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OF THE  
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CONTAINING PAPERS OF A MATHEMATICAL OR PHYSICAL CHARACTER.

VOL. 218.

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JULY, 1919.





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## A D V E R T I S E M E N T .

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THE Committee appointed by the *Royal Society* to direct the publication of the *Philosophical Transactions* take this opportunity to acquaint the public that it fully appears, as well from the Council-books and Journals of the Society as from repeated declarations which have been made in several former *Transactions*, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume ; the Society, as a Body, never interesting themselves any further in their publication than by occasionally recommending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the *Transactions* had happened for any length of time to be intermitted. And this seems principally to have been done with a view to satisfy the public that their usual meetings were then continued, for the improvement of knowledge and benefit of mankind : the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future *Transactions* ; which was accordingly done upon the 26th of March, 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them : without pretending to answer for the certainty of the facts, or propriety of the reasonings contained in the several papers so published, which must still rest on the credit or judgment of their respective authors.

It is likewise necessary on this occasion to remark, that it is an established rule of the Society, to which they will always adhere, never to give their opinion, as a Body.

upon any subject, either of Nature or Art, that comes before them. And therefore the thanks, which are frequently proposed from the Chair, to be given to the authors of such papers as are read at their accustomed meetings, or to the persons through whose hands they received them, are to be considered in no other light than as a matter of civility, in return for the respect shown to the Society by those communications. The like also is to be said with regard to the several projects, inventions, and curiosities of various kinds, which are often exhibited to the Society; the authors whereof, or those who exhibit them, frequently take the liberty to report, and even to certify in the public newspapers, that they have met with the highest applause and approbation. And therefore it is hoped that no regard will hereafter be paid to such reports and public notices; which in some instances have been too lightly credited, to the dishonour of the Society.



PHILOSOPHICAL TRANSACTIONS  
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ROYAL SOCIETY OF LONDON.

SERIES A, VOL. 218. TITLE, &c.

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THE SOLAR AND LUNAR DIURNAL VARIATIONS OF  
TERRESTRIAL MAGNETISM.

BY

S. CHAPMAN, M.A., D.Sc.,

FELLOW AND LECTURER OF TRINITY COLLEGE, CAMBRIDGE, AND CHIEF ASSISTANT  
AT THE ROYAL OBSERVATORY, GREENWICH.

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*Communicated by Sir F. W. DYSON, Astronomer Royal, F.R.S.*

Received March 12,—Read March 22, 1917.

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§ 1. *Introduction.*

THE regular daily changes of the earth's magnetism, considered as a world-wide phenomenon, afford a problem of much interest and importance. It is one, moreover, which the researches of BALFOUR STEWART and SCHUSTER have shown to be more vulnerable to attack than seem most of the problems of terrestrial magnetism. But in spite of their success, and of the contributions of subsequent writers, the comprehensive study of the subject has suffered undeserved neglect. It seems an unfortunate fact that the efforts of magneticians are unduly devoted to the accumulation of data, the time and labour spent in their discussion being, proportionately, inconsiderable.

The promising theory that the daily magnetic variations arise mainly from electric currents circulating in the upper atmosphere, under the impulsion of electromotive forces produced by the convective motion of the air across the earth's permanent magnetic field, was first propounded by BALFOUR STEWART.\* In a simple but penetrating discussion of the features both of the solar and lunar diurnal variations, he showed the power of this theory to account for the facts in a way which none of the other theories then current could do.

The theory was greatly developed, and rendered more definite, in two important memoirs by SCHUSTER in 1889 and 1907.† Adopting a suggestion by GAUSS, he applied the method of spherical harmonic analysis to the solar diurnal magnetic variations, to determine whether they had their origin mainly above or below the

\* Cf. his article on "Terrestrial Magnetism" in the 9th edition of the 'Encyclopædia Britannica' (1882). He made considerable use of BROUN'S admirable study of the lunar diurnal variation of declination at Trevandrum (1874).

† SCHUSTER, 'Phil. Trans.,' A, vol. 180, p. 467 (1889); and A, vol. 208, p. 163 (1907).

earth's surface. The result demonstrated the accuracy of BALFOUR STEWART'S conclusion that the origin must be external.

At the close of his first paper SCHUSTER suggested that the convective atmospheric motions indicated by the diurnal *barometric* changes are those which are responsible, in the manner proposed by the above theory, for the daily magnetic changes. In his second memoir this hypothesis was carefully examined, using the data of his former investigation as the basis of discussion. The general conclusion was favourable to the theory, although attention was drawn to several features of the phenomenon which remained difficult to explain.

Among other works on the subject which have appeared since the publication of SCHUSTER'S earlier memoir, those by FRITSCHÉ,\* G. W. WALKER,† and VAN BEMMELEN‡ may be noted here. The two former authors confined themselves to the solar diurnal magnetic variations, but VAN BEMMELEN broke fresh ground by applying harmonic analysis also to the lunar diurnal variations. The importance of the latter was fully recognized by both BALFOUR STEWART and SCHUSTER, who, in his second memoir (p. 181), urged the desirability of further study of them.

Some of the above, and other, writers reached conclusions adverse to the STEWART-SCHUSTER theory, partly owing to the fact that the results of their analyses of the observational data differed from SCHUSTER'S. The present paper embodies an attempt to resolve the points in dispute, and to remove other obscurities in the theory. New analyses are made both of the solar and lunar diurnal magnetic variations, so that the chief facts relating to each may be discussed together. It is taken as axiomatic, in view of the general resemblance between the two phenomena, that in the main the same theory and similar mechanisms must apply to each. Various modifications of SCHUSTER'S hypotheses and results are found to be necessary, but the essential points of the theory are confirmed by this investigation.

The discussion of the third and fourth, as well as the 24- and 12-hour, harmonics in the magnetic variations is one of the more novel features of this paper: previous discussions have generally been confined to the diurnal and semi-diurnal components, and doubts have been cast on the value of the higher frequency terms, which I hope the present investigation will remove. In the case of the lunar variations, only the semi-diurnal term has hitherto been used; this, however, was because, while other harmonics are present, their phases vary through a multiple of  $2\pi$  throughout each lunar month, so that they disappear from the ordinary mean monthly variation calculated as it has been in the past. In an earlier memoir § I have shown how all four harmonics can be determined by computing the variations

\* FRITSCHÉ, St. Petersburg, 1903, and Riga, 1905 and 1913 (these papers were apparently privately printed and circulated).

† G. W. WALKER, 'Roy. Soc. Proc.,' A, vol. 89, p. 379, 1913.

‡ VAN BEMMELEN, 'Meteorologische Zeitschrift,' 5, p. 218, 1912; 12, p. 589, 1913.

§ 'Phil. Trans.,' A, vol. 213, p. 279, 1913; and A, vol. 214, p. 295, 1914. Also see 'Phil. Trans., A, vol. 215, p. 161, 1915.

for groups of days all at the same lunar phase, afterwards correcting the phase of the resulting Fourier coefficients to the epoch of new moon. In this way a considerable similarity between the relative amplitudes and phases of the various components of the solar and lunar magnetic variations is revealed.

The changing phase of the non-semi-diurnal terms in the lunar variation is a result of the combination of a lunar semi-diurnal variation (a lunar atmospheric tide) with an effect depending on solar time. The latter is here identified with the variation in the electrical conductivity of the upper atmosphere, owing to some solar ionizing influence. At new moon the two effects are in phase, and the lunar magnetic variations resemble the solar; in the latter case, of course, both the atmospheric oscillation and the variable conductivity keep time with the one body, the sun.

SCHUSTER found that while the main cause of the solar diurnal variations was external to the earth, there was also an induced system of earth currents, partly neutralizing the vertical force variations. This result is confirmed here, though with numerical modifications. The external contribution to the horizontal force variations is estimated at about 2.5 times the internal, as against about four in his memoir; also whereas no phase difference between the two current systems was found, a difference of from  $10^\circ$  to  $25^\circ$  is here indicated. It is shown that the internal field could be produced through induction by the outer currents, provided that, beneath an upper non-conducting layer of 150 or 200 miles depth, the substance of the earth has a uniform specific resistivity of amount  $2.74 \cdot 10^{12}$  C.G.S. A conclusion of this kind was arrived at in 1889 by SCHUSTER, and this investigation only modifies his in detail; he made no estimate of the resistivity of the inner core, and suggested 1000 km. as the depth of the outer layer.

The lunar diurnal magnetic variations are undoubtedly due solely to a semi-diurnal atmospheric oscillation. The relative magnitudes of the various harmonic components in the magnetic variation afford information regarding the conductivity of the atmospheric layers in which they are produced. It appears that the currents flow mainly in the sunlit hemisphere, the conductivity in the dark hemisphere being very small. Its diurnal variation can be approximately ascertained, and its maximum value numerically estimated; this proves to be higher than the value originally suggested by SCHUSTER. The phenomena of electric wave transmission also suggest the existence of such a layer of variable electric conductivity, and, in addition, of a still higher layer of constant and uniform conductivity. The magnetic variations give no indication of the latter layer.

The main terms in the solar magnetic variation are so similar, in most respects, to those of the lunar variation that they too would appear to be produced mainly by a semi-diurnal atmospheric oscillation. The 24-hour components are relatively larger, however, than in the lunar magnetic variation, so that, although the phases of the 24- and 12-hour terms show remarkably close agreement, there is ground for supposing that a diurnal atmospheric oscillation may be involved in addition.



The seasonal spherical harmonics in the magnetic variations are also considered, and it is found that they are relatively twice or thrice as large in the lunar variation as in the solar variation, in comparison with the harmonics which persist uniformly throughout the year. This suggests that the main 12-hour oscillation in the solar case may produce seasonal harmonics which are partly neutralized by some other oscillation, such as that of 24-hour period, just mentioned.

The phase relations of the latter oscillation present some difficulty, and it is questionable whether it is connected with the 24-hour barometric variation, of thermal origin, which is observed at the earth's surface. The 12-hour barometric variation, on the other hand, is so much more fundamental in character that it is not unreasonable to suppose that it persists even up to the high levels here contemplated. The magnetic data suggest that its proportional amplitude ( $\delta p/p$ ) diminishes upwards to the extent of one-half its surface value.

The upper air currents responsible for the magnetic variations will have a heating effect which can be approximately calculated, and it appears that there is a possibility of the production, by this means, of an appreciable solar diurnal temperature and pressure variation in the conducting layer. It may be that the above-mentioned diurnal oscillation, peculiar to the solar diurnal magnetic variations, is to be accounted for in this way.

The questions of phase raised by this discussion prove to be very perplexing. As the theory would indicate, the phases of the annual mean harmonics of various periods agree amongst themselves, both in the solar and lunar variations. But these phases seem to possess little or no relation with those of the solar and lunar semi-diurnal *barometric* variations at the earth's surface. It would appear that the phase of the solar barometric variation diminishes with increasing height, by an amount which has been estimated at 80 or 90 degrees.\* But a much larger change of phase with height is required, affecting the lunar as well as the solar barometric variation, if these are to be brought into simple relation with the magnetic variations.

The other principal remaining difficulty is that the diurnal North force variations do not agree at all well with those calculated from the potential function which represents the diurnal West force variations. This does not seem to be explicable, as G. W. WALKER has suggested, by the presence of magnetic variations depending on the time of some fixed meridian.

In order that the present paper may be the better understood, it has seemed well to indicate the existing state of the problem, by giving a brief critical account (§§ 2 to 6) of the work of the previous writers already named. In the course of this historical survey mention is made of the chief modifications of previous methods, and of previous conclusions, which are introduced in the present discussion.

The burden of labour entailed by an investigation of this kind is very great, and could

\* This was not remarked on in SCHUSTER's second memoir, in which a measure of agreement seemed to be indicated between the phases of the barometric and magnetic variations.

not have been undertaken without considerable assistance. The heaviest part of the arithmetical work consisted in the computation of the lunar diurnal variations (§ 12); no reduced data of the desired kind were available, so that the variations had to be newly computed from the published hourly values of the magnetic elements, seven years' records from each of five observatories being used. Skilled assistance was obtained in this and all the other work of computation, wherever possible. In regard to this I wish to make grateful acknowledgment of the help placed at my disposal by the Government Grant Committee of the Royal Society, by Dr. SCHUSTER, and by the Astronomer Royal. Also in the preparation of the data of Tables I. to III. relating to the solar diurnal variation, I am indebted to the Astronomer Royal for computing assistance, and to Mr. W. W. BRYANT, Superintendent of the Magnetic and Meteorological Department at the Royal Observatory, Greenwich, who personally shared in and controlled the reduction of the published data to this form.

I wish also to acknowledge the courtesy of the following directors of observatories, who furnished me with manuscript records of such of their observations as I had need of, and which were at the time unpublished: Dr. ANGENHEISTER (Samoa), Mr. P. BARACCHI (Melbourne), Dr. SCHULZE (Pilar and Laurie Island), and Mr. SKEY (Christchurch, N.Z.).

The preparation of even the tables of initial data, such as Tables I. and II. and (much more) IV. to VI., is a task of considerable magnitude, which I believe must put a serious obstacle in the way of further advance in the subject. In order that future workers may not be repelled by such initial difficulties, it is very desirable that directors of magnetic observatories should reduce their own observations more completely, and publish them in a readily available form. With regard to the lunar diurnal variations I have already made suggestions as to the manner in which this might advantageously be done.\* The present discussion of these variations seems to confirm the desirability of further investigation. The same applies, though to a smaller extent, to the solar diurnal variations. In the latter case I would recommend that a threefold sub-division of the year should be adopted, as for the lunar diurnal variations in § 12; and that the variations from quiet days only for the mean of a number of years, should be used.

## PART I.—THE PRESENT STATE OF THE PROBLEM.

### § 2. SCHUSTER'S *first investigation* (1889).

The data used by SCHUSTER were the Fourier coefficients of the first four harmonics in the solar diurnal variations of North, West, and vertical magnetic force, taken separately over the summer and winter halves of the year 1870, from the observations at Bombay, Lisbon, Greenwich, and St. Petersburg. The year 1870 happened to be

\* 'Phil. Trans.,' A, vol. 214, p. 295, 1914.

a year of abnormally high solar and magnetic activity,\* so that the data were not typical, though this is no drawback so far as the investigation is self-contained. The first part of the discussion dealt with the determination of a potential function which, on differentiation, yields as close a representation as possible of the observed variations in the North and West components of force. It was provisionally assumed that such a potential function exists, and that it is symmetrical with respect to the earth's axis and remains constant in its relation to the sun as the earth revolves—*i.e.*, that the variations depend solely on local time. Moreover, since the number of stations from which data were used was small, it was necessary to assume symmetry also with respect to the equatorial plane. Thus the Northern winter variations were taken to represent† the variations, at corresponding Southern latitudes, contemporaneous with the observed Northern summer variations.‡ The period of the year to which the calculations apply is consequently a half-year centred at either solstice.

If such a potential function exists, data from the above four stations should suffice to indicate its main features, although the area of the earth's surface from which they are drawn is somewhat limited. It is desirable to have more stations, however, both in order to test the validity of the assumption, and to evaluate the function more exactly. WALKER states that the observed variations indicate the presence of important harmonics not depending solely on local time; the new data of this paper do not give much support to this conclusion, but they agree with FRITSCHÉ'S results in suggesting that an appreciable part of the variations at any one station is local and peculiar to the place. If data from only a few observatories are used it is nearly always possible to represent them closely by including a sufficient number of tesseral harmonics in the potential function; but from the above it is clear that only the main terms are likely to have significance as indicative of variations which are world-wide. For this reason it would now seem that SCHUSTER'S analysis of his data was unnecessarily elaborate, but at the time there was no previous experience to serve as a guide, and it was probably best to risk going too far in this direction, rather than to fall short of what the data might yield. Only the more important terms, however, which agree with those considered in this paper, were discussed. They are reproduced (in the notation of § 9) in Table D, p. 25, for comparison with other determinations by FRITSCHÉ and the present author. The various investigations give results which agree fairly well as regards the phase angles, and in the relative orders of magnitude of the various amplitude-coefficients. The absolute

\* WOLFER'S sunspot number for this year was 139, a value which has been approached only on one other known occasion, *viz.*, in 1848, when the sunspot number was 124.

† With suitable changes of sign in certain components.

‡ This was done only for the first two components of periods 24 and 12 hours. The seasonal terms were not considered in the case of the 8-hour and 6-hour components, for which the mean of summer and winter was taken to apply to each hemisphere alike.

magnitude of SCHUSTER'S results is in nearly every case greater than those here obtained, even for the year of sunspot maximum. This was to be expected in view of the exceptional character of the year 1870.

Having obtained a potential function which would account for the horizontal force variations, SCHUSTER compared the observed vertical force variations with those calculated from this function on the respective hypotheses that its origin was (*a*) external, (*b*) internal to the earth. Only from one of the four stations (Lisbon), unfortunately, were satisfactory vertical force data available for the year 1870. For the other three observatories data relating to later years had to be taken.\*

It appeared that the *phase* of the observed vertical force variations agreed completely with the assumption of an external cause (and was therefore opposite to that corresponding to the second hypothesis), but that the observed amplitude was only about half the calculated amplitude. This was explained by supposing the primary varying magnetic field, above the earth's surface, to be accompanied by a secondary field within the earth due to electric currents induced by the primary field. The secondary field would reinforce the horizontal force variations due to the primary, and would partly neutralize the vertical force variations. But an accompanying phase difference was to be expected between the calculated and observed vertical force results, and this appeared not to exist. Certain researches by LAMB,† indeed, indicated that if the earth were assumed uniformly conducting, a reduction of the amplitude of the vertical force variations by one-half (as in the Lisbon data) should be accompanied by a phase change of about 40 degrees. This difficulty was surmounted, however, in pursuance of a suggestion by LAMB, by assuming that the conductivity of the inner core of the earth exceeds that of the upper layers. In his second memoir (p. 169) SCHUSTER roughly estimated the thickness of the outer non-conducting crust to be about 1000 km.

The general conclusion as regards the diurnal and semi-diurnal components of the solar diurnal magnetic variation was that the potential of the external field agrees in phase with, but is four times the magnitude of, that for the internal field.‡ The components of shorter period were hardly at all discussed in either of his memoirs. The character of the vertical force data used, and the presence of local irregularities in the variations at single stations, naturally suggest that this separation of the internal and external fields may be somewhat uncertain. FRITSCHÉ'S and VAN BEMMELEN'S results are considerably different, and those also of the present paper, while confirming SCHUSTER'S main conclusions, differ from his results in some important respects.

\* As regards Greenwich and St. Petersburg this was because the temperature corrections to the vertical force records were not properly known in 1870. The vertical force magnetograph at Bombay did not come into operation till after 1870.

† LAMB, 'Phil. Trans.,' 1883, p. 536; also the appendix to SCHUSTER'S memoir of 1889.

‡ Cf. p. 170 of the second memoir: this conclusion was not explicitly stated in the first memoir.

§ 3. FRITSCHÉ'S *Investigations of the Solar Diurnal Magnetic Variations.*

FRITSCHÉ'S investigations of the solar diurnal magnetic variations are works of considerable magnitude and numerical detail, and are contained in three papers of 1902, 1905, and 1913.\* In the first paper a Gaussian potential function is determined to represent as closely as possible the variations in the North and West components of force at 27 stations. The function was determined separately for the summer and winter half-years. It was not necessary to assume symmetry about the equator, as SCHUSTER had done, since FRITSCHÉ'S stations included five in the Southern hemisphere; the assumption that the variations depend only on local time was, however, retained. The use of a much larger number of stations was in itself an improvement, but this was attained, in FRITSCHÉ'S case, by throwing over an important consideration to which SCHUSTER rightly gave much weight, viz., that the data should all relate to the same epoch. FRITSCHÉ'S data are drawn from series of observations extending in some cases only over a few months, and in others over several years, and their epochs range from 1841 to 1896. They are consequently far from homogeneous, both on account of the eleven-year cycle in the magnetic activity of the earth, and probably also because of varying degrees of observational accuracy.

