calculated from Mount Wilson observations. ζ = 20°.

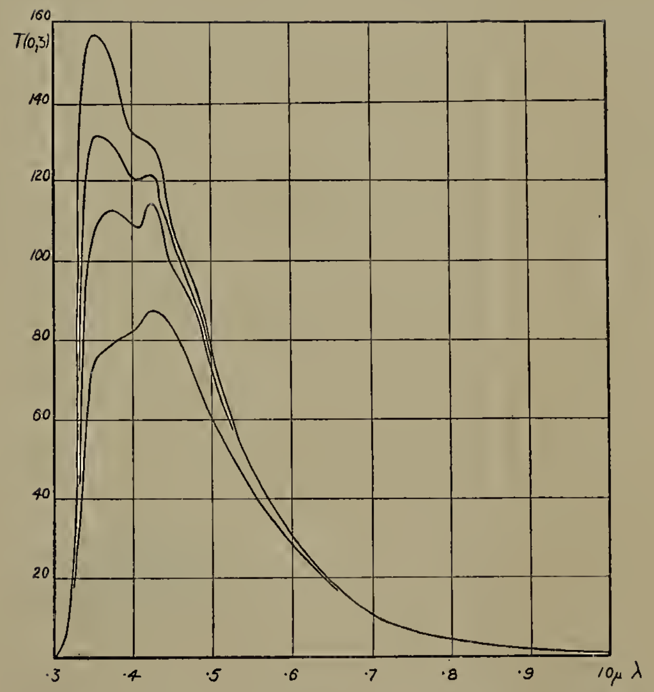


Diagram IV. Relative intensities from zenith sky calculated from Mount Wilson observations. ζ = 40°.

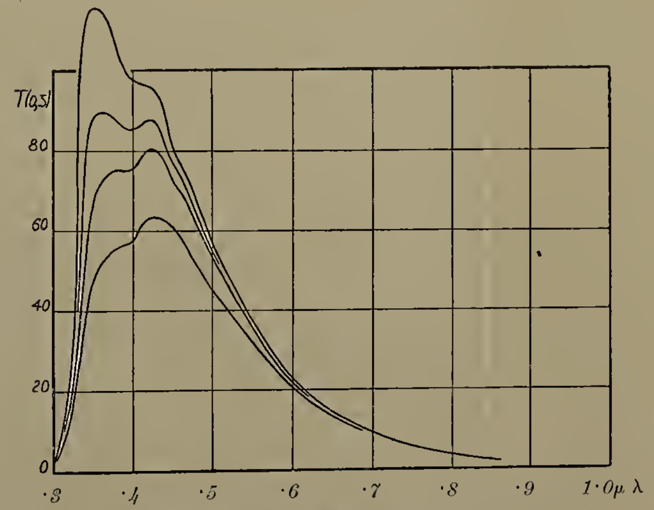


Diagram V. Relative intensities from zenith sky calculated from Mount Wilson observations. ζ = 60°.

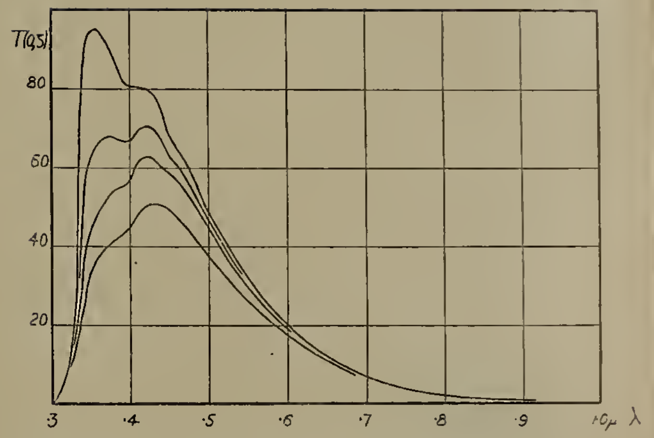


Diagram VI. Relative intensities from zenith sky calculated from Mount Wilson observations. ζ = 70°.

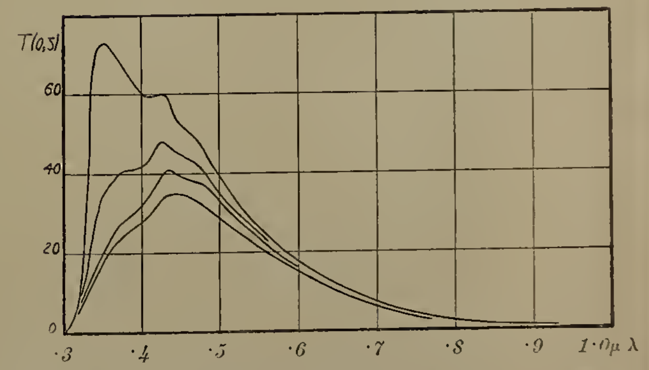


Diagram VII. Relative intensities from zenith sky calculated from Mount Wilson observations. ζ = 80°.