Of the 27 stations, nine were North of latitude  $60^\circ$  N., thirteen lay between  $0^\circ$  and  $60^\circ$  N., while the remaining five extended from  $0^\circ$  to  $60^\circ$  S. After deducing his potential functions from the North and West force data taken together, using the method of least squares,† FRITSCHÉ made an elaborate numerical comparison of the calculated and observed variations. The best agreement was found for the ten Northern observatories lying between the tropical circle and  $60^\circ$  N.; it was less good for the tropical and Southern stations, and very bad for the nine stations above  $60^\circ$  N. latitude. The last circumstance is perhaps not unnatural, owing to the divergence of the magnetic from the geographical poles of the earth. So long as the analysis of the magnetic variation is based on the assumption that they depend solely on local time, it seems best to use data only from stations between  $\pm 60^\circ$  latitude. All the other investigations described here conform to this rule, and FRITSCHÉ himself decided later that it was desirable to exclude the nine polar stations and to re-calculate the potential function from the remaining 18 observatories. This work is described in his 1913 paper. The 18 sets of data, combined

\* FRITSCHÉ, St. Petersburg, 1902, Riga, 1905, and Riga, 1913. The second paper, so far as it deals with the daily variation, is in the nature of an appendix to the first, and need not be separately considered.

† The 27 stations were combined into six groups, and the mean diurnal inequalities in each element were computed from those for the separate stations in each group. These mean inequalities (in the form of 24 hourly values) were harmonically analysed, and the Fourier coefficients were then treated by the method of least squares so as to fit a potential function to them as closely as possible. Two of the six groups included the stations North of  $60^\circ$  N.

into four groups only (as they were given in the 1902 paper), were treated by the method of least squares as before. While the resulting potential functions were not greatly different from those first obtained, the residuals for the given 18 stations were improved, without much affecting those for the other nine. The chief terms in the re-calculated functions are exhibited in Table D, § 10, in a form allowing comparison to be made with SCHUSTER'S and the new results of this paper. FRITSCHÉ'S values, like those here found for the years 1902 and 1905, are much less than SCHUSTER'S, for the reason already mentioned. But the agreement is more striking than the differences, considering the different material, epochs, and methods of analysis used in the various investigations.

FRITSCHÉ treated the vertical force data from the same stations in a precisely similar way, and thus deduced from them a potential function which was independent of the horizontal force variations. In Table E, p. 26, the re-calculated results of his 1913 paper are compared with the corresponding results obtained in this paper. The two sets of figures generally agree in sign, but numerically the agreement is much less good than for the horizontal force data of Table D. I can only attribute the difference to the greater difficulty of obtaining reliable observations of the *vertical* force variations.\* This renders it very necessary to use only the most modern and reliable data available.

The calculation of a separate potential function from the vertical force data makes possible a more satisfactory estimation of the respectively external and internal parts of the magnetic variation field than SCHUSTER'S limited material allowed. The method used by FRITSCHÉ, and also in this paper, is explained in §§ 8, 9, and only the results will be mentioned here. In place of SCHUSTER'S value, 4 : 1, the ratio of the surface potentials of the outer and inner portions of the field was given as 1·75 : 1 in the 1913 paper (in the 1902 paper the discordance was still greater, the stated ratio being 1·49 : 1). Another method used by FRITSCHÉ for estimating the same ratio gave the results 1·59 : 1 (1913) or 1·44 : 1 (1902). He concluded that the internal field was too nearly equal to the external field to allow it to be regarded merely as an induction product of the latter. It need hardly be stated how much the difficulties in the way of an explanation of the phenomenon would be increased if such a conclusion were substantiated; two independent mechanisms would then have to be co-ordinated and accounted for.

FRITSCHÉ did not discuss the phase relations of the internal and external potentials, nor did he consider SCHUSTER'S theory of a non-uniformly conducting earth. In view of the new analysis of improved data in this paper, it does not seem necessary to complete FRITSCHÉ'S discussion in this respect.

\* An error of another kind which has to some extent affected earlier investigations of the present nature may be mentioned, viz., that by a mistake in the formulæ of reduction the Batavian vertical force variations have been recorded at twice their true amount from their commencement in 1880 until the discovery of the error in 1913 ('Batavian Observations,' 35, 1912, Preface).

It may also be noticed that the comparison between the calculated and observed variations in his paper showed a much more satisfactory agreement for the West component than for the other two. This seems to be partly a consequence of greater freedom from local irregularities in this element, and is confirmed by the results of the present investigation.

#### § 4. G. W. WALKER'S *Investigation* (1913).

The investigation by WALKER was confined within narrower limits than FRITSCHÉ'S, both in respect of the data used and consequently also in their analysis. The data consisted of the annual mean solar diurnal variations of the North, West, and vertical components of force at nine observatories, and the components having periods of 24 and 12 hours were alone considered. The nine stations ranged in latitude from  $60^{\circ}$  N. to  $6^{\circ}$  S. While in every case the observations were of recent date, they did not all refer to the same year. It appeared that a potential function of simple type ( $Q_2^1$  and  $Q_3^2$  for the 24- and 12-hour periods,\* respectively) could be fitted fairly well to either the West or North force data separately, but that the same numerical coefficient would not apply to both. This was taken to indicate that the assumption of a potential function, at any rate of one depending solely on local time, was invalid. SCHUSTER and FRITSCHÉ, using the two components together, and including a considerable number of harmonics in their analyses, did not notice such a discrepancy (*cf.*, however, the last paragraph of § 3).

WALKER tried to overcome this difficulty by introducing harmonic functions not dependent solely on local time, and in this way he obtained a better representation of his data. But the crucial test of the existence of such additional harmonics must consist of the examination of data from stations of widely different longitudes, and, unfortunately, seven out of the nine stations used by WALKER lay between  $3^{\circ}$  W. and  $31^{\circ}$  E. The data of the present paper, which had been collected before the publication of Mr. WALKER'S paper, were chosen with a view to a decision upon this question,† and are from fairly widely distributed stations. While the simple potential functions of type  $Q_2^1$ ,  $Q_3^2$  do not well represent the North force data, the evidence for the existence of any considerable harmonics not depending on local time does not appear to be strong. For the components of period 12 hours or less, I am inclined to attribute the North force discordance to local irregularities, while leaving the question open in the case of the 24-hour component.

The terms in WALKER'S representation which depend on local time and are symmetrical about the equator are compared in § 10 with the corresponding annual terms obtained by other writers. The phases agree well, and the amplitudes found

\* These are the main annual terms of these periods which were found also in the other investigations summarized in Table D.

† In consequence of a suggestion made by SCHUSTER in his second memoir, p. 172.

by WALKER agree in order of magnitude with those tabulated, although his value for  $C_3^2$  is rather small. Since his data refer to the mean of a year, and are drawn almost entirely from the Northern hemispheres, the unsymmetrical terms in his analysis are not comparable with any results of this paper.

With regard to the vertical force data, WALKER showed that the 24-hour terms in the horizontal force potential would fit the vertical force observations if it was assumed that the internal and external fields agree in phase, and that their amplitude ratio, in the case of the second degree harmonics, is that found by SCHUSTER, viz., 4 : 1; the internal contribution to the harmonic of the first degree was taken to be nil. The 12-hour component was examined in more detail, and it was estimated that the internal contribution to the harmonics of degree three was about one-quarter the external, and that a phase difference between the two would improve the agreement with the vertical force data; as before, the minor harmonic (in this case  $Q_1^1$ ) was assumed to be entirely external. The phase differences alluded to amounted to 35 degrees in the case of  $Q_3^2$ , and 54 degrees in the case of  $Q_3^3$ , the internal field being in *advance* of the external. FRITSCHÉ'S data indicate a phase difference of smaller amount in the contrary sense. The theoretical significance of these differences was not considered, perhaps because the phase difference seemed to be absent in some cases and present in others. The data of the present paper indicate that in all the important, well-determined harmonics, both in the solar and lunar diurnal variations, the phase of the internal field is in advance of the external phase by amounts of the order of 20 degrees. In §§ 15–17 it is shown how these phase differences and the amplitude-ratios can be accounted for by a modified form of SCHUSTER'S hypothesis of a non-uniformly conducting earth.

#### § 5. VAN BEMMELEN'S *Study of the Lunar and Solar Semi-diurnal Magnetic Variations* (1912).

While the lunar diurnal magnetic variation has often been studied, and from many points of view, VAN BEMMELEN was the first to investigate it as a world-wide phenomenon after the manner of SCHUSTER and FRITSCHÉ. His data consisted of the Fourier coefficients  $a_2$ ,  $b_2^*$  for the lunar semi-diurnal variations of the geographical components of magnetic force, taken separately over the summer and winter half-years, from fifteen observatories. The latitude range of these was  $60^\circ$  N. to  $43^\circ$  S. The material was somewhat heterogeneous, relating to different epochs, and calculated in different ways from unequal periods of observation; but a careful

\* The first harmonic coefficients  $a_1$ ,  $b_1$  were also calculated and tabulated, but it was stated that they were irregular, and probably not a real part of the phenomenon. This is the case when they are calculated directly from the mean of a month, as for the semi-diurnal variation. A later paper ('Phil. Trans.,' A, vol. 213, p. 279, 1913) showed, however, that a real 24-hour component exists, which can be calculated only by separately considering the days of different lunar phase.



attempt was made to reduce the data to a common standard, so that the consequent drawback is less than in FRITSCHÉ'S investigations. Besides using various published data, new reductions were made for several stations, and the paper is valuable on this account as well as for its main purpose. For the present paper it was unfortunately necessary to re-calculate the lunar variation for some of these stations so recently dealt with by VAN BEMMELEN, since the harmonics of varying phase could not otherwise be determined. The circumstance does, however, render possible an interesting comparison (§ 14) between the results of the two sets of computations.

Although his data referred separately to the summer and winter half-years, VAN BEMMELEN discussed only the mean annual values, neglecting the seasonal variations. He concluded that the horizontal force variations had a potential, which he determined (after trial of SCHUSTER'S method) by the method of least squares; unlike FRITSCHÉ, however, he used the separate values of  $a_2$  and  $b_2$  from each station instead of combining them into groups, and apparently, also, only the West force data were used. The vertical force data were similarly treated, and a separation of the internal and external parts of the lunar magnetic variation field was then effected.

In a correcting paper of 1913 this calculation was revised, since the "least squares" method of determining the potential seemed to give too much weight to some rather irregular data of early epoch from the three Southernmost stations—the Cape of Good Hope, Melbourne, and Hobarton.\* SCHUSTER'S method was returned to as enabling more discrimination to be exercised between the various data in the course of the work. The resulting analysis was perhaps somewhat over-elaborate, but the principal harmonic, the one dealt with also in this paper, agrees moderately well with the result here obtained (*cf.* § 14). The original calculation had made it appear that the external variation field was actually *less* than the internal field; the revised paper reversed this conclusion, although the inner field was given as more nearly approaching the outer field, in magnitude, than the new analysis of this paper would suggest. VAN BEMMELEN, indeed, as the result of his calculations, still contemplated the possibility of a primary inner as well as a primary outer field.

In his first paper he had also attempted to bring the lunar semi-diurnal variation into relation with the lunar semi-diurnal barometric variation (as observed at Batavia), just as SCHUSTER had done for the solar diurnal variations in his 1907 memoir. The discrepancy between SCHUSTER'S and FRITSCHÉ'S analyses of the solar diurnal magnetic variation, which were both discussed by VAN BEMMELEN, rendered the conclusions somewhat indefinite, and they must, in any case, have been superseded after the revised calculation of the lunar diurnal variation potential. In his second paper VAN BEMMELEN avoided the ambiguity just alluded to, by making

\* Certain mistakes of sign had also been made in the first investigation, which were corrected. In the original paper the Bombay data were given as of thrice their true value, apparently through a numerical slip in the reductions, but on account of their discrepancy with other results they were excluded from the discussion.

a new determination of the semi-diurnal part of the solar diurnal variation potential. The data used were the  $a_2$ ,  $b_2$  coefficients of the annual mean solar diurnal variations in the three geographical components of magnetic force from fifteen observatories (nine North and six South of the equator). The epoch for most of the stations was 1901, a year of minimum solar activity; in other cases the data were corrected so as to correspond to such a year. In §10 the main symmetrical annual term in the horizontal force potential is compared with the corresponding results from other investigations. The agreement in phase is good; the amplitude determined by VAN BEMMELEN is a little smaller than in most of the other cases. VAN BEMMELEN'S analysis also includes a strong unsymmetrical element  $Q_2^2$ , which is somewhat surprising, considering that it relates to the *annual* mean variation. The present results do not seem to suggest much asymmetry between the two hemispheres.

In attempting to separate the internal and external parts of the field, Dr. VAN BEMMELEN remarked on the hazardous nature of the task, owing to the "strong irregularities" in the vertical force data. It appeared, as the result, that the internal potential for the solar semi-diurnal variation was equal to, or even slightly in excess of, the external potential. This differs so greatly from my own conclusion (and also from that of FRITSCHÉ) that I have carefully compared his and my vertical force data. The figures for the nine Northern stations in common were closely similar in the two cases, but the Southern data were far from accordant. Only Batavia was common to the two sets of Southern observatories; during 1901 and 1902 the reorganization of the magnetic work at Batavia and the transfer of the instruments to Buitenzorg interrupted the record, and the 1889 Batavian observations, corrected to 1901, were used. As the correction noted in §3 had not then been discovered, however, the  $a_2$ ,  $b_2$  coefficients as used have twice their true value. As regards the other Southern observatories, the date of three sets used, St. Helena, Cape of Good Hope, and Hobarton, was 1843, and the two latter series are very discordant. It would seem that too much weight has been given to the six Southern sets of vertical force data, and that here lies the explanation of the above discrepancy between the two separations of the external and internal variation fields.

#### § 6. SCHUSTER'S *Second Memoir* (1907).

The theory of the diurnal magnetic variations originally propounded by BALFOUR STEWART (§1) was shown by SCHUSTER, in his first memoir, to be so far correct in that the main part of these variations arises from electric currents circulating above the earth's surface. BALFOUR STEWART'S theory also involved the hypothesis that the electromotive forces which impel these currents are supplied by the permanent terrestrial magnetic field acting on masses of conducting air which, in their bodily motion, cut through the earth's lines of magnetic force. In this hypothesis two important factors were unspecified, viz., the atmospheric motions and the atmospheric conductivity. In his second memoir SCHUSTER made definite suggestions

on these points, and examined their consequences in connection with the results of his first memoir.

It may be stated at the outset that the direct magnetic effect of the convective motion of masses of electrified air was examined and found to be negligible (*loc. cit.*, § 10). Also it was shown (*loc. cit.*, § 8) that the horizontal magnetic field of the earth, and the vertical atmospheric motions, might be neglected, so that the investigation was concerned with the determination of the electromagnetic effect of a *horizontal* oscillation of the atmosphere, acting on the known *vertical* component of the earth's field. Initially the electrical conductivity of the upper atmosphere, where the currents flow, was supposed uniform and constant; afterwards examination was made of the modifications introduced into the theory by assuming the conductivity to be variable.

It was first proved that the atmospheric oscillations necessary for the production of the diurnal and semi-diurnal\* magnetic variations (the conductivity being uniform) are of types  $Q_1^1$  or  $Q_3^1$  and  $Q_2^2$  or  $Q_4^2$  respectively. These are the types of motion indicated by the diurnal and semi-diurnal barometric variations. The theory that the latter variations are closely connected with the daily magnetic variations had already been tentatively advanced in SCHUSTER'S first paper; he now submitted it to a detailed numerical test. The main difficulty confronting the theory was that the ratio of the diurnal to the semi-diurnal term in the magnetic variation ( $C_2^1/C_3^2$ ) is very much greater than the corresponding ratio ( $c_1^1/c_2^2$ ) in the barometric variation. The former ratio was found in his first paper to be 9.6,† while the calculated ratio was only 2.6; the latter calculation assumed the atmospheric conductivity to be uniform. As regards phase, the calculated variations lagged behind the observed by about  $1\frac{1}{2}$  hours (or from  $2\frac{1}{2}$  to 3 hours, on taking self induction into account).

In the above, the effect of barometric terms of type  $Q_3^1$  and  $Q_4^2$  was neglected, only  $Q_1^1$  and  $Q_2^2$  being considered. The nature of the diurnal term in the barometric variation is not known very definitely, however, and it was pointed out that by representing it in part by an oscillation of type  $Q_3^1$  the amplitude ratio 2.6 could be increased: also that such an oscillation may be present in the upper layers of the atmosphere, which do not greatly affect the barometer, even if it is not found in the surface variation.

The term  $Q_3^1$  would be called on to a smaller extent if the atmospheric conductivity is not uniform, but varies with the zenith distance ( $\omega$ ) of the sun. In this case the 12-hour oscillation  $Q_2^2$  would contribute to the 24-hour magnetic variation  $Q_2^1$ , and the 24-hour oscillation  $Q_1^1$  to the 12-hour magnetic variation  $Q_3^2$ , but the effect would be much more marked in the former case than in the latter. It was shown, in fact,

\* Variations of higher frequency were not considered.

† In equation (10) of the second memoir the coefficient of  $\psi_3^2$  should be 9.23 in place of 11.16 (this is the coefficient of  $\psi_2^2$  as found in the first memoir, p. 486).

that assuming the variation of conductivity to follow the law  $1 + \cos \omega$ ,\* the ratio 2.6 would be increased to 4.7 without drawing at all on  $Q_3^1$ .

As regards the seasonal change in the magnetic variations, it was stated that the large increase in summer could not be explained completely by the above variation of conductivity, and a cumulative seasonal change was suggested as a possibility, in addition to the variation with  $\omega$ . The weight of this difficulty, however, was chiefly thrown upon the uncertainties in the atmospheric motions. In this paper the problem is simplified by the evidence afforded by the lunar diurnal variations, which indicate how largely a semi-diurnal oscillation is able to account for the 24-hour magnetic variations, owing to a much more marked variation of conductivity, between day and night, than that represented by the formula  $1 + \cos \omega$ .

SCHUSTER estimated the order of the electric conductivity required by the theory, and discussed how far the high value thus found was physically possible or probable. He concluded that it was a possible value, which might perhaps be accounted for by ascribing the conductivity to the ionizing action of ultra-violet radiation from the sun. But it was remarked that the absorption of such radiation in the solar atmosphere might render this suggestion invalid.

The theoretical calculations of the paper dealt mainly with that part of the permanent magnetic field of the earth which is symmetrical about the geographical axis. It was pointed out, however, that the obliquity of the magnetic axis should result in the production of magnetic variations not depending solely on local time, and a search for these terms was suggested as a promising line of further work.

## PART II.—A NEW ANALYSIS OF THE SOLAR DIURNAL MAGNETIC VARIATION.

### § 7. *Description of the Data.*

The data used in this investigation consist of the Fourier coefficients  $a_n, b_n$  in the harmonic formula

$$(1) \quad \Sigma (a_n \cos nt + b_n \sin nt)$$

for the solar diurnal variations in the North, West and vertical components of magnetic force. Results from twenty-one observatories are utilised, of which fifteen are North and six South of the equator, between latitudes  $\pm 61$  degrees. The average number of stations represented in any particular section of the final results is slightly less than twenty, however, since data in every element were not available from quite all the selected observatories at the chosen epochs.

The stations were selected so as to obtain as wide a distribution in longitude as the available records allowed (*cf.* § 27). Particulars of their names and positions are given in Table A. For convenience in the subsequent numerical analysis they have been divided into nine groups, as indicated.

\* According to this law the conductivity evidently varies from a maximum at the point directly beneath the sun to zero at the antipodal point.

TABLE A.—The Sources of the Data Used for the Investigation of the Solar Diurnal Magnetic Variation.

No. of group.	No. of observatory.	Observatory.	Latitude (North+).	Co-latitude $\theta$ .	Longitude from Greenwich (East+).
			° ' .	° ' .	° ' .
I.	{	1 Pavlovsk . . . . .	59 41	30 19	30 29
		2 Sitka . . . . .	57 3	32 57	- 135 20
		3 Ekaterinburg . . . . .	56 50	33 10	60 38
		Mean . . . . .	57 51	32 9	—
II.	{	4 Potsdam . . . . .	52 23	37 37	13 4
		5 Irkutsk . . . . .	52 16	37 44	104 19
		6 Greenwich . . . . .	51 29	38 31	0 0
		Mean . . . . .	52 3	37 57	—
III.	{	7 Pola . . . . .	44 52	45 8	13 51
		8 Tiflis . . . . .	41 43	48 17	44 48
		Mean . . . . .	43 17	46 43	—
IV.	{	9 Baldwin . . . . .	38 47	51 13	- 95 10
		10 Cheltenham . . . . .	38 44	51 16	- 75 50
		Mean . . . . .	38 46	51 14	—
V.	{	11 Zi-Ka-Wei . . . . .	31 12	58 48	121 26
		12 Honolulu . . . . .	21 19	68 41	- 158 3
		Mean . . . . .	26 16	63 44	—
VI.	{	13 Bombay . . . . .	18 54	71 6	72 49
		14 Vieques, Porto Rieo . . . . .	18 9	71 51	- 65 26
		15 Manila . . . . .	14 35	75 25	120 58
		Mean . . . . .	17 13	72 47	—
VII.	{	16 Batavia . . . . .	- 6 11	96 11	106 50
		17 Samoa . . . . .	- 13 48	103 48	- 171 46
		Mean . . . . .	- 10 0	100 0	—
VIII.	{	18 Pilar . . . . .	- 31 41	121 41	- 63 51
		19 Melbourne . . . . .	- 37 50	127 50	144 59
		20 Christchurch . . . . .	- 43 32	133 32	172 37
		Mean . . . . .	- 37 41	127 41	—
IX.	21	Laurie Island, South Orkneys	- 60 45	150 45	- 45 1

The epoch of the data used is modern, the years 1902 and 1905\* being chosen; these were years of sunspot minimum and maximum in their eleven-year cycle, two such periods being considered in order that the influence of solar activity on the phenomenon might be definitely determined. Also, so that the seasonal changes might be studied, each year was divided into four quarters of three calendar months each, beginning with February, March and April as the spring quarter. In calculating the mean variation for each of these eight periods, all days were used except a very few which were so highly disturbed as of themselves to be able to modify the quarterly means appreciably. The published data in most cases gave the variations of horizontal force and declination instead of North and West force, to which they had to be transformed. In some cases changes of phase had also to be made, to reduce the data to the adopted time-origin, which is here the local mean time of noon at each station. In the formula (1),  $t$  represents local time reckoned in angle at the rate of 15 degrees per hour. The first *four* harmonics ( $n = 1, 2, 3, 4$ ) have been used throughout, the coefficients  $a_n, b_n$  being expressed in force units of amount  $0.1 \gamma$  ( $10^{-6}$  C.G.S.), and reckoned positive to North, West, and radially (or vertically upwards). The initial data of this paper, relating to the *solar* diurnal magnetic variations, are given at the end of the discussion in Tables I. and II. ( $\alpha$ ), ( $\beta$ ), (1)–(4), (pp. 74, *et seq.*).

### § 8. *General Outline of the Analysis of the Data.*

The data in the Tables I. and II. exhibit a considerable degree of regularity and of constancy in type; thus, save for the increased amplitude in the later year, the 1902 and 1905 values are closely similar: they show a general independence of longitude: and they are nearly symmetrical, or anti-symmetrical, with respect to the equatorial plane. These features are little less apparent in the terms of lower than in those of higher frequency.

Besides this, however, there is an irregularity about the numbers which seems to represent something peculiar to each station, persisting from year to year, and also affecting different elements unequally, the North component, perhaps, being the one most affected. In order to assist in eliminating this local part of the phenomenon from the analysis, nine group means of the data of Table I. have been formed, the groups being indicated and numbered in Table A. It would probably have been advantageous had each group included a still larger number of separate stations.

For the discussion of seasonal influence the method adopted was as follows: the mean of the spring and autumn data was taken to represent the main part of the phenomenon at the equinoxes, at which times there is a general similarity between

\* Or rather 1902, February, to 1903, January, and similarly for 1905. It may also be noted that the Batavian vertical force data for the 1902 summer quarter are drawn from June and July observations only, no records being available for May. WOLFER's sunspot numbers for these years were 5 (1902) and 64 (1905).

the variations in the Northern and Southern hemispheres. The summer and winter data are, of course, widely different, though the Northern summer bears considerable resemblance to the Southern winter, and *vice versa*. The mean,  $\frac{1}{2}$  (Summer + Winter), was taken to represent the part of the phenomenon common to both seasons—it is, indeed, as would be expected, nearly symmetrical about the equator—while the semi-difference,  $\frac{1}{2}$  (Summer – Winter), represents the variable, seasonal part of the phenomenon, which is anti-symmetrical about the equator. As will appear, the solstitial mean agrees very closely, in many respects, with the equinoctial mean, showing that a large part of the variation continues almost uniformly throughout the year. Even the residuals are very similar in the two cases.

These three sets of group means were taken separately for the years 1902 and 1905, and are to be found in Tables III. ( $\alpha$ ), ( $\beta$ ), ( $\gamma$ ). For the sake of completeness the equinoctial semi-differences,  $\frac{1}{2}$  (Spring – Autumn), were also examined (*cf.* Table III. ( $\delta$ )), but only for the mean of 1902 and 1905, as this set is less important than the others. It need hardly be pointed out that this analysis of the data can be immediately adapted so as to give the result for any single season,  $\frac{1}{2}$  (Summer + Winter) –  $\frac{1}{2}$  (Summer – Winter), for instance, giving the winter analysis alone.

In the investigation of these tables of group means, the aim kept always in view has been that of reproducing the broad features by as simple a mathematical representation as possible, considering, first of all, potential functions depending solely on local time. The residuals are discussed later, in connection with the question as to whether there are important terms varying with the longitude (§ 27).

On examination it became clear that the nearly constant, “annual” part of the phenomenon, corresponding to the equinoctial and solstitial group means of Tables III. ( $\alpha$ ) and II. ( $\beta$ ), can be represented with fair accuracy by a single harmonic function for each periodic term, as far as regards the West force variations. The seasonal portions (Tables III. ( $\gamma$ ) and III. ( $\delta$ )) can, for the same component of force, be represented in each case by two such functions. These harmonic functions, depending on local time only, agreed in type with the main terms in SCHUSTER’S and FRITSCHÉ’S analyses, so far as the three investigations are comparable.

If the diurnal magnetic variations have a potential, the North force variations must be deducible from the potential function which represents the West force data. In Table III. the calculated values are given both for the West and North force variations, using the functions chosen to represent the West force data alone. The agreement with the observed values may be considered satisfactory in the latter case, but it is not nearly so good for the North force variations. Perhaps the local irregularities in the data will account for the discrepancy, at any rate in the case of the three components of shorter period (12, 8, and 6 hours). The residuals for the 24-hour component are very systematic, however, and could not be accounted for by a mere change in the amplitude of the potential function derived from the West force variations (*cf.* § 4). Possibly the two sets of data could be more nearly represented

by the same potential function if more harmonics of higher degree were included. But I doubt whether any improvement thus made would be very substantial or of real value, and I have therefore judged it best not to discard the above simple and successful representation based on the West force variations alone. It may be added that if an independent attempt were made to determine, from the North force variations alone, the values of the harmonic functions present in them, of the type which represent the West force data, the results would differ little from those actually calculated from the latter.

The notation of the harmonic functions used in this analysis is described in § 9. In that notation a function

$$(2) \quad (A_m^n \cos nt + B_m^n \sin nt) Q_m^n(\cos \theta) \quad (n = 1, 2, 3, 4)$$

was used in Tables III. ( $\alpha$ ) and III. ( $\beta$ ) to represent the variations  $(a_n \cos nt + b_n \sin nt)$  at the individual stations of various co-latitudes  $\theta$ . The value of  $m$  in each case was found to be  $n+1$ . In Tables III. ( $\gamma$ ) and III. ( $\delta$ ) two such functions, corresponding to  $m = n$  and  $m = n+2$ , were used in each instance. The constants  $A_m^n$  and  $B_m^n$  are set out in Table C § (9).

As previous investigations have indicated, both inside and outside causes contribute to the magnetic field at the earth's surface, so that the vertical force variations cannot be deduced theoretically from the horizontal force variations. On the contrary, the potential function (if such exists), which represents and is calculated from the vertical force data alone, affords the means of separation of the respectively external and internal parts of the whole variation field. It proved on examination that functions (2), of precisely the same type as were used for the horizontal-force data, serve likewise for the vertical-force variations, only the numerical coefficients (denoted in this case by  $\mathbf{A}_m^n$  and  $\mathbf{B}_m^n$ ) being different. These also are given in Table C, alongside the values of  $A_m^n$  and  $B_m^n$ . The corresponding calculated values of  $a_n$  and  $b_n$  are given in Table III. for comparison with the observed data.

For the purpose of the subsequent discussion it was clearly advisable that  $A_m^n$  and  $B_m^n$ ,  $\mathbf{A}_m^n$  and  $\mathbf{B}_m^n$  should be determined on some definite plan which would at least give results which were comparable in the different cases. Where only one harmonic function was involved in the representation of a given set of Fourier coefficients, as in Tables III. ( $\alpha$ ) and III. ( $\beta$ ), the course adopted was very simple. The weighted mean of the various values of the function  $Q_m^n$ , corresponding to the mean latitude of each of the nine groups of observatories, was taken *numerically*, *i.e.*, negative values being treated as positive; the similarly weighted sum of the group mean values of  $a_n$  (or  $b_n$ ) was also taken, the signs being reversed where this had been done for the calculated (negative) values. A simple division then gave the required coefficient  $A_m^n$ ,  $B_m^n$ ,  $\mathbf{A}_m^n$ , or  $\mathbf{B}_m^n$ . As regards the weighting, the Northern group means were each given unit weight, and the Southern means each half a unit



of weight. The fifteen Northern observatories were thus given a total weight six, and the three, four, or five Southern observatories (according to the number available in the different cases) received a total weight one or one and a-half.

Where two harmonic functions were involved in the representation of one set of data, as in Tables III. ( $\gamma$ ) and III. ( $\delta$ ), the same general method of weighting and combining the data was used, except that two equations had to be formed, to give the two coefficients. Usually the middle four or five values of  $a_n$  or  $b_n$  were used in one equation, and the remainder in the other.

### § 9. *The Harmonic Representation of the Magnetic Variation Field.*

A potential function which varies with the local time, but is otherwise the same at all stations along any parallel of latitude, can always be expanded in a series of spherical harmonic functions of the form

$$(3) \quad \psi_m^n \equiv \left\{ \left( E_{m(a)}^n \frac{r^m}{R^{m-1}} + I_{m(a)}^n \frac{R^{m+2}}{r^{m+1}} \right) \cos nt + \left( E_{m(b)}^n \frac{r^m}{R^{m-1}} + I_{m(b)}^n \frac{R^{m+2}}{r^{m+1}} \right) \sin nt \right\} Q_m^n(\theta).$$

Here  $E_{m(a)}^n$ ,  $E_{m(b)}^n$ ,  $I_{m(a)}^n$ ,  $I_{m(b)}^n$  are numerical coefficients;  $t$  is the local time reckoned in angle at the rate of 15 degrees per hour ( $t = \lambda + t'$ , where  $\lambda$  is the longitude measured towards the East from some standard meridian, and  $t'$  is the time corresponding to that meridian);  $r$  is the distance from the earth's centre to the point considered, at colatitude  $\theta$  (in this paper measured from the North pole as origin), and  $R$  is the earth's mean radius. The function  $Q_m^n(\theta)$ , or  $Q_m^n$  as it will generally be written, is the ordinary tesseral harmonic of degree  $m$  and order  $n$ ; it can readily be calculated from the formula

$$(4) \quad Q_m^n = \frac{(2m)!}{2^m \cdot m! (m-n)!} \sin^n \theta \left\{ \cos^{m-n} \theta - \frac{(m-n)_2}{2^2 \cdot 1! (m-\frac{1}{2})_1} \cos^{m-n-2} \theta \right. \\ \left. + \frac{(m-n)_4}{2^4 \cdot 2! (m-\frac{1}{2})_2} \cos^{m-n-4} \theta - \dots \right\},$$

in which the factors of the form  $p_s$ , where  $s$  is a positive integer, denote

$$p(p-1)(p-2) \dots (p-s+1).$$

The part of (3) which depends on  $r^m$  is continuous and satisfies LAPLACE'S equation within the sphere  $r = R$ . In the case of the magnetic variation potential, consequently, it arises from an electric current system outside the earth. The remaining portion of (3), which depends on  $r^{-m-1}$ , similarly results from a current system within the earth. The letters E and I are chosen to indicate the respectively external and internal origins of the corresponding parts of the potential.

A term  $\psi_m^n$  in the magnetic variation potential would lead to the following

terms in the North, West, and vertical force variations at the surface of the earth ( $r = R$ ):—

$$(5) \quad \frac{d\psi_m^n}{R d\theta} = \{(\mathbf{E}_{m(a)}^n + \mathbf{I}_{m(a)}^n) \cos nt + (\mathbf{E}_{m(b)}^n + \mathbf{I}_{m(b)}^n) \sin nt\} \frac{dQ_m^n}{d\theta} \quad (\text{North}),$$

$$(6) \quad \frac{1}{R \sin \theta} \frac{d\psi_m^n}{d\lambda} = \{-(\mathbf{E}_{m(a)}^n + \mathbf{I}_{m(a)}^n) \sin nt + (\mathbf{E}_{m(b)}^n + \mathbf{I}_{m(b)}^n) \cos nt\} \frac{n}{\sin \theta} Q_m^n \quad (\text{West}),$$

$$(7) \quad -\frac{d\psi_m^n}{dr} = -\{(m\mathbf{E}_{m(a)}^n - \overline{m+1}\mathbf{I}_{m(a)}^n) \cos nt + (m\mathbf{E}_{m(b)}^n - \overline{m+1}\mathbf{I}_{m(b)}^n) \sin nt\} Q_m^n \quad (\text{Radial, outwards}).$$

These may be written in the form

$$(8) \quad (\mathbf{A}_m^n \cos nt + \mathbf{B}_m^n \sin nt) \mathbf{N}_m^n(\theta) \quad (\text{North}),$$

$$(9) \quad (\mathbf{B}_m^n \cos nt - \mathbf{A}_m^n \sin nt) \mathbf{W}_m^n(\theta) \quad (\text{West}),$$

$$(10) \quad -(\mathbf{A}_m^n \cos nt + \mathbf{B}_m^n \sin nt) Q_m^n(\theta) \quad (\text{Radial, outwards}),$$

the new notation being thus defined:—

$$(11) \quad \mathbf{A}_m^n \equiv \mathbf{E}_{m(a)}^n + \mathbf{I}_{m(a)}^n, \quad \mathbf{B}_m^n \equiv \mathbf{E}_{m(b)}^n + \mathbf{I}_{m(b)}^n,$$

$$(12) \quad \mathbf{A}_m^n \equiv m\mathbf{E}_{m(a)}^n - (m+1)\mathbf{I}_{m(a)}^n, \quad \mathbf{B}_m^n \equiv m\mathbf{E}_{m(b)}^n - (m+1)\mathbf{I}_{m(b)}^n.$$

The new symbols  $\mathbf{N}_m^n(\theta)$  and  $\mathbf{W}_m^n(\theta)$  are defined as follows:—

$$(13) \quad \mathbf{N}_m^n(\theta) = \frac{dQ_m^n}{d\theta}, \quad \mathbf{W}_m^n(\theta) = \frac{n}{\sin \theta} Q_m^n.$$

Table B contains a list of the particular values of the three functions  $Q_m^n$ ,  $\mathbf{N}_m^n$  and  $\mathbf{W}_m^n$  corresponding to the special values of  $m$  and  $n$  with which we are

TABLE B.

$Q_m^n(\cos \theta).$	$\mathbf{N}_m^n = \frac{d}{d\theta} Q_m^n.$	$\mathbf{W}_m^n = \frac{n}{\sin \theta} Q_m^n.$
$Q_1^0 = \cos \theta$	$\mathbf{N}_1^0 = -\sin \theta$	$\mathbf{W}_1^0 = 0$
$Q_1^1 = \sin \theta$	$\mathbf{N}_1^1 = \cos \theta$	$\mathbf{W}_1^1 = 1$
$Q_2^1 = 3 \sin \theta \cos \theta$	$\mathbf{N}_2^1 = 3(2 \cos^2 \theta - 1)$	$\mathbf{W}_2^1 = 3 \cos \theta$
$Q_3^1 = \frac{3}{2} \sin \theta (5 \cos^2 \theta - 1)$	$\mathbf{N}_3^1 = \frac{3}{2} \cos \theta (15 \cos^2 \theta - 11)$	$\mathbf{W}_3^1 = \frac{3}{2} (5 \cos^2 \theta - 1)$
$Q_2^2 = \frac{3}{2} \sin^2 \theta$	$\mathbf{N}_2^2 = 6 \sin \theta \cos \theta$	$\mathbf{W}_2^2 = 6 \sin \theta$
$Q_3^2 = 15 \sin^2 \theta \cos \theta$	$\mathbf{N}_3^2 = 15 \sin \theta (3 \cos^2 \theta - 1)$	$\mathbf{W}_3^2 = 30 \sin \theta \cos \theta$
$Q_4^2 = \frac{15}{2} \sin^2 \theta (7 \cos^2 \theta - 1)$	$\mathbf{N}_4^2 = 30 \sin \theta \cos \theta (7 \cos^2 \theta - 4)$	$\mathbf{W}_4^2 = 15 \sin \theta (7 \cos^2 \theta - 1)$
$Q_3^3 = 15 \sin^3 \theta$	$\mathbf{N}_3^3 = 45 \sin^2 \theta \cos \theta$	$\mathbf{W}_3^3 = 45 \sin^2 \theta$
$Q_4^3 = 105 \sin^3 \theta \cos \theta$	$\mathbf{N}_4^3 = 105 \sin^2 \theta (4 \cos^2 \theta - 1)$	$\mathbf{W}_4^3 = 315 \sin^2 \theta \cos \theta$
$Q_5^3 = \frac{105}{2} \sin^3 \theta (9 \cos^2 \theta - 1)$	$\mathbf{N}_5^3 = \frac{315}{2} \sin^2 \theta \cos \theta (15 \cos^2 \theta - 7)$	$\mathbf{W}_5^3 = \frac{315}{2} \sin^2 \theta (9 \cos^2 \theta - 1)$
$Q_4^4 = 105 \sin^4 \theta$	$\mathbf{N}_4^4 = 420 \sin^3 \theta \cos \theta$	$\mathbf{W}_4^4 = 420 \sin^3 \theta$
$Q_5^4 = 945 \sin^4 \theta \cos \theta$	$\mathbf{N}_5^4 = 945 \sin^3 \theta (5 \cos^2 \theta - 1)$	$\mathbf{W}_5^4 = 3780 \sin^3 \theta \cos \theta$
$Q_6^4 = \frac{945}{2} \sin^4 \theta (11 \cos^2 \theta - 1)$	$\mathbf{N}_6^4 = 945 \sin^3 \theta \cos \theta (33 \cos^2 \theta - 13)$	$\mathbf{W}_6^4 = 1890 \sin^3 \theta (11 \cos^2 \theta - 1)$

concerned in this paper. These functions were numerically evaluated for each of the twenty-one values of  $\theta$  in Table A, and the group means I. to IX. were formed; by means of these the coefficients  $A_m^n$  and  $B_m^n$ ,  $\mathbf{A}_m^n$  and  $\mathbf{B}_m^n$  were determined as described in § 8, the West and vertical force Fourier coefficients being compared with the formulæ (9) and (10). The North force values of  $a_n$  and  $b_n$  were then calculated from  $A_m^n$  and  $B_m^n$  by means of (8). The observed and calculated values of  $a_n$  and  $b_n$  for the various components and seasons are tabulated in Tables III. ( $\alpha$ ) to ( $\delta$ ), and the values of  $A_m^n$ , &c., are given below in Table C.