Diagram VIII.—*Comparison of Formulæ for the Relative Intensities of Sky Radiation Calculated from Mount Wilson Observations for* $\zeta = 60°$.

It is of some interest to compare with the formula for sky intensity derived in the present paper the various formulæ which have been employed by various writers in the interpretation of sky observations. The results are shown graphically in Diagram VIII. for a zenith distance of the sun of 60°, and refer to intensities of zenith sky.

Curve I. is given by the formula (63)

$$(4\pi)^{-1}\,\mathrm{S}\tfrac{3}{4}\,(1+\cos^2\zeta)\,\mathrm{C},$$

and is the same as that given by Kelvin[*] and employed by Perrin[†] in an estimate of the number of molecules per unit volume of a gas.

Curve II. is given by the formula

$$(4\pi)^{-1}\,\mathrm{S}\,\{\tfrac{3}{4}\,(1+\cos^2\zeta)\}\,e,$$

and is seen to give a considerably smaller value of sky intensity in the red, agreeing closely with the value $\mathrm{T}(0, \zeta)$ for wave-lengths greater than $\cdot 45\mu$.

Curve III. is given by the mean solution (64) for $\mathrm{T}(0, \zeta)$ which takes into account the effect of self-illumination.

Curve IV. gives the intensity of zenith sky neglecting self-illumination but taking into consideration the attenuation of both the incident and scattered radiation.

---

[*] Kelvin, 'Baltimore Lectures' (1904), p. 313.

[†] Perrin, J., 'Annales de Chimie et de Physique,' 8^{me} Série, September, 1909. See p. 79 of 'Brownian Movement and Molecular Reality' (F. Soddy, 1910), published by Taylor and Francis, London.

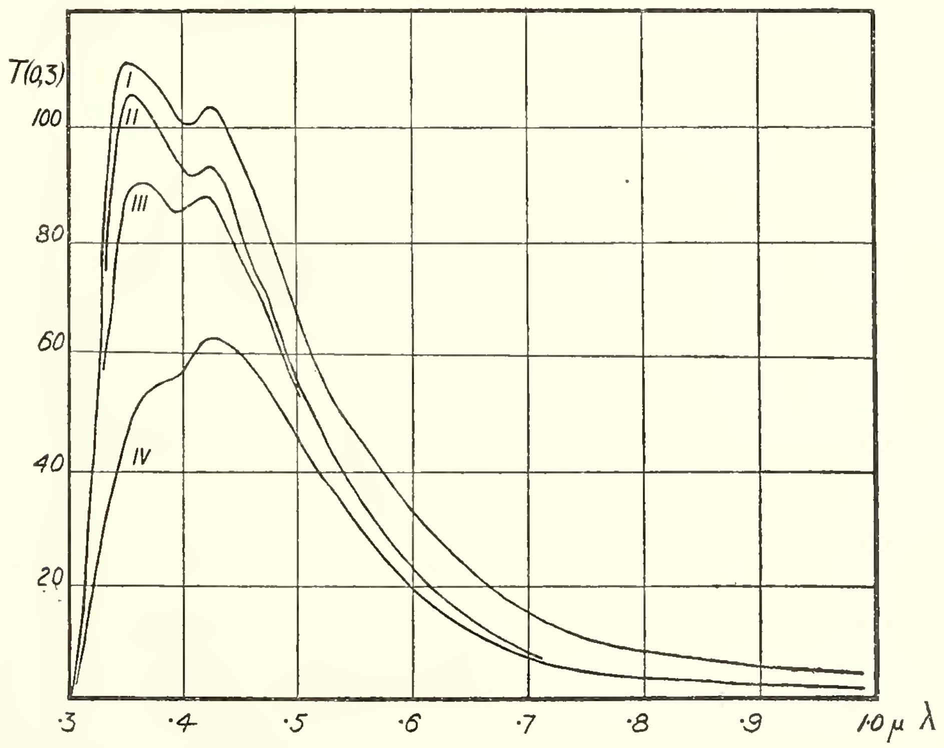


Diagram VIII. Comparison of formulæ for intensities from zenith sky, Mount Wilson, $\zeta = 60°$.

DIAGRAMS IX. AND X.—*Total Radiation Calculated from Mount Wilson and Washington Observations.*

The curves drawn on Diagrams IX. and X. are drawn from the data calculated in Tables VII. and IX. for the values of total solar and sky radiation at Mount Wilson and Washington respectively. The various curves denoted by I., II., III., IV., refer to the following quantities:—

Curve I. gives the total intensity of solar radiation in calories per square centimetre per minute normal to the sun's rays; *i.e.*, the curve represents the variation of

$$\int_0^\infty \mathrm{E}(\zeta)\,d\lambda \text{ with } \zeta.$$

Curve II. gives the total intensity of solar radiation in calories per square centimetre per minute on a horizontal plane; *i.e.*, the curve represents the variation of

$$\cos\zeta \int_0^\infty \mathrm{E}(\zeta)\,d\lambda \text{ with } \zeta.$$

Curve III. represents the total intensity in calories per square centimetre per minute of the radiation from the entire sky on a horizontal plane; *i.e.*, the curve represents the variation of

$$\int_0^\infty \mathrm{H}(\zeta)\,d\lambda \text{ with } \zeta.$$

Curve IV. represents the total radiation from sun and sky on a horizontal plane; *i.e.*, the curve represents the variation of

$$\int_0^\infty \{\cos\zeta\mathrm{E}(\zeta)+\mathrm{H}(\zeta)\}\,d\lambda \text{ with } \zeta.$$

The calculations are only given as far as $\zeta = 80°$. Curves I. and II. fall to zero at $\zeta = 90°$. Curve III. is arbitrarily carried on beyond this point (in dotted lines) to $\zeta = 100°$, and represents to some extent the intensity of scattered radiation due to the "twilight" following the sunset or preceding the sunrise. The effect of the earth's curvature makes it practically impossible to calculate the scattered radiation when the sun is below the horizon. The heat reaching the earth before sunrise shows itself in continuous air-temperature records in the fact that the minimum in the diurnal inequality of temperature occurs about one-half hour before the sun actually rises.

The curve just described are intended for use in meteorological problems.