It is clear from the Tables III. that the above harmonic analysis, although of a very simple character, gives a fair representation of the main features of the daily magnetic variation, except for the 24-hour component of the North force variation; for the other periodic terms of the latter variation the agreement with the potential calculated from the West force is better—perhaps even satisfactory, when the irregular “run” of the North force is considered.

#### § 10. *Comparison with Previous Harmonic Analyses of the Solar Diurnal Magnetic Variation.*

It is of interest to examine how far the various studies of the solar diurnal magnetic variation, which have been made by different methods and with different data, agree in their main results. The principal terms in SCHUSTER'S, FRITSCHÉ'S (1913), and the present analyses, so far as they are comparable with one another, are collected in Tables D and E. In the former table the potential functions derived from the North and West force variations (or, in the present paper, from the West force variations only) are given. Instead of  $A_m^n$  and  $B_m^n$ , however, the amplitude  $C_m^n$  and phase  $\alpha_m^n$  are given, where

$$(14) \quad A_m^n \cos nt + B_m^n \sin nt = -C_m^n \cos (nt + \alpha_m^n).$$

All the results have been modified where necessary, to conform to the notation of this paper. In some cases the authors cited carried their analysis further than in the present instance, in others, as the table indicates, they stopped short of it; but the principal terms were in all cases the same.

In Tables D and E, the figures for the present paper, under the heading “annual terms,” are obtained from the mean of the solstitial and equinoctial results in Table B. They therefore represent the mean for a whole year, as in the case of SCHUSTER'S and FRITSCHÉ'S results. The seasonal terms in the present analysis, on the contrary, refer to a half-year only, *i.e.*, the two quarters centred at the solstices. They may be expected to be of somewhat larger amplitude than if they had been derived from the two half-years, as in the previous discussions.

TABLE C.—The Spherical Harmonic Representation of the Solar Diurnal Variations of West and Vertical Magnetic Force.

Values of  $A_m^n$ ,  $B_m^n$ ,  $A_m^n$ ,  $B_m^n$ .The Unit of Force is  $10^{-6}$  C.G.S.

n.	m.	Sunspot maximum, 1905.				Sunspot minimum, 1902.			
		West.		Vertical.		West.		Vertical.	
		$A_m^n$ .	$B_m^n$ .	$A_m^n$ .	$B_m^n$ .	$A_m^n$ .	$B_m^n$ .	$A_m^n$ .	$B_m^n$ .
Mean Equinox, $\frac{1}{2}$ (Spring + Autumn).									
1	2	-54	26	-41	14	-34	25	-34	4
2	3	-7.2	3.7	-8.5	0.1	-5.1	3.6	-5.4	0.3
3	4	-0.45	0.40	-0.87	0.29	-0.31	0.37	-0.71	0.30
4	5	-0.0123	0.0203	-0.040	0.022	-0.0082	0.0156	-0.037	0.027
Mean Solstice, $\frac{1}{2}$ (Summer + Winter).									
1	2	-52	22	-37	12	-31	22	-31	7
2	3	-6.4	3.1	-7.3	-0.5	-4.6	2.9	-5.6	0.6
3	4	-0.34	0.29	-0.71	0.30	-0.24	0.24	-0.46	0.23
4	5	-0.0086	0.0091	-0.020	0.010	-0.0039	0.0068	-0.015	0.013
Solstitial Inequality, $\frac{1}{2}$ (Summer - Winter).									
1	1	-42	21	-4	-1	-40	17	-10	0
	3	-10.6	-4.5	-14.0	-2.5	-8.1	-2.3	-7.7	-3.5
2	2	-3.9	7.8	-1.5	2.6	-2.7	5.3	-3.4	2.5
	4	-0.60	0.35	-1.41	-0.37	-0.78	0.37	-0.85	-0.40
3	3	0.17	0.70	-0.038	0.070	0.01	0.63	-0.056	0.046
	5	0.036	-0.011	-0.030	-0.072	0.016	-0.006	-0.024	-0.051
4	4	0.048	-0.007	0.048	0.035	0.028	-0.010	0.030	0.040
	6	0.0045	-0.0099	-0.013	-0.040	0.0020	-0.0101	-0.013	-0.053
Mean of 1902 and 1905.									
Solstitial inequality.					Equinoctial inequality.				
1	1	-41	19	-7	0	13	-13	0.61	-0.42
	3	-9.4	-3.4	-10.8	-3.0	-0.60	1.64	-0.99	1.49
2	2	-3.3	6.6	-2.4	2.6	0.2	-5.5	1.5	-3.2
	4	-0.69	0.36	-1.13	-0.38	-0.047	-0.104	-0.19	0.43
3	3	0.09	0.66	-0.047	0.058	-0.29	-0.60	0.00	-0.58
	5	0.026	-0.008	-0.027	-0.062	-0.0024	0.0039	-0.017	0.010
4	4	0.038	-0.009	0.039	0.038	-0.037	-0.013	-0.014	-0.037
	6	0.0032	-0.0100	-0.013	-0.046	0.0038	-0.0032	-0.013	0.009

TABLE D.—Comparison of the Potential Functions determined by SCHUSTER and FRITSCHÉ from North and West Force Data, with those here determined from West Force Data alone.

Annual terms.					Seasonal terms.				
Ampli- tude. — Phase.	Present paper.		SCHUSTER, 1870.	FRITSCHÉ.	Ampli- tude. — Phase.	Present paper.		SCHUSTER, 1870.	FRITSCHÉ.
	1902.	1905.				1902.	1905.		
$C_2^1$ $\alpha_2^1$	40 35°	58 24°	89 24°	59 30°	$C_1^1$ $\alpha_1^1$	43 23°	47 27°	54 27°	59 28°
$C_3^2$ $\alpha_3^2$	5·8 35°	7·6 27°	9·2 31°	6·2 25°	$C_3^1$ $\alpha_3^1$	8·4 344°	11·5 337°	10·1 311°	6·2 347°
$C_4^3$ $\alpha_4^3$	0·41 47°	0·53 40°	0·63 67°	0·42 35°	$C_2^2$ $\alpha_2^2$	6·0 63°	8·7 63°	11·2 75°	8·4 62°
$C_5^4$ $\alpha_5^4$	0·0127 62°	0·0180 55°	0·0202 78°	— —	$C_4^2$ $\alpha_4^2$	0·86 25°	0·69 30°	0·66 -18°	0·73 6°
					$C_3^3$ $\alpha_3^3$	0·63 91°	0·72 104°	— —	0·76 88°
					$C_4^4$ $\alpha_4^4$	0·030 200°	0·49 188°	— —	0·33 173°

The horizontal force harmonics in Table D show a considerable degree of agreement in regard to phase, especially for the main terms  $Q_2^1$ ,  $Q_3^2$ ,  $Q_1^1$ , and  $Q_2^2$ . The amplitudes obtained by SCHUSTER generally exceed those of FRITSCHÉ and the present paper, including those for the maximum sunspot year 1905. The year 1870 was, however, one of abnormally great solar and magnetic activity. Detailed numerical agreement between the various sets of results is not to be looked for, owing to this and other reasons, and it is satisfactory that the different determinations yield values of amplitudes and phases which show such general agreement.

The papers by WALKER and VAN BEMMELEN referred to in §§ 4, 5 contained the following results, which may be compared with the above :—

WALKER.	Annual terms.	$C_2^1 = 55$	$\alpha_2^1 = 25^\circ$
	„ „	$C_3^2 = 4\cdot3$	$\alpha_3^2 = 23^\circ$
VAN BEMMELEN.	„ „	$C_3^2 = 4\cdot3$	$\alpha_3^2 = 26^\circ$

In Table E the coefficients  $A_m^n$ ,  $B_m^n$  obtained by FRITSCHÉ are compared with those of the present paper. The agreement for these vertical force results is much less good than for the horizontal force results in Table D. The reason for this is discussed in § 3 (*cf.* also § 5). The other authors quoted have not analysed the vertical force

potential in a way which allows of a comparison with FRITSCHÉ's and the present results.

TABLE E.—Comparison of the Potential Functions determined by FRITSCHÉ and in this Paper, from Vertical Force Data.

	Annual terms.			Seasonal terms.			
	Present paper.		FRITSCHÉ.	Present paper.			FRITSCHÉ.
	1902.	1905.		1902.	1905.		
$A_2^1$	-32	-39	-25	$A_1^1$	-10	-4	-25
$B_2^1$	6	13	31	$B_1^1$	0	-1	-16
$A_3^2$	-5.5	-7.9	-3.4	$A_3^1$	-7.7	-14.0	-12.4
$B_3^2$	0.5	-0.2	3.3	$B_3^1$	-3.5	-2.5	0.0
$A_4^3$	-0.58	-0.79	-0.66	$A_2^2$	-3.4	-1.5	-3.9
$B_4^3$	0.26	0.30	0.30	$B_2^2$	2.5	2.6	5.6
				$A_4^2$	-0.8	-1.4	0.1
				$B_4^2$	-0.4	-0.4	-1.4

§ 11. *The Separation of the External and Internal Solar Diurnal Variation Fields.*

The equations (11) and (12) indicate how we may determine the respectively internal and external parts of the magnetic variation fields by means of the horizontal and vertical force potential coefficients  $A_m^n$ ,  $B_m^n$ ,  $\mathbf{A}_m^n$ ,  $\mathbf{B}_m^n$ . Thus we have

$$(15) \quad E_{m(a)}^n = \frac{(m+1)A_m^n + \mathbf{A}_m^n}{2m+1}, \quad E_{m(b)}^n = \frac{(m+1)B_m^n + \mathbf{B}_m^n}{2m+1},$$

$$(16) \quad I_{m(a)}^n = \frac{mA_m^n - \mathbf{A}_m^n}{2m+1}, \quad I_{m(b)}^n = \frac{mB_m^n - \mathbf{B}_m^n}{2m+1}.$$

At the earth's surface ( $r = R$ ) the value of the term  $\psi_m^n/R$  in the magnetic variation potential is (*cf.* (3))

$$(17) \quad \begin{aligned} \psi_m^n/R &= \{(E_{m(a)}^n + I_{m(a)}^n) \cos nt + (E_{m(b)}^n + I_{m(b)}^n) \sin nt\} Q_m^n \\ &= -\{\mathbf{E}_m^n \cos(nt + \mathbf{e}_m^n) + \mathbf{I}_m^n \cos(nt + \mathbf{i}_m^n)\} Q_m^n, \end{aligned}$$

where in the last two lines the external and internal parts have been transformed in terms of their amplitudes and phases; these are connected with  $E_{m(a)}^n$ , &c., by the equations

$$(18) \quad E_{m(a)}^n = -\mathbf{E}_m^n \cos \mathbf{e}_m^n, \quad E_{m(b)}^n = \mathbf{E}_m^n \sin \mathbf{e}_m^n,$$

$$(19) \quad I_{m(a)}^n = -\mathbf{I}_m^n \cos \mathbf{i}_m^n, \quad I_{m(b)}^n = \mathbf{I}_m^n \sin \mathbf{i}_m^n.$$

The values of  $E_m^n$ ,  $e_m^n$ ,  $I_m^n$ ,  $i_m^n$ , deduced from Table C by means of equations (15), (16), (18), (19), are given in Table F. For the solstitial as well as for the equinoctial inequality only the mean results for 1902 and 1905 are given.

TABLE F.—Amplitudes and Phases of the Spherical Harmonic Coefficients of the External and Internal Solar Diurnal Magnetic Variation Fields.

The unit is  $10^{-6}$  C.G.S.

n.	m.	Sunspot maximum, 1905.				Sunspot minimum, 1902.			
		External.		Internal.		External.		Internal.	
		$E_m^n$ .	$e_m^n$ .	$I_m^n$ .	$i_m^n$ .	$E_m^n$ .	$e_m^n$ .	$I_m^n$ .	$i_m^n$ .
Mean Equinox, $\frac{1}{2}$ (Spring + Autumn).									
1	2	44.6	24	15.4	29	31.5	30	11.5	53
2	3	5.7	22	2.5	40	4.3	30	2.1	47
3	4	0.43	35	0.18	56	0.35	44	0.14	65
4	5	0.0167	52	0.0075	75	0.0135	55	0.0046	85
Mean Solstice, $\frac{1}{2}$ (Summer + Winter).									
1	2	41.2	22	14.8	25	28.8	30	9.7	50
2	3	5.0	20	2.2	39	3.8	27	1.7	45
3	4	0.33	35	0.12	55	0.24	42	0.10	53
4	5	0.0088	42	0.0038	57	0.0060	54	0.0019	78
Mean of 1902 and 1905.									
Solstitial inequality, $\frac{1}{2}$ (Summer - Winter).					Equinoctial inequality, $\frac{1}{2}$ (Spring - Autumn).				
1	1	32	23	13	30	12.5	225	5.9	226
2	2	5.1	61	2.2	69	3.9	264	1.5	262
3	3	0.46	87	0.23	119	0.46	292	0.21	305
4	4	0.025	182	0.015	212	0.025	333	0.015	352
1	3	7.3	341	2.7	338	1.52	72	0.50	76
2	4	0.53	17	0.27	48	0.048	348	0.094	270
3	5	0.016	220	0.014	178	0.0042	46	0.0010	61
4	6	0.009	264	0.003	199	0.0014	225	0.0039	213

As regards the reliability of the results in Table F, this is, of course, greater for the annual (*i.e.*, mean equinoctial and mean solstitial) terms than for the seasonal terms (solstitial and equinoctial inequalities). In the latter case the harmonics  $Q_m^n$ , where  $m = n$ , are fairly well determined, but the higher harmonics  $m = n+2$  are much less certainly evaluated. Among the components of different periods the semi-diurnal one is probably most free from accidental error, but the agreements in phase and amplitude for the other periods in the various parallel cases seem to indicate that the harmonics  $Q_{n+1}^n$  and  $Q_n^n$  for all four periodic terms have definite terrestrial significance. It should be remembered that  $Q_m^n$  contains a numerical factor which increases rapidly with  $m$  (*cf.* Table B), so that the small amplitudes  $E_m^n$ ,  $I_m^n$  for the higher harmonics represent magnetic variations much less small, in proportion to the diurnal and semi-diurnal terms, than their numerical values suggest at first sight.

This completes the actual analysis of the solar diurnal magnetic variation field, although the original data, and the residuals between these and the values of  $a_n$  and  $b_n$  calculated from the analytical representation, will be discussed later in connection with the possible existence of a portion varying with the longitude. Before discussing the relation between the external and internal variation fields already determined, a similar analysis of the lunar diurnal magnetic variation will be described in order that the results of the two analyses may be considered together.

### PART III.—A NEW ANALYSIS OF THE LUNAR DIURNAL MAGNETIC VARIATION.

#### § 12. *Description of the Data and of the Method of Analysis.*

The data used in this analysis consist of the  $a_n$ ,  $b_n$  Fourier coefficients in the analysis of the lunar diurnal magnetic variation according to the formula (1). But the time  $t$  in (1) is now local mean lunar time, reckoned at the rate of 15 degrees per mean lunar hour, which is approximately  $\frac{29}{28}$  times as long as a mean solar hour. The time of origin is the local time of upper culmination of the moon, at the epoch of new moon. The conventions as regards the signs of the three geographical components of force are the same as in § 7. The unit of force in which the Fourier coefficients are expressed is  $10^{-7}$  C.G.S., or  $0.01\gamma$ , only one-tenth as large as the unit used in Part II.

The lunar diurnal magnetic variation is of very small amount, and it can be computed with any approach to accuracy only by the use of a long series of observations, so as to eliminate accidental errors arising from fortuitous disturbances of much larger magnitude than the variation itself. In the present case seven years' observations at each observatory have been used, and the years chosen were "quiet" as regards solar and magnetic activity. Except in the case of Batavia, the same seven years (1897 to 1903) were used for each station. Owing to the reorganization of the Batavian observatory during this period the years 1899 to 1901 had in this instance to be replaced by the correspondingly quiet years 1888 to 1890 of a previous



solar cycle. A longer period than seven years would, of course, have been advantageous, but the labour of computation was already great.

The method of computation adopted, and in particular the method of calculation of the non-semi-diurnal harmonic components, of changing phase, has been described in an earlier paper, and a reference to this must suffice here.\* In that paper are given the data, so obtained, from observations made at Pavlovsk and Pola. These are two of the five observatories chosen for consideration in this research; the other three are Zi-Ka-Wei, Manila and Batavia. The results obtained for the three latter have not hitherto been published; they are to be found in Tables IV. and V. The first of these contains the Fourier coefficients corresponding to the different phases of the moon, reduced to the epoch of new moon; these data are subject to certain corrections to amplitude and phase (*cf.* § 6 of the paper cited) which for convenience have been applied only to the mean results. The latter, transformed in terms of the geographical components of force, are given in Table V. The results for all the five observatories are collected in Tables VI. (*a*) to (*d*).

The method of treating the seasonal changes is slightly different from that adopted for the solar diurnal variations. Instead of dividing the year into four quarters it was divided into three equal parts, November to February representing the winter solstice, May to August the summer solstice, and the intervening four months the equinoxes. It would have been better, for purpose of comparison, if this method of sub-division had been adopted also for the solar diurnal variations; and, as Dr. CHREE points out, this sub-division of the year corresponds more closely than the one adopted with the actual seasonal changes in the solar diurnal variation.

As regards the solstitial data, since the semi-sum and semi-difference form the basis of analysis (*cf.* Tables VI. (*c*) and (*d*), corresponding to the solar diurnal Tables II. ( $\beta$ ) and ( $\gamma$ )), the mean solstitial and the seasonal harmonics of Table G result from eight months' material, while the equinoctial material is based on only four months of the year. Less weight must accordingly be attached to the latter than to the former. It may also be remarked that the mean solstitial and equinoctial epochs are slightly different for the two sub-divisions of the year, and that therefore some allowance must be made for this when comparing the solar and diurnal results.