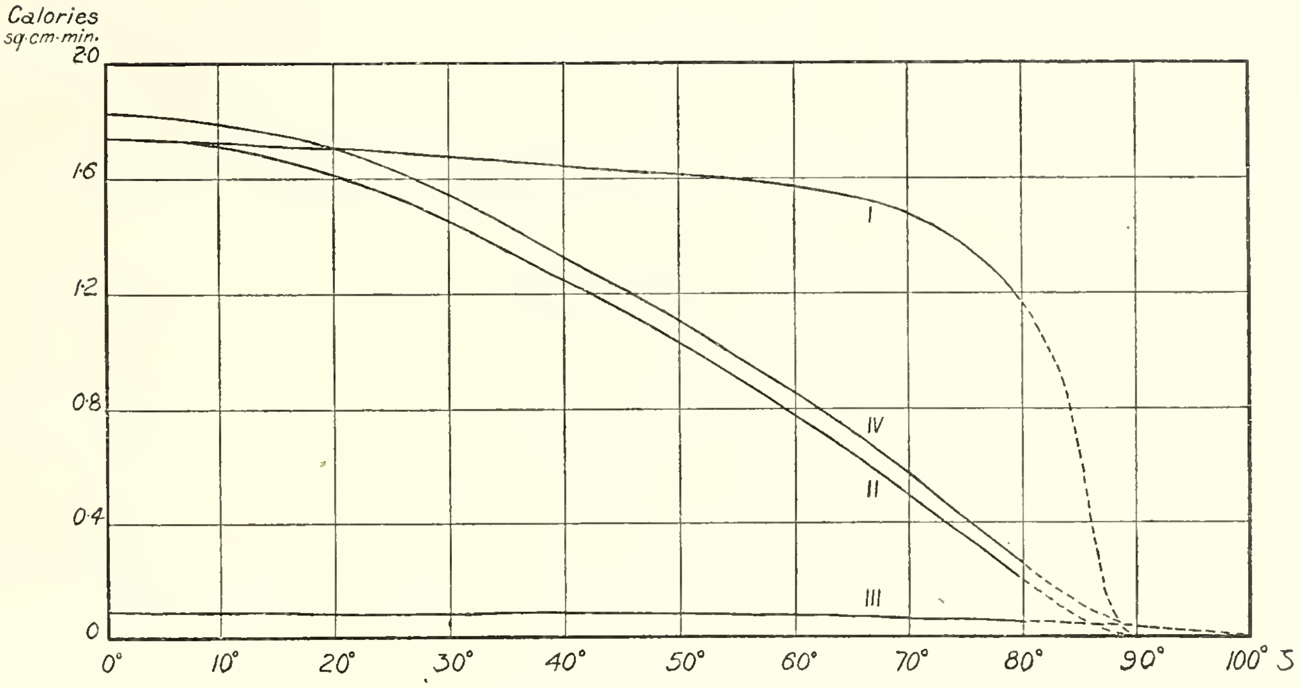


Diagram IX. Total solar and sky radiation calculated from Mount Wilson observations.

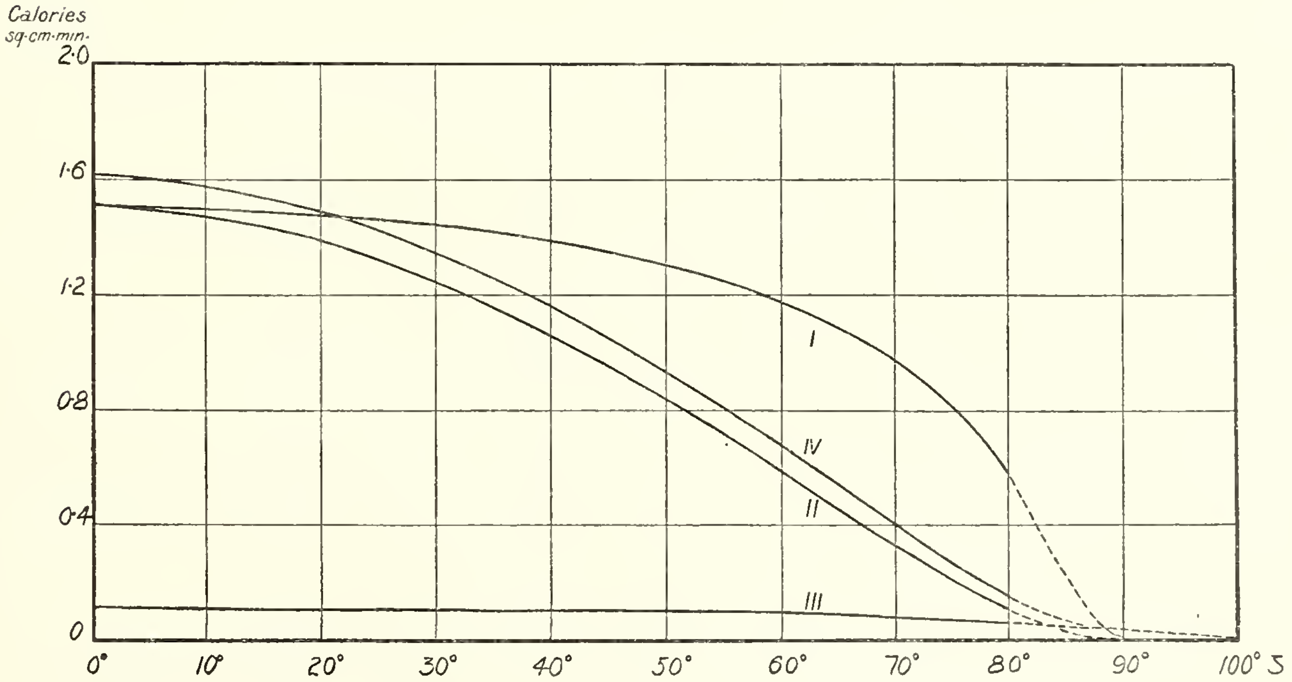


Diagram X. Total solar and sky radiation calculated from Washington observations.

DIAGRAM XI.—*Relative Intensities from Sky and Sun Calculated from Mount Wilson and Washington Observations.*

The curves given in Diagram XI. represent the ratio *zenith sky/sun* for equal solid angles, the total radiation covering all wave-lengths being taken in both cases. The curve represents the formula

$$\omega \int_0^\infty \mathrm{T}(0, \zeta)\, d\lambda \bigg/ \int_0^\infty \mathrm{E}(\zeta)\, d\lambda,$$

where ω is the solid angle subtended by the sun, *i.e.*, $\omega = 2\pi(1 - \cos 16') = 6 \cdot 80 \times 10^{-5}$.

Curves I. refer to Mount Wilson and include the extreme and mean solutions in the expression for $\mathrm{T}(0, \zeta)$.

Curve II. refers to Washington and represents the mean solution of the integral equation only.

Since the ratio just described is that most easily obtained in measurements of sky radiation, the curves just given are appropriate for a comparison of theory with observation.

DIAGRAM XII.—*Relative Intensities from Zenith Sky, Calculated for Different Wave-Lengths from Washington Observations.*

The curves given in Diagram XII. are drawn on the same plan as those described in Diagrams II.–VII. for Mount Wilson. In the present instance the numerical values from which the curves are drawn are given in Table VIII. Intensities corresponding to the mean solution of the integral equation are alone given, since the presence of "dust" at low-level stations is an extremely variable factor. This factor gives rise to a sharp bend in the attenuation curve for Washington shown in Diagram I. in the neighbourhood of $\cdot 610\mu$. The effect on the intensity of zenith sky is very sharply marked and gives rise to a finite discontinuity in the intensity curve corresponding to that wave-length. In reality the bend of the attenuation curve in Diagram I. cannot be as sharp as the intersection of two straight lines, so that the discontinuity in the sky intensity curve in this neighbourhood is probably represented by a sharp peak (represented in the drawing by the dotted portions of the curves) which arises from the effect of "dust" in scattering the long-wave radiation. The prominence of this peak in the intensity curve must be an extremely variable factor, and may possibly account for discrepancies in observations on sky-radiation; *e.g.*, NICOLS[*] mentions as a result of his measurements that sky intensities show far greater relative intensities in the longer wave-lengths than one would expect from RAYLEIGH'S theory. The effect of "dust" is an illustration of the effect of several groups of molecular complexes or small particles on radiation travelling through a medium containing them; each group which is able to produce a sharp bend in the attenuation-curve at any wave-length is also able to produce a corresponding maximum in the intensity-curve of the scattered radiation, the whole effect resembling a broad emission band in its spectrum.[†]

---

[*] NICOLS, *loc. cit.*, p. 502.

[[†] Important experiments describing the transition from lateral scattering to selective reflection are described by WOOD, R. W., under the name "resonance radiation." These are described in the 'Clark University Lectures,' Clark University, 1912, p. 101.—*Note added December* 31, 1912.]