The analysis of the "observed" data of Tables IV. (*a*) to (*d*) is similar to that explained in § 8; owing to the small number of observatories dealt with, however, no

\* 'Phil. Trans.,' A, 214, p. 295, 1914; *cf.* also A, 213, p. 279, 1913. It should be noted that in § 6 of the former paper a phase correction is given with the wrong sign, viz.,  $-2L/29$  degrees instead of (as it should be)  $+2L/29$  degrees. In applying the correction it is to be understood that the time of lunar transit at Greenwich has been used as the local time of lunar transit on the *same civil day* at the other stations, otherwise 360 degrees would have to be added to or subtracted from L degrees. The phase angles given in Table VI. (*a*), p. 316 of the former paper, need to be diminished by 4.2 degrees (Pavlovsk) and 2.0 degrees (Pola) on the above account.

grouping was possible, so that the five observatories were each treated as were the groups in the former analysis. Equal weight was accorded to each of the five observatories.

Another divergence from the course described in Part II. was that the equinoctial inequality was not considered (with the adopted sub-division of the data, this was not possible). Also the harmonics  $Q_{n+2}^n$  in the solstitial inequality were left out of consideration, since the functions  $Q_n^n$ , as with the solar diurnal variations, represented the greater part of the seasonal change, and the data hardly sufficed to determine the small coefficients of the remaining harmonics  $Q_{n+2}^n$ .

§ 13. *Results of the Analysis of the Lunar Diurnal Magnetic Variation.*

The results of the harmonic analysis of the data in Tables VI. are collected in Table G, which includes also the values of the separated internal and external parts

TABLE G.—The Spherical Harmonic Representation of the Lunar Diurnal Variations of West and Vertical Magnetic Force, and of the Separated External and Internal Fields.

The Unit is  $10^{-7}$  C.G.S.

$n.$	$m.$	West.		Vertical.		External $E_m^n$ .		Internal $I_m^n$ .	
		$A_m^n$ .	$B_m^n$ .	$A_m^n$ .	$B_m^n$ .	(a.)	(b.)	(a.)	(b.)
Mean Solstice, $\frac{1}{2}$ (Summer + Winter).									
1	2	8.8	28.5	- 5.0	23.3	4.3	21.8	4.5	6.7
2	3	0.4	7.4	- 6.0	4.6	- 0.6	4.9	1.0	2.5
3	4	0.16	0.42	0.00	0.79	0.09	0.32	0.07	0.10
4	5	0.0106	0.0106	0.005	0.048	0.0063	0.0102	0.0044	0.0005
Equinox, Spring and Autumn.									
1	2	0.4	30.6	- 17.5	9.4	- 3.3	20.2	3.7	10.4
2	3	- 0.7	9.0	- 8.2	1.5	- 1.6	5.3	0.9	3.6
3	4	- 0.03	0.59	- 0.31	0.89	- 0.05	0.43	0.02	0.16
4	5	0.009	0.032	- 0.009	0.051	0.004	0.022	0.005	0.010
Solstitial Inequality, $\frac{1}{2}$ (Summer - Winter).									
1	1	- 9	57	- 21.4	5.5	- 13.1	39.8	4.1	17.2
2	2	- 3.3	22.2	- 6.1	5.5	- 3.2	14.4	- 0.1	7.8
3	3	0.23	1.68	- 0.42	1.02	0.07	1.11	0.16	0.57
4	4	0.009	0.022	0.010	0.039	0.006	0.016	0.003	0.0054

of the field. The notation is the same as that explained in §§ 9 and 11, only the seasonal divisions and the unit of force (here  $0.01\gamma$  in place of  $0.1\gamma$ ) being different. In Tables VI. (b) to (d) the calculated values of  $a_n$  and  $b_n$ , corresponding to these harmonic functions, are placed for comparison beside the values computed from the observational data.

The agreement between observation and calculation is naturally less good than for the solar diurnal variation, both because the accidental error in the data is greater in the present case (the whole effect being smaller) and because single observatories are here used in place of groups of observatories, so that the local irregularities are larger. The agreement is better, on the whole, in Tables VI. (c), (d) than in Table VI. (b), which rests on only half as much observational material as the two former; it is also better for the West than for the North component of force, as in Part II. The agreement is surprisingly good in Table VI. (d) for the horizontal force components. The vertical force variations are smaller than the horizontal force variations, and some of the values of  $\mathbf{A}_m^n$  and  $\mathbf{B}_m^n$ , determined from the former, are very uncertain. On the whole, however, while the present data might be very considerably improved upon, the results prove more satisfactory than I had expected, at any rate for the horizontal force potential  $\mathbf{A}_m^n$  and  $\mathbf{B}_m^n$ . In judging the success of the analysis, regard may be had to the agreement of phase between the harmonic components of different periods and the reproduction of other features of the analysis of the solar diurnal magnetic variation, which show the close parallelism of the two phenomena. Although some of the tables of observed and calculated data in Table VI. do not seem to show much correspondence between the two, the results in Table G suggest that the assumptions underlying the analysis (*i.e.*, that the variations can be represented by the functions  $Q_{n+1}^n$  or  $Q_n^n$ ) are sound, and that the discordances from the results of calculation arise from a relatively large amount of accidental error in the observational data.

The use of so small a number of observations is, of course, a fit ground for criticism, and calls for a repetition of this part of the investigation on a larger scale. The present is to be considered as merely a pioneer attempt. For this reason the analysis has been narrowly restricted, and the results must be discussed with due recognition that the percentage error is not small.

#### § 14. Comparison with VAN BEMMELEN'S Data.

As bearing upon the question of the accidental error of the initial data of Tables VI. (a) to (d), it is interesting to compare the present values of  $a_2$ ,  $b_2$ , with those calculated by VAN BEMMELEN for the same observatories (only the  $a_2$ ,  $b_2$  coefficients are given by the latter author). It should be borne in mind, however, that neither the epoch, the amount of observational material dealt with, nor the method of computation, was the same in the two cases. Dr. VAN BEMMELEN divided

the year, for the purposes of his paper, into summer and winter halves, and in comparing with his results the summer and winter data of this paper, allowance has been made for this by incorporating with them the equinoctial results, with half weight. Table H contains all the material for comparison, and will sufficiently indicate the probable accuracy of our present knowledge of the lunar diurnal magnetic variation.

TABLE H (*a*).—Comparison of the Lunar Semi-diurnal Magnetic Variations at Five Observatories, as determined by VAN BEMMELLEN (1) and in this Paper (2).

The Unit is  $10^{-7}$  C.G.S.

Observatory.	West.				North.				Radial.			
	$a_2$ .		$b_2$ .		$a_2$ .		$b_2$ .		$a_2$ .		$b_2$ .	
	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.
Summer.												
Pavlovsk . . . .	110	112	- 18	5	56	5	58	86	- 19	- 2	- 9	- 3
Pola . . . . .	137	122	- 9	33	85	51	117	103	16	34	- 55	- 34
Zi-Ka-Wei . . .	191	210	- 68	23	30	9	9	6	111	112	- 18	27
Manila . . . . .	119	132	- 47	- 21	- 10	- 22	- 29	- 60	- 8	20	- 78	- 86
Batavia . . . . .	14	- 5	- 3	- 13	- 27	- 40	- 43	- 70	- 3	- 4	- 38	- 34
Winter.												
Pavlovsk . . . .	- 5	8	14	18	- 35	- 12	- 28	11	- 1	3	- 15	1
Pola . . . . .	10	- 2	27	33	19	28	0	11	23	23	- 19	- 19
Zi-Ka-Wei . . .	35	64	- 56	- 40	73	65	- 33	- 50	89	88	0	38
Manila . . . . .	- 34	- 6	- 72	- 80	- 48	- 27	- 102	- 112	- 54	- 29	- 62	- 87
Batavia . . . . .	- 178	- 195	- 4	- 11	- 49	- 66	- 60	- 99	- 3	- 10	13	10
Year.												
Pavlovsk . . . .	53	60	- 2	12	11	- 3	15	48	- 10	0	- 12	- 1
Pola . . . . .	74	60	9	33	52	40	59	57	20	28	- 37	- 26
Zi-Ka-Wei . . .	113	137	- 62	- 8	52	37	- 12	- 22	100	100	- 9	32
Manila . . . . .	43	63	- 60	- 50	- 29	- 25	- 66	- 86	- 31	- 5	- 70	- 86
Batavia . . . . .	- 82	- 100	- 4	- 12	- 38	- 53	- 52	- 85	- 3	- 7	- 13	- 12

TABLE H (b).—Comparison of the Lunar Semi-diurnal Magnetic Variations at Five Observatories, as determined by VAN BEMMELEN (1) and in this Paper (2).

The Unit is  $10^{-7}$  C.G.S.

Observatory.	West.				North.				Radial.			
	$c_2$ .		$\theta_2$ .		$c_2$ .		$\theta_2$ .		$c_2$ .		$\theta_2$ .	
	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.
Summer.												
Pavlovsk . . .	111	112	99	87	82	86	44	3	21	4	245	214
Pola. . . . .	137	126	94	75	145	115	36	26	57	48	164	135
Zi-Ka-Wei . .	203	211	110	84	31	11	73	56	112	115	99	76
Manila . . . .	128	134	112	99	31	64	199	200	79	88	186	167
Batavia . . . .	14	14	102	201	51	81	212	210	38	34	185	187
Winter.												
Pavlovsk . . .	15	20	340	24	45	16	219	133	15	3	184	—
Pola. . . . .	29	33	20	357	19	30	90	68	30	30	129	129
Zi-Ka-Wei . .	66	75	148	122	80	82	114	128	89	96	90	67
Manila . . . .	80	80	205	184	113	115	205	247	82	92	221	198
Batavia . . . .	178	195	269	267	77	119	219	214	13	14	347	315
Year.												
Pavlovsk . . .	53	61	92	79	18	48	35	356	16	1	220	—
Pola. . . . .	75	68	83	61	79	70	41	35	42	38	152	133
Zi-Ka-Wei . .	129	137	119	93	53	43	103	121	101	105	95	72
Manila . . . .	74	80	144	128	72	90	204	196	77	86	204	183
Batavia . . . .	82	101	267	263	64	100	216	212	13	14	193	210

The comparison may be completed by giving the results of VAN BEMMELEN'S harmonic analysis of the semi-diurnal part of the variation, so far as they are comparable with our present result. Only the annual mean values of  $E_3^2(a)$ ,  $E_3^2(b)$ ,  $I_3^2(a)$ ,  $I_3^2(b)$  can be compared in this way. They are as follows :—

	$E_3^2(a)$ .	$E_3^2(b)$ .	$I_3^2(a)$ .	$I_3^2(b)$ .
VAN BEMMELEN . . . . .	1.2	4.2	0.1	3.5
Present paper . . . . .	0.3	4.9	1.7	2.8

The values in the last line are formed from those given in Table G for the mean solstice (weight 2) and equinoxes (weight 1). The order of magnitude of the above

two sets of determinations is the same, and although there are phase differences the amplitudes are closely similar.

We now pass on to consider the connection between the external and internal fields determined from the solar and lunar diurnal variations, the material being the results contained in Tables F and G.

PART IV.—THE CONNECTION BETWEEN THE EXTERNAL AND INTERNAL MAGNETIC VARIATION FIELDS.

§ 15. *The Observed Values of the Amplitude Ratios and Phase Differences.*

In the present section the subject of discussion will be the relation between the external and internal magnetic variation fields, as measured by the amplitude ratio  $\mathbf{E}_m^n/\mathbf{I}_m^n$  and the phase difference  $\mathbf{e}_m^n - \mathbf{i}_m^n$ . We shall not be concerned, for the time being, with the actual values of  $\mathbf{E}_m^n$  and  $\mathbf{e}_m^n$ . The values of the amplitude ratios and phase differences for the solar diurnal magnetic variation are given in Table I. The values of  $\mathbf{E}_m^n$ ,  $\mathbf{I}_m^n$ ,  $\mathbf{e}_m^n$ ,  $\mathbf{i}_m^n$  and the amplitude ratios and phase differences for the lunar diurnal variation, calculated from Table C, are given in Table J (*cf.* the first six columns).

TABLE I.—Comparison of the External and Internal Solar Diurnal Magnetic Variation Fields.

n.	m.	Sunspot maximum, 1905.				Sunspot minimum, 1902.				Mean.	
		Mean equinox.		Mean solstice.		Mean equinox.		Mean solstice.			
		$\mathbf{E}_m^n/\mathbf{I}_m^n$ .	$\mathbf{e}_m^n - \mathbf{i}_m^n$ .	$\mathbf{E}_m^n/\mathbf{I}_m^n$ .	$\mathbf{e}_m^n - \mathbf{i}_m^n$ .	$\mathbf{E}_m^n/\mathbf{I}_m^n$ .	$\mathbf{e}_m^n - \mathbf{i}_m^n$ .	$\mathbf{E}_m^n/\mathbf{I}_m^n$ .	$\mathbf{e}_m^n - \mathbf{i}_m^n$ .	$\mathbf{E}_m^n/\mathbf{I}_m^n$ .	$\mathbf{e}_m^n - \mathbf{i}_m^n$ .
1	2	2.9	- 5	2.8	- 3	2.7	- 23	3.0	- 20	2.8	- 13
2	3	2.4	- 18	2.3	- 19	2.0	- 17	2.2	- 18	2.2	- 18
3	4	2.4	- 21	2.7	- 20	2.5	- 21	2.4	- 21	2.5	- 21
4	5	2.2	- 23	2.3	- 15	2.9	- 30	3.2	- 24	2.7	- 23
Mean		2.5	- 17	2.5	- 14	2.5	- 23	2.7	- 21	2.55	- 19
Mean of 1902 and 1905.											
		$Q_n^n$ .				$Q_{n+2}^n$ .					
		$\frac{1}{2}$ (Summer - Winter).		$\frac{1}{2}$ (Spring - Autumn).		$\frac{1}{2}$ (Summer - Winter).		$\frac{1}{2}$ (Spring - Winter).			
1	1, 3	2.5	- 7	2.1	- 1	2.7	+ 3	3.0	- 4		
2	2, 4	2.3	- 8	2.6	+ 2	2.0	- 31	0.5	+ 78		
3	3, 5	2.0	- 32	2.2	- 13	1.1	+ 42	4.2	- 15		
4	4, 6	1.7	- 30	1.7	- 19	3.0	+ 65	0.4	+ 12		
Mean		2.1	- 19	2.2	- 8						

TABLE J.—Comparison of the External and Internal Lunar Diurnal Magnetic Variation Fields.

The unit is  $10^{-7}$  C.G.S.

n.	m.	External.		Internal.		$\frac{E_m^n}{I_m^n}$	$e_m^n - i_m^n$	f' calculated.	z calculated.
		$E_m^n$	$e_m^n$	$I_m^n$	$i_m^n$				
Mean Solstice, $\frac{1}{2}$ (Summer + Winter).									
1	2	22.2	101	7.9	124	2.8	-23	2.6	-21
2	3	4.9	83	2.7	112	1.8	-29	2.5	-20
3	4	0.33	106	0.12	125	2.7	-19	2.5	-20
4	5	0.0120	121	0.0044	173	2.7	-52	2.7	-22
Equinox, Spring and Autumn.									
1	2	20.5	81	11.0	110	1.9	-29	2.6	-21
2	3	5.5	73	3.7	104	1.5	-29	2.5	-20
3	4	0.43	83	0.16	97	2.7	-14	2.5	-20
4	5	0.022	100	0.011	117	2.0	-17	2.7	-22
Solstitial Inequality, $\frac{1}{2}$ (Summer - Winter).									
1	1	41.9	72	17.7	103	2.4	-31	2.8	-13
2	2	14.8	77	7.8	83	1.9	-6	2.3	-15
3	3	1.11	94	0.59	106	1.9	-12	2.3	-16
4	4	0.017	110	0.006	93	2.8	+17	2.4	-18

The numbers in Table I, relating to the solar diurnal magnetic variation, are remarkable for the almost unbroken uniformity (neglecting the uncertain values for  $Q_{n+2}^n$ ) with which they indicate that the external magnetic field is about 2.5 times as great—reckoning by the surface values of the potentials—as the internal field, and that the latter is in *advance* of the former, in phase, by about 20 degrees. The differences between the values for the various harmonic terms, of different degrees and periods, are much less noteworthy than the accordance exhibited: the differences, moreover, appear to be in part real (§ 17). If the sixteen values of  $E_m^n/I_m^n$  for the annual harmonics  $Q_{n+1}^n$  are treated as if their differences were altogether accidental, the probable error of the mean, 2.55, is found to be only 0.06. It may also be noticed that the nearly constant value 2.5 corresponds to very different values of  $A_m^n/A_m^n$ ,  $B_m^n/B_m^n$ , for the various values of  $m$ , and that these different ratios are actually observed.

The general result that the external field is about  $2\frac{1}{2}$  times as great as the internal field, at the earth's surface, lies between the conclusions of SCHUSTER ( $E_m^n/I_m^n = 4$ , approximately) and FRITSCHÉ ( $E_m^n/I_m^n = 1.5$ , approximately); VAN BEMMELEN obtained

still lower values, both for the solar and lunar semi-diurnal variations. Hitherto the evidence afforded by the third and fourth harmonics has never been examined. There seems now no reason to doubt that the internal field is merely an induction product of the external field.

If the latter be so, the mechanism by means of which the internal solar variation field is produced must also be that responsible for the internal lunar variation field, and the relation between the external and internal fields will be very similar in the two cases. Table J does, indeed, show results very similar, in general, to those of Table I, especially when the small magnitude and accidental error of the determined lunar variation are considered. The mean amplitude ratio of the external and internal fields in the lunar case is 2·3, while the mean of the phase differences (all of which, save one, have the negative sign) is  $-21$  degrees. The results for the mean of the corresponding solar variation fields are 2·4 and  $-19$  degrees. There seems, therefore, no reason to question the similarity of the two phenomena in this respect, although a more precise discussion of the point, with more adequate data, would be of value.

As might be anticipated, the results of Tables I and J show little dependence on season or on solar activity. The only notable difference between 1902 and 1905 is found in connection with the diurnal "annual" harmonic  $Q_2^1$ , for which the mean phase differences are  $-4$  degrees (1902) and  $-21$  degrees (1905). The solstitial and equinoctial results separately indicate these divergent differences, and thus tend to establish the reality of the divergence. It remains to be seen whether other pairs of years will manifest the same result, but for the present no theoretical explanation of it will be attempted. Only the mean of the two values of  $e_2^1 - i_2^1$  will be used, but the uncertainty of this mean should be kept in mind during the discussion.

#### § 16. *The Hypothesis of a Uniformly Conducting Earth.*

In § 2 a brief account has already been given of the theory proposed by SCHUSTER to explain the results of his separation of the external and internal solar diurnal magnetic variation fields. At that time the problem was to account for the induction of an internal field of one-quarter the magnitude of the primary without the production of a phase difference. It now appears that a phase difference does exist, and it may be expected that the difficulty of explanation will be lessened. The sign of the difference agrees with that predicted by the theory of induction in a uniformly conducting sphere, as Prof. LAMB'S researches\* show (and this was kindly confirmed by him on enquiry). The hypothesis of induction being so far substantiated, it remains to consider the actual numerical relations between the external and internal fields; the theory can be regarded as completely satisfactory only when the same amount and distribution of conducting matter in the earth will suffice in relation to all the harmonics of the many periods and degrees concerned.

\* Cf. the appendix to SCHUSTER'S first memoir, p. 513, and also 'Phil. Trans.,' 1883, p. 526.