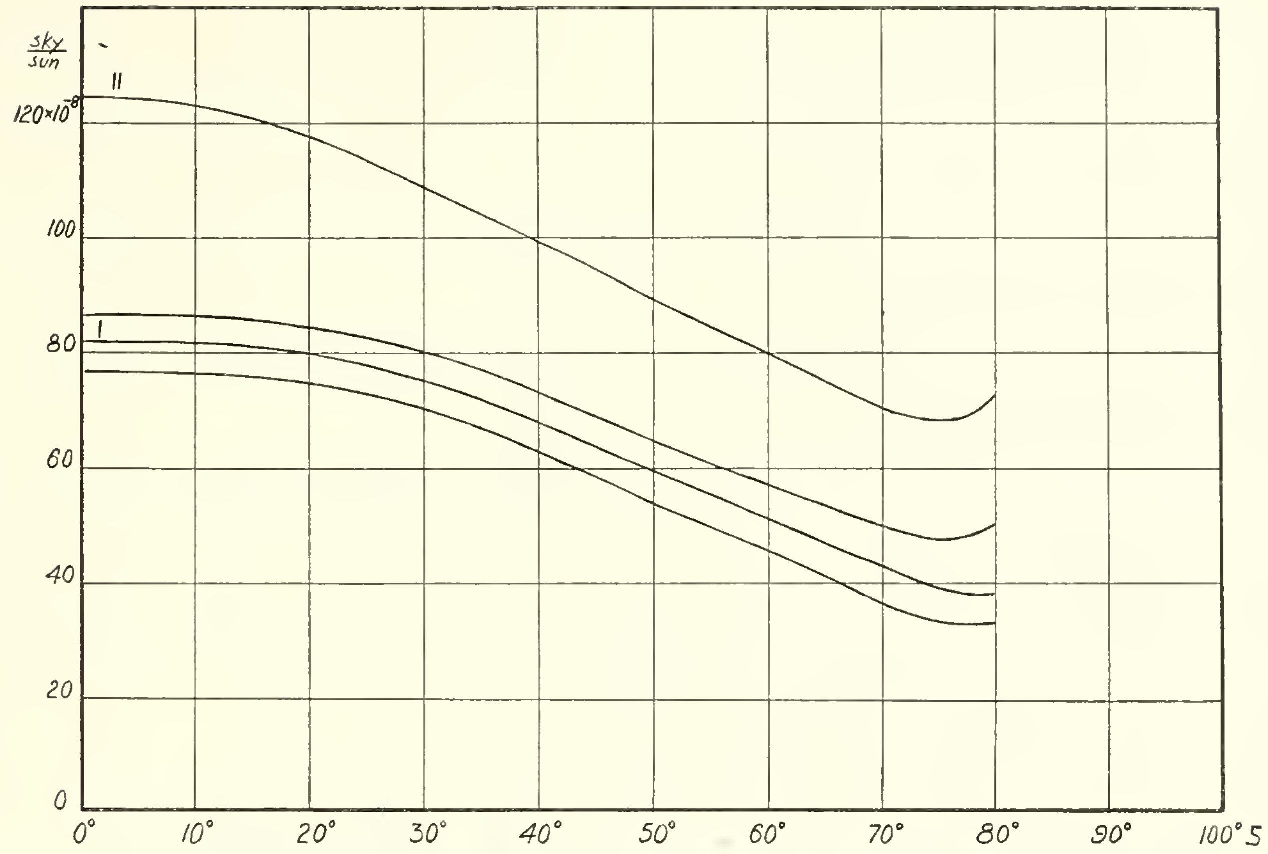


Diagram XI.—Ratio *zenith sky/sun* for equal solid angles calculated from Mount Wilson and Washington observations.

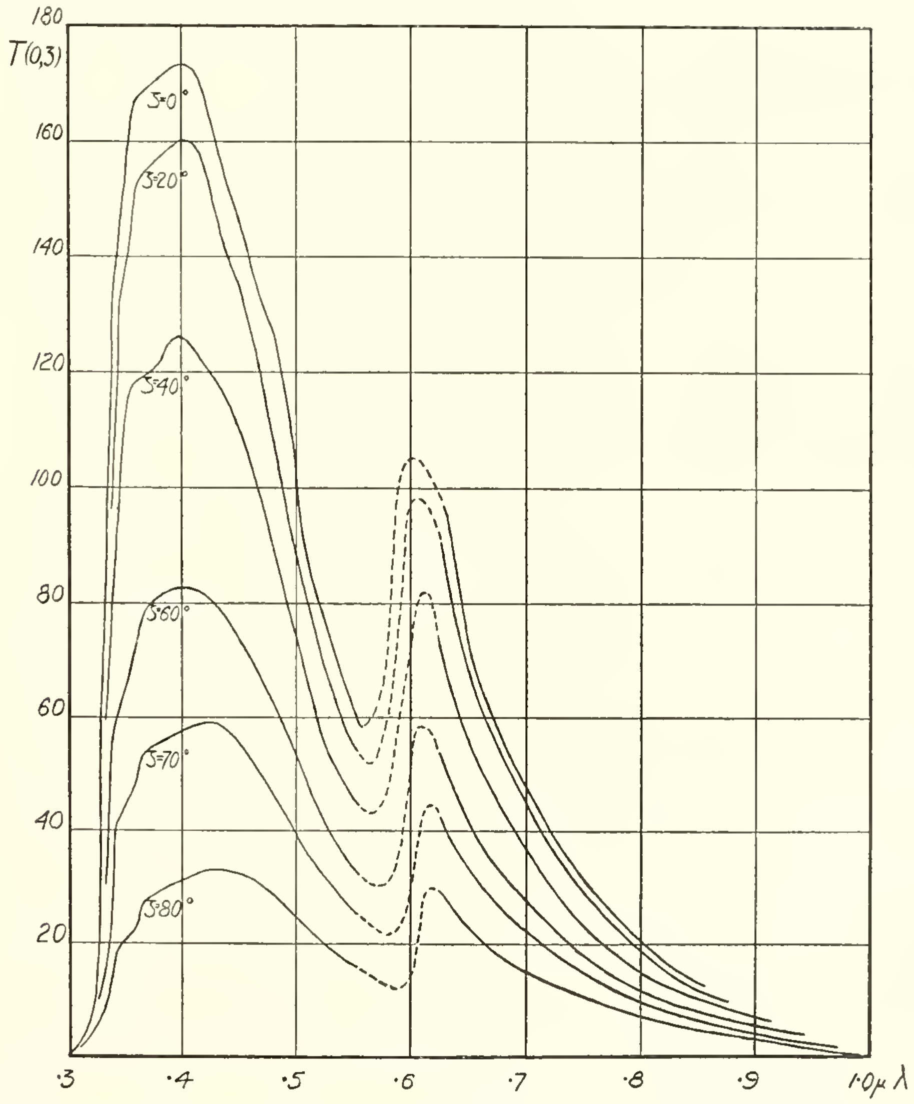


Diagram XII. Relative intensities from zenith sky, calculated from Washington observations.

DIAGRAM XIII.—*Quality of Sky Radiation Calculated at Mount Wilson and Compared with Observations.*

The curves (i), (ii), (iii) of Diagram XIII. are plotted from the results of Table X., and show graphically how observed values of sky radiation agree with values calculated from mean attenuation coefficients at Mount Wilson. The curves corresponding to the extreme and mean values of the solution of the integral equation are retained throughout. Observed points are denoted by small circles, and lie fairly close to the calculated curves.

DIAGRAM XIV.—*Polarization of Zenith Sky Calculated from Washington and Mount Wilson Observations.*

The curves given in Diagram XIV. are drawn from data calculated in Table XIII., and represent the ratio of the component intensities of zenith sky polarized in the principal plane to the component polarized at right angles to that plane. This ratio is represented roughly by the formula

$$\frac{T_1(0,\zeta)}{T_2(0,\zeta)}=\frac{1+Q(0,\zeta)/P(0,\zeta)}{\cos^2\zeta+Q(0,\zeta)/P(0,\zeta)}.$$

Curves are given for various zenith distances of the sun, making use of the constants for Mount Wilson and Washington. In the latter case the effect of "dust" gives rise to a discontinuity in the neighbourhood of $\cdot 610\mu$, represented in an actual case by a peak in the curves (represented by dotted lines). The characteristic just mentioned is actually observed in curves of polarization of zenith sky obtained by NICOLS.* In comparatively "dust-free" air as at Mount Wilson this peak is wanting, and the curve represents a type obtained by NICOLS† which rises with increasing wave-length. Since the forms of the curves just described depend essentially on the effects of self-illumination, these will be extremely sensitive to the presence of "dust," and will therefore vary greatly with time and place. Reflection of solar radiation from the earth's surface (*e.g.*, a snow-covered landscape) will affect in a marked manner the polarization of sky radiation independently of effects of self-illumination, and may therefore account for the great variety of results obtained by observation on this point.

---

[*] NICOLS, *loc. cit.*, p. 508, fig. 10, Curves (*b*) and (*b'*).

[†] NICOLS, *loc. cit.*, fig. 10, Curve (*c*).