The simplest hypothesis, that of a uniformly conducting earth, will first be considered. LAMB'S theory enables the amplitude ratio  $f$ , and phase difference  $\alpha$ , to be calculated for a uniformly conducting sphere of radius  $R$  and specific resistance  $\rho$  for any harmonic term  $Q_m^n$  in the potential of the external primary variation field. Tables giving equivalent results for certain values of  $\rho$  and  $m$  are to be found in SCHUSTER'S paper, but as they are insufficient for the more extensive observational data of Table I further calculations have been made which are summarized in Table K. Where the two sets of values of  $f$  and  $\alpha$  overlap they are in agreement. The Table K gives the values of  $f$  and  $\alpha$  corresponding to the two variables  $m$  and  $\delta$  on which they depend;  $\delta$  is defined by the equation

$$(20) \quad \delta = \frac{1}{N} \frac{8\pi^2 n R^2}{\rho},$$

where  $N$ , the number of seconds in a day (the period corresponding to  $n = 1$ ), is equal to 86,400 in the case of the solar diurnal magnetic variation, and 89,500 (approximately) in the case of the lunar diurnal variations.

On the hypothesis that the whole earth is uniformly conducting, we must take  $R = R$  (§ 9), and  $2\pi R = 4 \cdot 10^9$  cm. Hence for the solar diurnal magnetic variations

$$(21) \quad \delta = \frac{4 \cdot 10^{14} n}{1 \cdot 08 \rho},$$

and for the lunar diurnal variations

$$(22) \quad \delta = \frac{4 \cdot 10^{14} n}{1 \cdot 12 \rho}.$$

TABLE K.—Amplitude Ratios  $f$  and Phase Difference  $\alpha$  between a Primary (External) and Secondary (Internal) Magnetic Field, Induced in a Sphere of Uniform Conductivity corresponding to Spherical Harmonics of Various Degrees  $m$ , and for Various Values of  $\delta$ , or the Ratio Frequency/Resistivity.

$\delta$ .	$m = 1.$		$m = 2.$		$m = 3.$		$m = 4.$		$m = 5.$	
	$f.$	$\alpha.$	$f.$	$\alpha.$	$f.$	$\alpha.$	$f.$	$\alpha.$	$f.$	$\alpha.$
10	4.21	47.9	5.82	66.5	8.73	75.4	12.60	80.4	17.32	83.1
20	3.24	31.9	3.59	50.5	4.82	63.5	6.62	71.5	8.89	76.5
30	2.95	25.2	2.96	41.1	3.64	54.2	4.73	63.8	6.17	70.5
50	2.70	18.9	2.50	31.2	2.80	42.6	3.35	52.5	4.12	60.5
80	2.53	14.6	2.24	24.3	2.36	33.6	2.65	42.1	3.07	50.0
100	2.47	13.1	2.14	21.6	2.21	29.9	2.43	37.8	2.76	45.0
162	2.36	10.1	1.98	16.7	1.98	23.3	2.10	29.5	2.27	35.9
200	2.32	9.0	1.93	15.0	1.90	20.9	1.98	26.7	2.11	32.3
288	2.27	7.3	1.85	12.4	1.79	17.4	1.83	22.2	1.92	27.0
338	—	—	—	—	1.75	15.9	1.77	20.4	1.85	24.9
450	—	—	—	—	1.68	13.8	1.69	17.7	1.74	21.5
612	—	—	—	—	—	—	—	—	1.65	18.4

A brief inspection of Tables I and K suffices to show that no single value of  $\rho$  can be found for which the calculated and observed values of  $f$  and  $\alpha$  are in agreement. Indeed, even if we leave out of account the constancy of  $\rho$  for the different harmonics, no calculated values of  $f$  and  $\alpha$  are to be found in Table K which agree with those which are deduced from observation. Thus, considering only the mean results for the "annual" harmonics  $Q_{n+1}^n$ , we may notice the following comparative figures:—

TABLE L.—Illustrating the Failure of the Hypothesis of a Uniformly Conducting Earth.

Harmonic.	Theoretical $\alpha$ (corresponding to observed $f$ ).	Observed $\alpha$ .	Theoretical $f$ (corresponding to observed $\alpha$ ).	Observed $f$ .
$Q_2^1$	37	13	1.9	2.8
$Q_3^2$	30	18	1.8	2.2
$Q_4^3$	39	21	1.8	2.5
$Q_5^4$	43	23	1.8	2.7

These figures indicate clearly that the observed relations between the external and internal fields could not arise from a uniformly conducting earth whatever its conductivity. The observed phase differences are smaller than the amplitude ratios would suggest on this assumption. The discrepancy is in the same sense as in SCHUSTER'S paper, where no observed phase difference was found; but as his determination of the amplitude ratio was also larger than those of this paper, his data indicated a more outstanding failure of the hypothesis than do our present results.

#### § 17. *The Hypothesis of a Non-uniformly Conducting Earth.*

The simplest form of non-uniformly conducting earth which we can consider is that discussed by SCHUSTER in his first paper, viz., a sphere containing an inner core of one degree of conductivity and an outer concentric layer of another degree. There is observational evidence for the belief that the outer crust of the earth, down to a depth which is considerable in comparison with that of the oceans and of the surface inequalities, possesses high electrical resistance. For this reason, and because of the mathematical simplicity of the hypothesis, we shall suppose that the outer layer of the earth is an absolute non-conductor. If  $R_c$  is the radius of the inner core, and  $\rho$  its resistivity, the theory referred to in § 16 will, as before, enable us to calculate the amplitude ratio  $f$  and phase difference  $\alpha$  between the potentials of the primary external, and induced internal, fields, at the surface of the inner core ( $\mathbf{R} = R_c$ ). Corresponding to a harmonic of degree  $m$ , however, the earth-surface potential of the primary external field will at the surface of the inner core be reduced

in the ratio  $(R_c/R)^m$  (*cf.* § 9). Similarly, the amplitude of the induced field, which is  $(1/f)$  times the amplitude of the inducing field at the surface of the core, will at the surface of the earth be reduced in the ratio  $(R_c/R)^{m+1}$ . Hence the amplitude ratio of the primary and secondary fields, at the earth's surface, will be equal to  $(R/R_c)^{2m+1} f$ ; we shall denote this by  $f'$ , so that

$$(23) \quad f' = (R_c/R)^{2m+1} f.$$

The phase differences  $e_m^n - i_m^n$ , on the other hand, remain invariable at all radii, so that the modified form of the theory enables us to account for larger amplitude ratios, corresponding to given phase differences, than was possible in § 16. The right half of Table L shows that this is the direction in which change is required in order to fit the observational results.

The adopted procedure was as follows. The phase differences  $\alpha$  in Table I were taken as the more fundamental observed data, and the various corresponding values of  $\delta/n$  (or  $R^2\rho$ ), appropriate to the several "annual" harmonics  $Q_{n+1}^n$ , were read off from Table K. The weighted mean of the deduced values of  $\delta/n$  was then formed, less weight being given to the value corresponding to  $Q_2^1$  than to  $Q_3^2, Q_4^2, Q_5^4$ , on account of the discrepancy between the 1902 and 1905 values of  $e_2^1 - i_2^1$ . The adopted value of  $\delta/n$  was 125. The values of  $\alpha$  calculated on this basis are given in Table M, both for the annual harmonics used in determining  $\delta/n$ , and for the larger of the seasonal harmonics,  $Q_n^n$ . The value of  $\rho/R_c^2$  calculated from (20), when  $\delta/n$  is 125, is  $7.31 \cdot 10^{-6}$ .

Table M.—Phase Differences Corresponding to a Conducting Sphere for which  $\rho/R_c^2 = 7.31 \cdot 10^{-6}$ .

Annual harmonics.			Seasonal harmonics.		
	Phase difference.			Phase difference.	
	Observed.	Calculated.		Observed.	Calculated.
$Q_2^1$	(13)	18.9	$Q_2^1$	4	11
$Q_3^2$	18	18.7	$Q_3^2$	3	13
$Q_4^3$	21	19.3	$Q_4^3$	27	15
$Q_5^4$	23	20.5	$Q_5^4$	24	17
Mean . . .	19	19.3	Mean . . .	15	14

The agreement between the observed and calculated values of  $\alpha$  in Table M is good, especially for the annual harmonics, which are better determined than are the

seasonal harmonics (*cf.* Table I). The differences are in most cases easily within the limits of accidental error.

As regards the lunar diurnal magnetic variation, the corresponding value of  $\delta/n$  is 121, and, as Table K shows, the above values of  $\alpha$  would hardly be affected by the change. The calculated values for the lunar variation are given in Table J, alongside the observed data. Considering the uncertainties in the determination of the small quantities concerned, the agreement between the two sets of values is good. The observed phase differences are, with one exception, of the right sign, and their mean ( $-20^{\circ}6$ ) is in satisfactory accordance with the mean value of  $\alpha$  ( $-19^{\circ}0$ ). The lunar variation, therefore, supports the above hypothesis as fully as the reliability of the data allows one to expect.

The theoretical values of  $f$  corresponding to the values of  $\alpha$  in Table M were then compared with the observed amplitude-ratios (which we denote by  $f'$ ), and in accordance with (23), the values of  $(f'/f)^{1/2m+1}$ , or  $R/R_c$ , were calculated for each of the annual harmonics  $Q_{n+1}^n$ . The four values found were

$$(23a) \quad 1.068, \quad 1.030, \quad 1.041, \quad 1.041 \quad (R/R_c).$$

Adopting the value 1.04, the following calculated values of  $f'$  were deduced from the formula

$$(24) \quad f'_{\text{calc.}} = (1.04)^{2m+1} f_{\text{calc.}}$$

both for the annual and seasonal harmonics:—

TABLE N.—Amplitude Ratios of the Surface Potentials of the External and Internal Diurnal Magnetic Variation Fields.

Annual harmonics.				Seasonal harmonics.			
—	$f_{\text{calc.}}$	$f'$		—	$f_{\text{calc.}}$	$f'$	
		Calculated.	Observed.			Calculated.	Observed.
$Q_2^1$	2.05	2.49	2.8	$Q_1^1$	2.42	2.72	2.3
$Q_3^2$	1.83	2.41	2.2	$Q_2^2$	1.88	2.29	2.45
$Q_4^3$	1.74	2.47	2.5	$Q_3^3$	1.73	2.27	2.1
$Q_5^4$	1.70	2.61	2.7	$Q_4^4$	1.67	2.37	1.7
Mean . . . .		2.50	2.55	Mean . . . .		2.41	2.14

Again the agreement with observation must be considered satisfactory, so that with the aid of only two disposable constants ( $\rho$  and  $R_c/R$ ) a good account has been

given of the values of sixteen observational quantities (eight values of the amplitude ratio and eight of the phase difference). Naturally, however, the hypothesis of a non-uniformly conducting earth such as we have considered must be regarded as giving only a convenient idealized representation of the real facts.

The theoretical values of  $f'$  calculated for the lunar diurnal variation are given in Table J; they differ but little from those of Table N. The observed values in Table J are somewhat irregular, but their mean (2.3) is in satisfactory agreement with the calculated mean (2.5), when the accidental error of the lunar data is considered.

§ 18. *The Electrical Conductivity of the Earth as Deduced from the Diurnal Magnetic Variations.*

In § 17 the following two quantities were determined, in connection with the theory that the earth has a conducting nucleus of radius  $R_c$  and specific resistance  $\rho$ , surrounded by a non-conducting layer:—

$$(25) \quad \rho/R_c^2 = 7.31 \cdot 10^{-6}, \quad R/R_c = 1.04.$$

Here  $R$  denotes the radius of the earth ( $2\pi R = 4 \cdot 10^9$  cm.).

The thickness of the outer layer is given by

$$(26) \quad R - R_c = R(1 - R_c/R) = 245 \text{ km.},$$

or about 160 miles. The specific resistance  $\rho$  of the inner core is similarly found to be as follows:—

$$(27) \quad \rho = 7.31 \cdot 10^{-6} \cdot R_c^2 = 2.74 \cdot 10^{12} \text{ C.G.S.}$$

These values may be compared with those deduced by SCHUSTER in his second memoir.\* The calculation there made was intended to give only a rough estimate, and in order to explain the apparent absence of phase difference between the external and internal fields (*cf.* § 2) it was necessary to assume a high—practically infinite—conductivity of the inner core. Hence no comparison with (27) is possible. On this basis, however, the deduced value of the thickness of the non-conducting layer was 1000 km., in place of the present value 245 km. The difference seems altogether beyond the probable limit of error in the latter result, and 1000 km. must be regarded as definitely too large. The estimate 245 km. can hardly be liable to so much as 50 per cent. error, so that the outer layer is probably from 200 to 300 km., or 100 to 200 miles in depth. It should not be forgotten, however, that we have no evidence for a sharp line of demarcation between the outer non-conducting and the inner conducting matter.

\* 'Phil. Trans.,' A, vol. 208, 1907, p. 169.

As regards the resistivity  $2.74 \cdot 10^{12}$ , we may note that this is considerably less than that of the *dry* constituents of the outer rocky crust of the earth. Ordinary sea water is more conducting; thus while for distilled water  $\rho$  is about  $1.4 \cdot 10^{15}$ , and for rain water  $6 \cdot 10^{13}$ , SCHMIDT\* found that for North Sea salt water  $\rho$  is  $2.5 \cdot 10^{10}$ , and ULLER† states that water from the Mediterranean Sea may be only two-thirds as resisting as this. ULLER also finds that the resistivity of moist earth ranges from  $10^{13}$  to  $10^{14}$ , but that for dry earth it is about  $10^{15}$ . LÖWY‡ has measured the specific resistance of the ordinary constituents of the earth's crust (rock, stone, and so on) and concluded that for the majority of specimens  $\rho$  is greater than  $10^{16}$ , though the results varied somewhat with the moisture in the stone. It would seem, therefore, that apart from the comparatively shallow oceanic or water-bearing strata at or near the earth's surface, the outer crust is from 100 to 1000 times as resisting as, from our calculations, the inner core appears to be.

The above data apply only to the solid crust, which geologists consider, on the evidence of seismological and gravity measurements and the study of radio-activity, to extend down to a depth of 30 or 40 miles only.§ Very little is known of the nature or condition of the underlying substance. The above value of  $\rho$ ,  $2.74 \cdot 10^{12}$ , is much greater than the resistivity of metals such as iron at ordinary temperatures (for which  $\rho$  is about  $10^7$ ); their resistance, however, increases with temperature, and may also be affected by the great pressures to which the interior layers of the earth must be subject.

As regards the depth of the non-conducting layer, 200 to 300 km., it may be noticed that HELMERT||, and also TITTMANN and HAYFORD¶, have concluded that the inequalities in the distribution of mass near the earth's surface extend down to a depth of 120 km.; variations in the electrical properties of the earth seem therefore to extend below this region of variation of elasticity.

## PART V.—ON CERTAIN PROPERTIES OF THE EARTH'S ATMOSPHERE.

### § 19. *The Solar Diurnal Barometric Variation.*

As was remarked in § 6, the atmospheric motions to which the daily magnetic variations are to be attributed, on the STEWART-SCHUSTER theory, are the horizontal and not the vertical movements. Before proceeding with the study of the magnetic variations, a brief statement will be made of the principal relevant facts regarding the daily circulation and electrical conductivity of the atmosphere.

\* SCHMIDT, 'Jahrbuch d. Drahtlosen Telegraphie,' vol. 4, p. 636, June, 1911.

† ULLER, *ibid.*, p. 638.

‡ LÖWY, 'Ann. d. Physik,' 36, p. 125, October 3, 1911.

§ Cf. Sir A. GEIKIE'S Article on Geology, 'Encyc. Brit.' (11th ed.), vol. 11, p. 654.

|| HELMERT, 'Encyc. d. Math. Wiss.,' VI., 1, B, vol. 2, 1910.

¶ "Geodetic Operations in the U.S.A., 1906-9." 'Report to 16th Conference of the International Geodetic Association,' by O. H. TITTMANN and T. HAYFORD.

As regards the former, the sources of information are the diurnal variations of barometric pressure, of air temperature, and of wind. ANGOT\* and HANN† have studied the daily barometric variations in great detail, and DINES‡ has discussed the daily changes of wind at St. Helena. GOLD§ has examined the theoretical relations between these phenomena and the air-temperature variations.

The 24-hour component of the barometric variation is very irregular in its distribution over the earth, varying greatly both in amplitude and phase with season, situation (continent, land or ocean, mountain or valley), and weather conditions. The 12-hour component, on the contrary, is one of the most regular of all meteorological phenomena. Its phase is almost exactly the same over the whole region between latitudes  $\pm 60$  degrees (at least), its amplitude shows a regular diminution with increasing latitude, while it is practically independent of longitude, weather conditions, and local situation. Mountain records indicate that the 24-hour component diminishes with increasing height, vanishing and re-appearing with reversed phase. The 12-hour component likewise diminishes in amplitude, but almost proportionately to the pressure,|| while its phase is gradually retarded. GOLD assigns 90 degrees as the probable total diminution in the corresponding phase.

The annual changes in the 24-hour barometric variation are not very regular; those in the 12-hour component, on the contrary, are simple and definite. The phase is constant throughout the year, while the amplitude has maxima at the equinoxes and unequal minima at the solstices, the total variation, however, being small. The solstitial minima are simultaneous in the two hemispheres, the principal minimum occurring at aphelion in June.

ANGOT has shown that there is also a harmonic of period eight hours having a regular annual variation, but it is too small to require consideration in this paper.

The dependence on latitude of the amplitude of the 24-hour component is rather uncertain; ANGOT gives the law as  $\sin^2 \theta$ ,  $\theta$  being the co-latitude. SCHUSTER, in his second memoir (§ 6), used the harmonic  $Q_1^1$  or  $\sin \theta$ , stating however, that the harmonic  $Q_3^1$  might also be present. Expressed in millimetres of mercury, the value actually used was, at the equator,

$$(28) \qquad 0.3 \sin t.$$

ANGOT found that the amplitude of the 12-hour component was mainly proportional to  $\sin^4 \theta$ , but contained in addition a term proportional to  $\sin^2 \theta$ , as ADOLF SCHMIDT

\* ANGOT, 'Annales du Bureau Central Météorologique de France,' 1887, pp. 237-344.

† HANN, "Lehrbuch," and also numerous papers in the 'Met. Zeitschrift' and the publications of the Vienna Academy.

‡ DINES, 'Meteorological Office Publication No. 203,' 1910.

§ GOLD, 'Phil. Mag.,' 19, p. 26, 1910.

|| The diminution of amplitude seems to be slightly more rapid for the 12-hour amplitude than for the total pressure.

has also remarked; GOLD has used the law  $\sin^3 \theta$ , which fits the observations very closely. SCHUSTER adopted the law  $\sin^2 \theta$  (or  $Q_2^2$ ), which represents the facts moderately well, though distinctly less well than  $\sin^3 \theta$ . SCHMIDT's expression was

$$(29) \quad (0.31 Q_2^2 - 0.082 Q_4^2) \sin(2t + 154^\circ).$$

The seasonal variation of amplitude has been represented by ANGOT by the formula

$$(30) \quad \cos^2 \delta / d^2,$$

where  $\delta$  is the sun's declination and  $d$  its distance. Its magnitude is well illustrated by the following results of an analysis of the Batavian barometric observations for the period 1866 to 1905 :—

Spring (February to April) . . . .	1.026 $\sin(2t + 156^\circ.0)$ ,
Autumn (August to October) . . . .	1.022 $\sin(2t + 163^\circ.9)$ ,
Summer (May to July). . . . .	0.935 $\sin(2t + 158^\circ.5)$ ,
Winter (November to January). . . .	1.009 $\sin(2t + 161^\circ.9)$ ,
Mean equinox. . . . .	1.021 $\sin(2t + 159^\circ.9)$ ,
Mean solstice . . . . .	0.971 $\sin(2t + 160^\circ.3)$ .