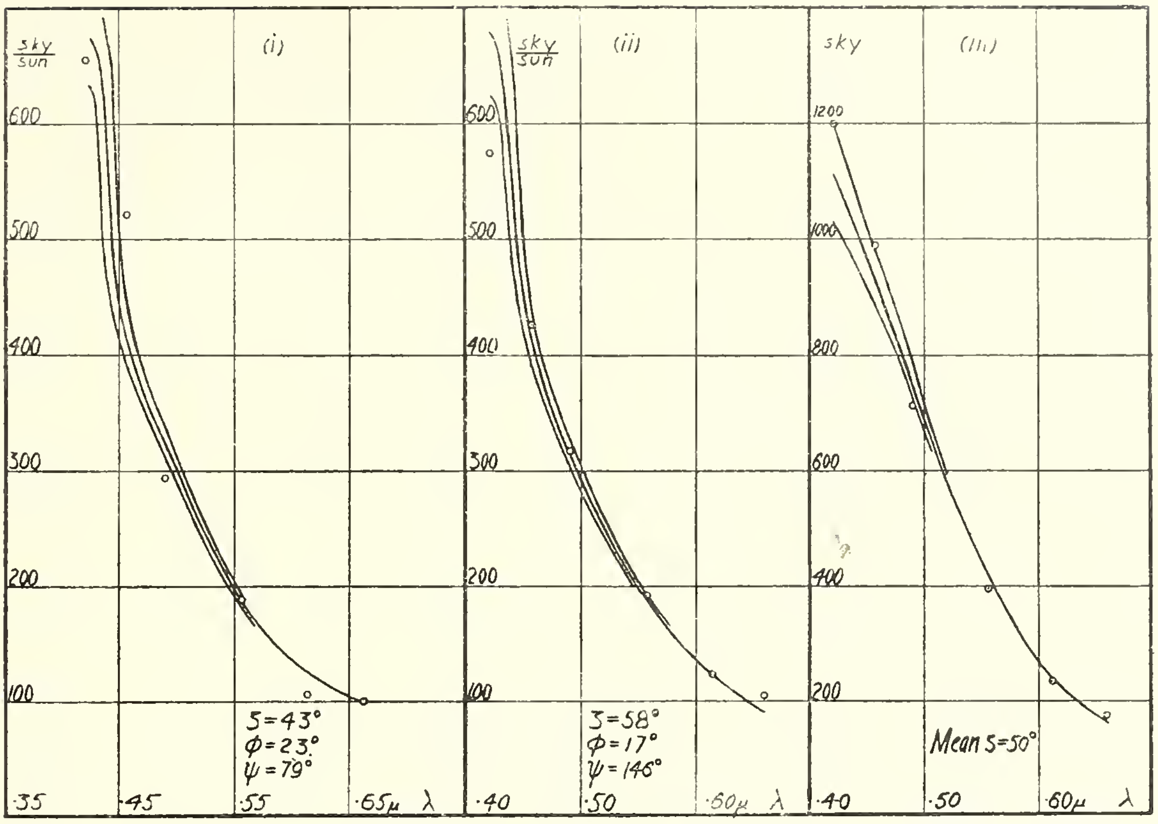
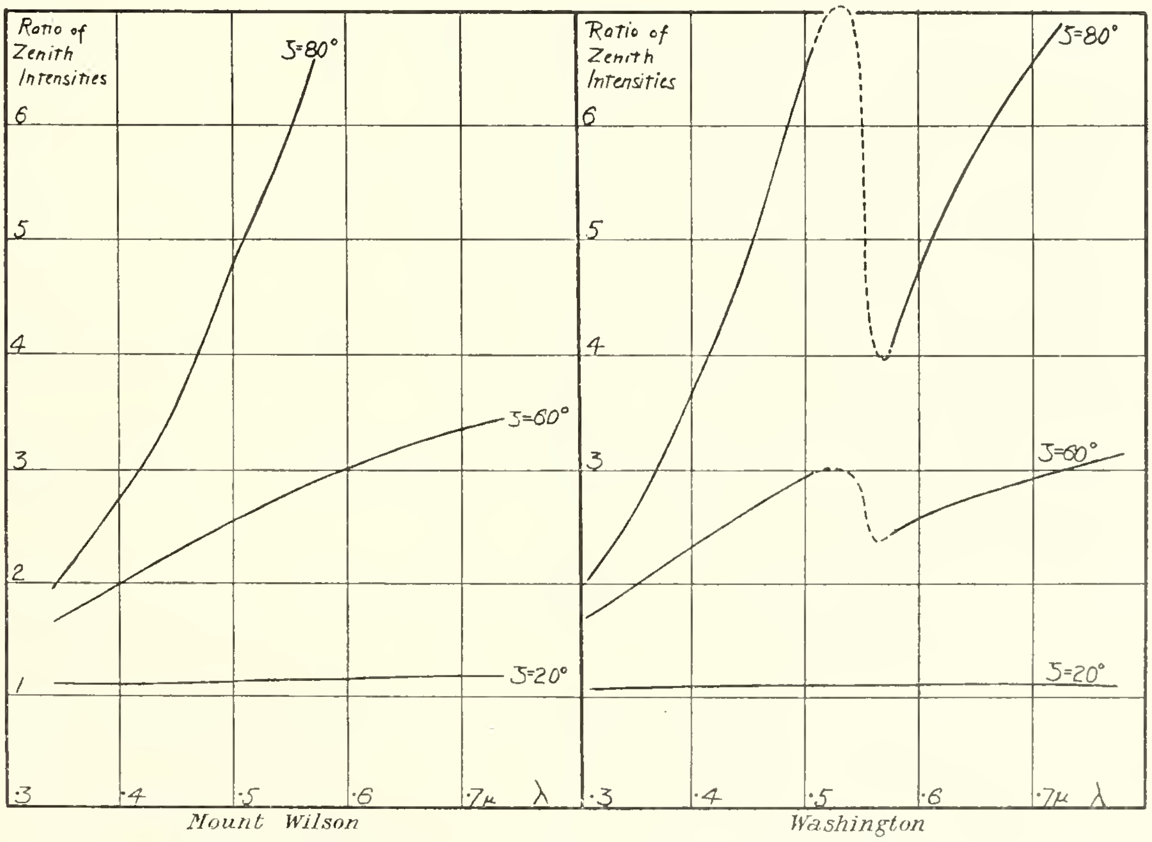


Diagram XIII. Quality of sky radiation, calculated from Mount Wilson observations, October 17, 1906.



Mount Wilson

Washington

Diagram XIV. Polarization of zenith sky calculated from Mount Wilson and Washington observations.

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