The mode of origin of the daily barometric variation has been much discussed, but the question whether the important semi-diurnal component is of tidal or thermal origin, or both, seems still open. If it is fundamentally a tidal effect, resonance with a free atmospheric period of 12 hours must be assumed, since the lunar diurnal barometric variation (which can hardly be of other than tidal origin) is of much smaller magnitude. Probably resonance is necessarily involved also if the cause is thermal, as the KELVIN-MARGULES theory supposes. In any case, however, the 12-hour variation is clearly much more fundamental than the 24-hour component, a fact which has an interesting bearing on the magnetic variations.

If  $\Phi$  is the velocity potential of the atmospheric motion, so that  $\frac{\partial \Phi}{\partial s}$  is the velocity in the direction of  $ds$ , the simplest theory connecting  $\psi$  and the pressure variation  $\delta p$  asserts that

$$(31) \quad \frac{1}{v^2} \frac{d\Phi}{dt} = - \frac{\delta p}{p},$$

where  $v$  is the velocity of sound. At the earth's surface, taking  $\delta p$  as

$$(32) \quad 0.3 Q_1^1 \sin(\lambda + t') + (0.31 Q_2^2 - 0.082 Q_4^2) \sin\{2(\lambda + t') + 154^\circ\}$$

in millimetres of mercury (so that  $p$  in the same units is 760), we find that

$$(33) \quad \Phi = (Nc^2/2\pi p) [0.3 \cos(\lambda + t') + \{0.16 Q_2^2 - 0.041 Q_4^2\} \cos\{2(\lambda + t') + 154^\circ\}].$$



The numerical value of  $Nv^2/2\pi p$  is  $1.99 \cdot 10^{10}$  ( $N = 86400$ ,  $v^2 = 11.0 \cdot 10^8$ ) or  $31.3R$ , where  $R$  is the radius of the earth.

The calculated values of the semi-diurnal components of velocity to east and south, at the latitude of St. Helena ( $16^\circ$  S.), are approximately given by

$$(34) \quad \begin{cases} \text{(East)} & -21 \sin(2nt + 154^\circ) \text{ cm./sec.}, \\ \text{(South)} & 9 \sin(2nt + 244^\circ) \text{ cm./sec.} \end{cases}$$

J. S. DINES has determined the actual values at St. Helena to be

$$(35) \quad \begin{cases} \text{(East)} & -22 \sin(2nt + 158^\circ), \\ \text{(South)} & 35 \sin(2nt + 237^\circ). \end{cases}$$

The agreement in phase is therefore very good, and also in amplitude for the easterly component; the southerly component variation is, on the contrary, much larger than the simple theory would predict.

It has already been remarked that  $\delta p/p$  seems to diminish upwards, so that in accordance with (31), the value of  $\Phi$  in (33) should diminish in amplitude with increasing height.\* The phase should also vary with height in the same way as for the pressure variation.†

### § 20. *The Lunar Diurnal Barometric Variation.*

LAPLACE, in the 'Mécanique Céleste,' xiii., ch. 1, seems to have been the first to mention that tidal motions should be present in the atmosphere as well as in the oceans. He also discussed a series of barometric observations made in France and found definite evidence of a very small lunar semi-diurnal variation, which he inclined to attribute to the indirect (rather than direct) tidal action of the moon working through the lunar tidal motion of the sea. SABINE ('Phil. Trans.,' 1847) proved from the discussion of two years' barometric observations at St. Helena that the magnitude of the lunar semi-diurnal barometric variation was of the order of 0.1 mm. of mercury. The most complete determination of the effect, however, has been made at Batavia ('Observations,' 1905); as in the case of the solar diurnal variations, the

\* As regards the magnitude of the diminution, some European mountain observations discussed by HANN, 'Wien. Denkschriften,' 59, 1892, may be quoted, although mountain observations may not be altogether representative of the conditions in the free atmosphere at the same height. Considering the whole amplitude of the barometric variation, reduced to sea-level according to the formula  $\delta p/p$ , the results from heights of  $1\frac{1}{2}$  to  $2\frac{1}{2}$  km. were found to be 0.28 mm., or even less, whereas the normal sea-level value in the same latitude is 0.32 mm.

† HANN (*ibid.*) shows that, at the mountain stations referred to, the phase angles range from 110 or 120 degrees to 140 degrees, in place of 154 degrees.

lunar *diurnal* term is variable and irregular, while the semi-diurnal term is constant, its value (calculated from forty years' observations) being, in millimetres of mercury,

$$(36) \quad 0.063 \sin(2t + 65^\circ).$$

WAGNER ('Göttingen Abh.,' ix., 4, 1913), has also discussed six years' hourly barometric observations at Samoa, with the aim of determining the various characteristics of the lunar semi-diurnal barometric variation. The material was insufficient for the attempted purpose of investigating the effect of season, lunar distance, declination, and phase, but the mean result for the semi-diurnal tide may be quoted, viz.,

$$(37) \quad 0.039 \sin(2t + 33^\circ).$$

The data do not suffice to determine the dependence of phase and amplitude on latitude, but we shall assume that the phase is constant, while the amplitude is specified by the function  $Q_2^2$ . The Samoan result does not support this conclusion very strongly when compared with the Batavian determination, but the material is insufficient to enable a definite judgment to be made as yet. For the present the Batavian result will be adopted as the basis for discussion in this paper. The corresponding value of the velocity potential  $\Phi$  is given by

$$(38) \quad \Phi = 32.4R \cdot 0.010Q_2^2 \cos(2t + 65^\circ).$$

### § 21. *The Electrical Conductivity of the Upper Atmosphere.*

It has already been mentioned (§ 6) that the electrical conductivity of the upper atmosphere was discussed by SCHUSTER in his second memoir. The possibility of the production of a conducting layer such as was suggested in that discussion by the agency of ultra-violet radiation from the sun has recently been considered by SWANN,\* in connection with recent physical data bearing on the problem. Assuming the ionized constituent of the atmosphere to be oxygen, it is possible to determine the rate of supply of energy of ultra-violet radiation necessary to maintain the proposed conductivity ( $10^{-13}$  C.G.S. electro-magnetic units, in a layer 300 km. thick, where the average pressure is  $10^{-6}$  atmosphere). The ionization potential for oxygen is 9 volts, and only the radiation of wave-length less than  $\lambda$  1350 is available for ionization.† Considering the solar spectrum to be that of a black body at  $6000^\circ$  C., it appears that  $1.6 \cdot 10^{-5}$  of the whole solar radiation would be thus available; it is found, however, that even if the total radiation of all wave-lengths were absorbed in the act of ionization, the rate of ionization would still be only one-sixteenth of what is required. SWANN points out that the simplest method of overcoming the

\* SWANN, 'Terrestrial Magnetism,' XXI., p. 1, 1916.

† HUGHES, 'Proc. Camb. Phil. Soc.,' 15, p. 483, 1910; 'Phil. Mag.,' 25, p. 685, 1913.

difficulty may be the assumption of a smaller pressure in the conducting layer. He shows, indeed, that if the variation of the quantities involved in his calculations follow the same laws at low pressures as those actually determined at ordinary pressures, the conductivity should theoretically tend to an infinite value with increase of altitude. Perhaps the inference to be drawn from this is that whatever ultra-violet light is present is absorbed only in some particular layer of the atmosphere of appropriate constitution.

SWANN does not discuss the pressures and composition actually existing in the upper atmosphere. It appears likely, however, that at about 100 km. height the atmosphere contains roughly equal proportions of hydrogen and nitrogen, with only about 2 or 3 per cent. of oxygen; the pressure is approximately  $3 \cdot 10^{-6}$  atmosphere. At 170 km. hydrogen is altogether the preponderant constituent, the only other which is at all appreciable being helium (6 per cent.); the pressure is approximately  $6 \cdot 10^{-7}$  atmosphere. Owing to the lightness of hydrogen, the pressure diminishes with height much more slowly than near the base of the stratosphere. Even at 800 km. height, where hydrogen is the sole constituent (within a small fraction of 1 per cent.), the pressure is probably  $10^{-9}$  atmosphere.\* Perhaps at such high levels as these the ultra-violet radiation ( $\lambda < 1350$ ) of the amount considered by SWANN might be sufficient to produce the required conductivity; his calculation related to oxygen, however, and how far it would be modified in the case of hydrogen is uncertain—I am not aware of the existence of the data necessary to examine this point. But it may be doubted whether, in any case, the suggested agency can be sustained as a probable cause of the ionization. In the first place, even though the solar atmosphere should allow such short-wave radiation to escape, its intensity must be much diminished, relatively to the red end of the spectrum, by scattering, and its total energy must be much less than that appropriate to a black body spectrum at  $6000^{\circ}$  C. Moreover it seems likely, in view of the close connection between solar and magnetic activity and the auroral, that the two latter terrestrial phenomena may originate in similar regions of the atmosphere. Recent observations indicate that the level of auroræ is generally between 90 and 140 km.†; SWANN'S calculation seems to preclude ultra-violet radiation as the ionizing agency in the conducting layer, if this is indeed situated at the auroral level.

Whatever the origin and situation of the conducting layer, the main cause of its ionization must be in the sun, since the magnetic data of this paper indicate a very strongly marked diurnal variation. Hence spontaneous ionization, uninfluenced by

\* For these atmospheric data *cf.* JEANS' 'Dynamical Theory of Gases' (2nd ed.), p. 356. If, however, as some authorities believe, there is no appreciable amount of free hydrogen in the atmosphere, the pressure will fall off much more rapidly than is described above, and the conclusions would be modified accordingly.

† STÖRMER, 'Terrestrial Magnetism,' XX., p. 159, 1915; SWINNE, 'Phys. Zeit.,' 17, p. 529, 1916, has discussed 2500 parallax determinations of the auroræ, and finds that 2098 lie between 90 and 130 km., and 322 between 130 and 200 km.

the sun, cannot be an important factor. Some form of corpuscular emission may be supposed to be responsible. SCHUSTER, in his second memoir, showed that only very rapidly moving corpuscles could possibly be so regarded; these would act as fertilizers in the absorbing layer by producing ions through collisions with molecules. Such corpuscles might be few in number compared with the total number of ions thus liberated; but if they are supposed to be of both signs, their speed of transmission from the sun must be great in order that re-combination may not take place on the way, while, if they are of one sign only, the accumulation of charge in the earth's atmosphere may present difficulties. The hypothesis therefore stands in need of numerical examination similar to SWANN'S discussion in the case of ultra-violet radiation, but at present the necessary data for this are wanting. It is difficult to imagine further alternatives, however, and the existence of the conducting layer itself can hardly now be questioned.

It may be mentioned that, since the intensity of the ionizing agent varies as the square of the resulting conductivity, the former must be from 100 to 150 per cent. greater at times of sunspot maximum than at times of minimum, the increase in the conductivity being from 35 to 60 per cent.

The phenomena of electric wave transmission also afford evidence on the present subject, and some conclusions of ECCLES\* may be mentioned. Three strata of the atmosphere are proposed, the highest one (first suggested by HEAVISIDE in 1900) being strongly and permanently conducting, while the lowest is permanently non-conducting. The middle layer, the lower surface of which was roughly estimated to be 50 miles high, is a conductor by day and a non-conductor at night, the transitional region being fairly definite. The magnetic phenomena discussed in this paper indicate a layer resembling the middle stratum in Dr. ECCLES' theory, but give no evidence of the higher, permanently conducting layer.

#### PART VI.—THE THEORY OF THE EXTERNAL SOLAR AND LUNAR DIURNAL MAGNETIC VARIATION FIELDS.

##### § 22. *Outline of the Mathematical Theory for the General Law of Atmospheric Conductivity.*

In Parts II. and III. of this paper it has been shown that the major portion of the solar and lunar diurnal magnetic variations is due to magnetic forces which possess a potential, and are therefore attributable to electric currents. These were found to be situated mainly above the earth's surface, and in Part IV. the internal current system was shown to be probably caused through induction by the external current system. The remaining task involved in the explanation of the whole phenomenon consists, therefore, in accounting for the externally circulating system of electric

\* ECCLES, 'Roy. Soc. Proc.,' A, vol. 87, p. 79, 1912.

currents. The STEWART-SCHUSTER theory of their origin will form the basis of this enquiry, and the data to be considered will be those of Table F, p. 27, for the solar diurnal magnetic variations, and Table J, p. 35, for the lunar diurnal variations. The former data are the more accurate, and are alone suitable for exact numerical comparison with the results of theoretical calculation. But it will be found that great advantage accrues from the possession of data relating to these two closely similar yet independent sets of magnetic variations.

For convenience later in the discussion it is necessary at this stage to outline the mathematical analysis of the above theory. The following investigation is a continuation of two earlier studies of the same problem by SCHUSTER\* and the present writer.† It is more general than the first of these, and also embodies certain simplifications of the methods of both papers. The details of the calculations are in all cases similar, however, and will be omitted here.

We suppose that the phenomenon takes its rise in a spherical shell of mean radius  $r$  and thickness  $e$  (small compared with  $r$ ). The conductivity of the air in this shell will be denoted by  $\rho$ , and we shall suppose that  $\rho$  (or  $\rho e$ ) is a function of  $\omega$  (the zenith distance of the sun from the point considered) expressible in the most general terms as a power series in  $\cos \omega$ . Clearly, if  $\delta$  is the declination of the sun, and  $\theta, \lambda$  are the co-latitude and longitude of the point, we shall have

$$(39) \quad \cos \omega = \sin \delta \cos \theta + \cos \delta \sin \theta \cos t$$

at local time  $t$  ( $t = \lambda + t'$ , *cf.* § 9). We suppose, therefore, that

$$(40) \quad \rho e = K \sum_{s=0}^{\infty} a_s \cos^s \omega. \quad (a_0 = 1)$$

Consequently

$$(41) \quad (\rho e)^2 = K^2 \sum_{s=0}^{\infty} b_s \cos^s \omega, \quad (b_0 = 1)$$

where

$$(42) \quad b_s = \sum_{r=0}^s a_r a_{s-r}.$$

It is convenient to transform  $\rho e$  and  $(\rho e)^2$  into Fourier series in  $\cos st$  as follows:—

$$(43) \quad \rho e = K \sum_{-\infty}^{\infty} f_s \cos st, \quad (\rho e)^2 = K^2 \sum_{-\infty}^{\infty} g_s \cos st.$$

Here

$$(44) \quad f_s = f_{-s} \equiv \sum_{q=0}^{\infty} C_q^{s+2q} \cdot d_{s+2q} \cdot \left(\frac{1}{2} \cos \delta \sin \theta\right)^{s+2q},$$

$$(45) \quad g_s = g_{-s} \equiv \sum_{q=0}^{\infty} C_q^{s+2q} \cdot e_{s+2q} \cdot \left(\frac{1}{2} \cos \delta \sin \theta\right)^{s+2q},$$

\* SCHUSTER, 'Phil. Trans.,' A, vol. 208, p. 185.

† 'Phil. Trans.,' A, vol. 213, p. 288.

and

$$(46) \quad d_r = \sum_{l=0}^{\infty} c_{l+r} C_r \cdot \alpha_{l+r} \cdot (\sin \delta \cos \theta)^l, \quad e_r = \sum_{l=0}^{\infty} c_{l+r} C_r \cdot b_{l+r} \cdot (\sin \delta \cos \theta)^l,$$

so that  $f_s, g_s$  are power series in  $\sin \theta$  and  $\cos \theta$ .

For the present we may consider an atmospheric oscillation of the general harmonic type, for which the velocity potential is

$$(47) \quad \Phi = K_{\sigma} r Q_{\sigma} r \sin(\tau t - \alpha).$$

The radial magnetic intensity of the earth's field (measured positive outwards) will be denoted by  $V$ . The components of electric force,  $X$  and  $Y$ , measured towards the south and east respectively, are given by

$$(48) \quad X = \frac{V}{r \sin \theta} \frac{d\Phi}{d\lambda}, \quad Y = -\frac{V}{r} \frac{d\Phi}{d\theta}.$$

If we express  $X$  and  $Y$  in the form

$$(49) \quad X = \frac{1}{r} \frac{d\mathfrak{S}}{d\theta} + \frac{1}{r\rho e \sin \theta} \frac{d\mathfrak{R}}{d\lambda}, \quad Y = \frac{d\mathfrak{S}}{r \sin \theta d\lambda} - \frac{1}{r\rho e} \frac{d\mathfrak{R}}{d\theta},$$

the function  $\mathfrak{R}$  will be the current function of the electric currents produced by  $X$  and  $Y$ .\*

In order to obtain  $\mathfrak{R}$  from (49), SCHUSTER first determined  $\mathfrak{S}$  by eliminating  $\mathfrak{R}$ , and afterwards determined  $\mathfrak{R}$  by the use of  $\mathfrak{S}$ . In my own earlier treatment of the problem I sought to avoid the calculation of  $\mathfrak{S}$  by using the resistivity in place of the conductivity, so that  $1/\rho e$  was the function which was expressed in the form (40). But it is better to keep  $\rho$  as the fundamental function, and this is easily effected, and  $\mathfrak{R}$  directly determined, by the use of the following method.

On eliminating  $\mathfrak{S}$  and multiplying both sides of the resulting equations by  $(\rho e/\sin \theta)^2$ —this being the step which yields the improvement of method—we obtain the following result:—

$$(50) \quad \frac{(\rho e)^2 r}{\sin \theta} \left\{ \frac{dX}{d\lambda} - \frac{d}{d\theta} (Y \sin \theta) \right\} = \frac{\rho e}{\sin^2 \theta} \left\{ \frac{d^2 \mathfrak{R}}{d\lambda^2} + \sin \theta \frac{d}{d\theta} \sin \theta \frac{d\mathfrak{R}}{d\theta} \right\} \\ - \left\{ \frac{1}{\sin^2 \theta} \frac{d\mathfrak{R}}{d\lambda} \frac{d\rho e}{d\lambda} + \frac{d\mathfrak{R}}{d\theta} \frac{d\rho e}{d\theta} \right\}.$$

\* Here we neglect the effect of self-induction for the present (see, however, § 26). We define  $\mathfrak{R}$  by the property that the flow across an element of length  $ds$ , measured from left to right, is  $\frac{d\mathfrak{R}}{ds} ds$ .

We may suppose that the solution  $\mathfrak{R}$  is expressible in the form of a series of spherical harmonic functions, thus

$$(51) \quad \mathfrak{R} \equiv K_{\sigma} \tau C K \sum_{m=0}^{\infty} \sum_{n=-\infty}^{\infty} p_m^n Q_m^n \sin (nt - \alpha_n).$$

In this equation  $Q_m^{-n}$ , when  $n$  is positive, will be defined as equal to  $Q_m^n$ . When  $m$  is numerically less than  $n$ ,  $Q_m^n$  is zero.

When the above values of  $\mathfrak{R}$  and  $\rho e$  are substituted on the one side, and of  $X$  and  $Y$  on the other, (50) becomes

$$(52) \quad \sum_{s=-\infty}^{\infty} g_s \left[ \left\{ \frac{dV}{d\theta} \frac{dQ_{\sigma}^{\tau}}{d\theta} - \sigma(\sigma+1) V Q_{\sigma}^{\tau} \right\} \sin (\overline{\tau+st} - \alpha) + \frac{\tau Q_{\sigma}^{\tau}}{\sin^2 \theta} \frac{dV}{d\lambda} \cos (\overline{\tau+st} - \alpha) \right] \\ = -C \sum_{m=0}^{\infty} \sum_{n=-\infty}^{\infty} \sum_{s=-\infty}^{\infty} p_m^n R_m^n (s) \sin \{(n+s)t - \alpha_n\},$$

where

$$(53) \quad R_m^n (s) \equiv \{m(m+1) - ns/\sin^2 \theta\} Q_m^n f_s + f_s' \frac{dQ_m^n}{d\theta}$$

and

$$(54) \quad f_s' \equiv \frac{df_s}{d\theta}.$$

By equating corresponding periodic functions of  $t$  and  $\theta$  on the two sides of (52), we may determine the values of  $p_m^n$  and  $\alpha_n$ .

For the time being we will now limit the problem to the determination of the part of  $\mathfrak{R}$  which depends solely on local time, *i.e.*, to the case in which  $\alpha_n$  is independent of  $\lambda$ , so that on the left-hand side of (52) the term  $dV/d\lambda$  will be omitted. This is the same thing as omitting from  $V$  the part which depends on  $\lambda$ . If we regard the earth as a uniformly magnetized sphere, with its magnetic axis inclined at an angle  $\phi$  to the geographical axis, we may write

$$(55) \quad V = C \cos \theta + C \tan \phi \sin \theta \cos \lambda_0,$$

where  $C$  is a constant (approximately equal to  $-\frac{2}{3}$ , having regard to our conventions of sign) while  $\lambda_0$  is the longitude measured from the meridian ( $68^\circ$  West of Greenwich) which contains the earth's north magnetic pole. The constant  $C$  has, for convenience, been already introduced in (51).

Neglecting, therefore, for the present, the second term in  $V$ , (45) becomes

$$(56) \quad \sum_{m=0}^{\infty} \sum_{n=-\infty}^{\infty} \sum_{s=-\infty}^{\infty} p_m^n R_m^n (s) \sin \{(n+s)t - \alpha_n\} \\ = \frac{1}{2\sigma+1} \{ \sigma(\sigma+2)(\sigma-\tau+1) Q_{\sigma+1}^{\tau} + (\sigma^2-1)(\sigma+\tau) Q_{\sigma-1}^{\tau} \} \sum_{s=-\infty}^{\infty} g_s \sin \{(s+\tau) - \alpha\}.$$

Hence it appears that for all values of  $n$ ,

$$(57) \quad \alpha_n = \alpha.$$

and on equating the factors of corresponding periodic terms on the two sides of the equation (56), we find that

$$(58) \quad \frac{1}{2\sigma+1} \{ \sigma(\sigma+2)(\sigma-\tau+1) Q_{\sigma+1}^{\tau} + (\sigma^2-1)(\sigma+\tau) Q_{\sigma-1}^{\tau} \} g_s = \sum_{m=0}^{\infty} \sum_{n=-\infty}^{\infty} p_m^n R_m^n(s')$$

where

$$(59) \quad s' = s + \tau - n.$$

There are an infinity of equations of type (58), one for each positive and negative integral value of  $s$ . Both sides of (58) may be expressed as the sum of a series of spherical harmonics of type  $Q_r^{s+\tau}$ , where (*cf.* 44, 45)  $r$  may take all integral values. By equating the factors of corresponding harmonics on the two sides, a doubly infinite set of equations is obtained, from which the doubly infinite set of constants  $p_m^n$  may be determined.

If the atmospheric conductivity is uniform,  $f_s$  and  $g_s$  are zero except when  $s = 0$ , so that only the central equation of the set (58) appears, and on the right-hand side  $R_m^n(s')$  vanishes except when  $s' = 0$ , *i.e.*, when  $n = \tau$ . Also  $R_m^{\tau}(0) = m(m+1)Q_m^{\tau}$ , and  $g_0 = 1$ . Thus, comparing the two sides of the equation, the only two values of  $m$  for which  $p_m^n$  is not zero are  $\sigma \pm 1$ . Consequently, a term  $Q_{\sigma}^{\tau}$  in the velocity potential of the atmospheric oscillation produces harmonics of types  $Q_{\sigma+1}^{\tau}$  and  $Q_{\sigma-1}^{\tau}$ , and no others, in the electric current function  $\mathfrak{R}$ , when the conductivity is uniform. If also  $\sigma = \tau$ , as in the atmospheric oscillations  $Q_1^1$  and  $Q_2^2$ ,  $Q_{\sigma-1}^{\tau}$  is zero and only the single harmonic  $Q_{\tau+1}^{\tau}$  will appear in  $\mathfrak{R}$ . In this case the value of  $p_{\tau+1}^{\tau}$  is found to be

$$(60) \quad \tau/(\tau+1)(2\tau+1).$$

If the atmospheric conductivity, or  $\rho e$ , is of the form  $K(1+a_1 \cos \omega)$ ,  $s$  in (58) can take five values ( $-2$  to  $+2$ ), while  $s'$  on the right can take three values ( $-1$  to  $+1$ ). Hence  $n$  may range from  $\tau-3$  to  $\tau+3$ , by (59), while  $m$  may range from  $\sigma-3$  to  $\sigma+3$ . Only  $p_{\sigma+1}^{\tau}$  and  $p_{\sigma-1}^{\tau}$  contain  $a_0$ , as before, and they also contain only even powers of  $a_1$ ;  $p_{\sigma\pm 1}^{\tau}$ ,  $p_{\sigma\pm 1}^{\tau\pm 1}$  contain  $a_1$  to the first and odd powers, and so on. The coefficients  $p_m^n$  have been worked out by SCHUSTER, for this law of conductivity, to the fourth power of  $a_1$ , for the two harmonics  $Q_1^1$  and  $Q_2^2$  in the velocity potential. The more important of these coefficients, which will be required in the subsequent discussion, may be obtained from Table O by writing  $a_2 = 0$ .

For more complicated forms of  $\rho e$  the calculation of the values of  $p_m^n$ , although straightforward and simple in principle, becomes increasingly laborious. In my



previous investigation the calculation was carried as far as  $a_1^2$  and  $a_2$  for the law  $K (a_0 + a_1 \cos \omega + a_2 \cos^2 \omega)$ , but this degree of approximation proves to be insufficient for the purposes of this paper. The terms have therefore been computed as far as the fourth order, for the same law and for the atmospheric oscillation  $Q_2^2$ . In this case (58) takes the form

$$(61) \quad 24g_s \sin^2 \theta \cos \theta = \Sigma \Sigma p_m^n R_m^n (s').$$

The values of the more important coefficients  $p_m^n$  calculated from this equation are given in the following table:—

TABLE O.

*Annual terms—*

$$p_2^1 = \frac{16}{63} a_1 \cos \delta + \frac{1}{1134} a_1 \cos \delta (2a_1^2 - 9a_2) (5 \cos^2 \delta - 4 \sin^2 \delta)$$

$$p_2^{-1} = -\frac{1}{189} a_1^3 \cos^3 \delta + \frac{1}{42} a_1 a_2 \cos^3 \delta$$

$$p_3^2 = \frac{2}{15} - \frac{1}{270} a_1^2 + \frac{2}{45} a_2 - \frac{1}{24.81} a_1^4 \left( \frac{53}{32} \cos^4 \delta + \frac{1}{20} \sin^2 \delta \cos^2 \delta + \frac{11}{5} \sin^4 \delta \right) \\ + \frac{1}{16.810} a_1^2 a_2 (59 \cos^4 \delta - 8 \sin^2 \delta \cos^2 \delta + 80 \sin^4 \delta) \\ - \frac{1}{2700} a_2^2 (11 \cos^4 \delta - 8 \sin^2 \delta \cos^2 \delta + 16 \sin^4 \delta)$$

$$p_3^{-2} = \frac{29}{103,680} a_1^4 \cos^4 \delta + \frac{1}{540} a_2^2 \cos^4 \delta$$

$$p_4^3 = \frac{1}{140} a_1 \cos \delta + \frac{1}{2100.240} a_1 \cos \delta (15a_1^2 - 64a_2) (4 \cos^2 \delta - \sin^2 \delta)$$

$$p_4^{-3} = 0$$

$$p_5^4 = \frac{1}{3150} a_2 \cos^2 \delta + \frac{1}{600.9450} (10a_1^4 - 51a_1^2 a_2 + 40a_2^2) \cos^2 \delta (3 \sin^2 \delta - 2 \cos^2 \delta)$$

$$p_5^{-4} = 0$$

*Seasonal terms—*

$$p_1^1 = \frac{2}{105} a_2 \sin \delta \cos \delta - \frac{1}{210} a_1^4 \sin \delta \cos^3 \delta \\ - \frac{1}{24} a_1^2 a_2 \sin \delta \cos \delta \left( \frac{4}{945} - \frac{1057}{45.1024} \cos^2 \delta \right) \\ + \frac{1}{2520} a_2^2 \sin \delta \cos \delta \left( \frac{26}{3} - \frac{83}{4} \cos^2 \delta \right)$$

TABLE O (continued).

*Seasonal Terms* (continued) —

$$p_1^{-1} = \frac{1}{2100} (30a_1^4 - 160a_1^2a_2 - 744a_2^2) \sin \delta \cos^3 \delta$$

$$p_3^1 = \frac{1}{360} (5a_1^2 + 24a_2) \sin \delta \cos \delta - \frac{1}{2160} a_1^2 a_2 \sin \delta \cos \delta (13 \cos^2 \delta - 43 \sin^2 \delta) \\ + \frac{1}{51,840} a_1^4 \sin \delta \cos \delta (191 \sin^2 \delta - 41 \cos^2 \delta) \\ - \frac{1}{270} a_2^2 \sin \delta \cos \delta (27 \cos^2 \delta + 8 \sin^2 \delta)$$

$$p_3^{-1} = \frac{1}{2700.48} (145a_1^4 - 690a_1^2a_2 + 48.83a_2^2) \sin \delta \cos^3 \delta$$

$$p_2^2 = \frac{8}{63} a_1 \sin \delta + \frac{1}{1134} a_1 \sin \delta (2a_1^2 - 9a_2) (2 \sin^2 \delta - \cos^2 \delta)$$

$$p_2^{-2} = 0$$

$$p_4^2 = \frac{1}{35} a_1 \sin \delta + \frac{1}{252,000} a_1 \sin \delta (15a_1^2 - 64a_2) (8 \sin^2 \delta + 3 \cos^2 \delta)$$

$$p_4^{-2} = 0$$

$$p_3^3 = \frac{1}{2160} (5a_1^2 + 24a_2) \sin \delta \cos \delta + \frac{1}{311,040} a_1^4 \sin \delta \cos \delta (133 \cos^2 \delta - 41 \sin^2 \delta) \\ + \frac{1}{12,960} a_1^2 a_2 \sin \delta \cos \delta (13 \sin^2 \delta - 29 \cos^2 \delta) \\ + \frac{1}{540} a_2^2 \sin \delta \cos \delta (\cos^2 \delta - \sin^2 \delta)$$

$$p_4^4 = -\frac{1}{13,440} a_1^3 \sin \delta \cos^2 \delta + \frac{1}{3150} a_1 a_2 \sin \delta \cos^2 \delta.$$

We may now also take into account the second term in V, depending on longitude (*cf.* 55). On substituting this term in place of V in (52), and taking  $\sigma = \tau = 2$  (so that we consider only a semi-diurnal atmospheric oscillation of type  $Q_2^2$ ), the left-hand side is found to be

$$(62) \quad \frac{2}{5} K_2^2 K C \tan \phi \sum_{s=-\infty}^{\infty} g_s [(9Q_1^1 - 4Q_3^1) \sin \{(s+2)t - \lambda_0 - \alpha\} + 2Q_3^3 \sin \{(s+2)t + \lambda_0 - \alpha\}].$$

When the conductivity is uniform it follows that the corresponding parts of  $\mathfrak{K}$ , the current function, are as follows:—

$$(63) \quad \frac{1}{15} K_2^2 K C \tan \phi [(27Q_1^1 - 2Q_3^1) \sin (2t - \lambda_0 - \alpha) + Q_3^3 \sin (2t + \lambda_0 - \alpha)].$$

The general form of  $\mathfrak{R}$  may be written thus

$$(64) \quad 6K_2^2 KC \tan \phi \sum_{m=0}^{\tau} \sum_{n=-\infty}^{\infty} [q_m^n \sin \{(n-1)t + \lambda_0 - \alpha\} + r_m^n \sin \{(n+1)t - \lambda_0 - \alpha\}] Q_m^n$$

in place of (51), and from (50) and (62) we obtain the following equations for  $q_m^n$  and  $r_m^n$  :—

$$(65) \quad -g_s (\sin \theta - 2 \sin^3 \theta) = \Sigma \Sigma r_m^n R_m^n (s' - 1),$$

$$(66) \quad 2g_s \sin^3 \theta = \Sigma \Sigma q_m^n R_m^n (s' + 1).$$

We shall only consider the simple law  $(\alpha_0 + \alpha_1 \cos \omega)$  for the conductivity, and we shall neglect the seasonal terms containing  $\sin \delta$ . To the first order in  $\alpha_1$  the following are the values of  $q_m^n$  and  $r_m^n$  for the principal 24- and 12-hour longitude harmonics :—

$$(67) \quad \left\{ \begin{array}{lll} r_1^1 = \frac{3}{10}, & r_3^1 = -\frac{1}{45}, & q_3^3 = \frac{1}{90}, \\ r_2^0 = -\frac{1}{2} \frac{9}{52} \alpha_1 \cos \delta, & r_4^0 = \frac{1}{70} \alpha_1 \cos \delta, & \\ q_2^2 = \frac{2}{63} \alpha_1 \cos \delta, & q_4^2 = -\frac{1}{840} \alpha_1 \cos \delta, & \end{array} \right.$$

The values in the first line of (67) necessarily agree with (63). This calculation is very incomplete, but it will sufficiently illustrate the discussion of the longitude terms in the magnetic variation, and until the main part of the phenomenon is better accounted for, it is hardly worth while to make a more elaborate determination of  $q_m^n$  and  $r_m^n$ .

The above investigation gives the method by which the electric current function  $\mathfrak{R}$  is obtained. MAXWELL has shown that the magnetic potential corresponding to a term  $Q_m^n$  in  $\mathfrak{R}$ , at a radius  $R$  within the spherical current sheet, is given by

$$(68) \quad -4\pi (m+1) R^m Q_m^n / (2m+1) r^m.$$

Since the lower limit of the current sheet is probably fifty\* or more miles above the earth's surface (the radius of which we denote by  $R$ ), the mean value of  $r$  may be perhaps 2 per cent. greater than  $R$ . In this case, for some of the higher harmonics in the Tables F and J, such as  $Q_5^4$ , the factor  $(R/r)^m$  will not be quite negligible, and later it will be again referred to (§ 23).

We have so far assumed that  $\tau$ ,  $n$ ,  $s$  are all integers, so that the periodicities, with regard to time, of the atmospheric oscillation and conductivity are commensurate. In the case of the lunar diurnal atmospheric oscillation and the atmospheric conductivity (which depends on solar time) this is not the case. The difficulty may be overcome in a fairly accurate way by regarding the conductivity as a function whose

\* Cf. §§ 21, 24.

period is a lunar day, and allowing for the slight difference between this and the time period by supposing it to have a slowly varying phase. Thus if  $t$  in the above investigation represents solar time, and  $t_0$  represents lunar time, we may write

$$(69) \quad t = t_0 + \nu, \quad t_0 = t - \nu,$$

where  $\nu$  measures the lunar phase, and increases from 0 to  $2\pi$  during the interval between successive epochs of new moon. The atmospheric oscillation (47) now has the time factor  $\sin(\tau t_0 - \alpha)$  in place of  $\sin(\tau t - \alpha)$ . Now  $\tau t_0 - \alpha = \tau t - (\alpha + \tau \nu)$ . Hence, if we replace  $\alpha$  by  $\alpha + \tau \nu$ , the above investigation remains unchanged. The result must be interpreted in lunar time, however, so that a term  $p_m^n Q_m^n \sin(nt - \alpha)$  now becomes

$$(70) \quad p_m^n Q_m^n \sin(nt_0 - \alpha + \overline{n - \tau \nu}).$$

Thus the phase of the magnetic variation of the same period ( $n = \tau$ ) as the atmospheric oscillation remains invariable, while the phases of other components increase or decrease by whole multiples of  $2\pi$  during the lunar month. This is what is actually observed in the lunar magnetic variation, and the data of Part III. have been obtained by allowing for this. It will be noticed, however, that the components for which  $n$  is negative vary very rapidly in phase (by  $2(n' + \tau)\pi$  per lunar month,  $n'$  denoting the numerical value of  $n$ ). These terms are included in the solar diurnal magnetic variation (where their phase is constant), but not in the lunar diurnal magnetic variation as here computed.

### § 23. *The Relative Amplitudes of the Magnetic Variations.*

The theoretical results of § 22 will now be applied to the discussion of the *relative* amplitudes of the magnetic variations, leaving the absolute amplitudes and phases to be considered later.

In the case of the lunar diurnal magnetic variation, the nature of the monthly changes of phase for the different periodic components indicates that the fundamental atmospheric oscillation here concerned is semi-diurnal. The type is not known (§ 20), but our assumption of the form  $Q_2^2$  is perhaps not far from the truth.

According to the theory of § 22, the presence of components of other periods (with varying phases) indicates that the electrical conductivity of the atmosphere is not uniform and constant throughout the (solar) day. We will first consider what evidence is afforded, concerning the nature of the daily variation of conductivity, by the relative amplitudes of the harmonics of different periods.

The simplest law of variation for the latter is given by

$$(71) \quad 1 + a_1 \cos \omega.$$

The amplitudes of the magnetic variations  $Q_m^n$  produced by an atmospheric oscillation  $Q_2^2$ , corresponding to this law of variation of conductivity, are proportional to the values of  $\{m+1\}/\{2m+1\} p_m^n$ , where  $p_m^n$  is obtainable from Table O by writing  $\alpha_2 = 0$ . For the present we shall consider only the "annual" harmonics  $Q_{n+1}^n$  at the equinoxes, so that we shall also write  $\delta = 0$ . Since the atmospheric conductivity cannot be negative,  $\alpha_1$  cannot exceed unity. Table O shows that the subsidiary (*i.e.*, non-semi-diurnal) harmonics are greater the greater the value of  $\alpha_1$ . If we take  $\alpha_1 = 1$ , the theoretical amplitudes are found to have the following relative values,  $k$  being an undetermined constant; the observed equinoctial amplitudes in the lunar diurnal magnetic variation are added for comparison (*cf.* Table J); the ratios of the two sets of numbers are also given, assuming  $k$  to be such that the ratio for  $Q_3^2$  is unity:—

TABLE P.

	$Q_2^1$ .	$Q_3^2$ .	$Q_4^3$ .	$Q_5^4$ .
Theoretical relative amplitudes . . . . .	$15 \cdot 8k$	$7 \cdot 3k$	$0 \cdot 41k$	$-0 \cdot 00019k$
Observed amplitudes . . . . .	20·5	5·5	0·43	0·022
Ratio . . . . .	0·68	1·00	0·71	-0·007

The law (71) would clearly account for a considerable proportion of the harmonics  $Q_2^1$  and  $Q_4^3$ , but wholly fails in the case of the fourth harmonic  $Q_5^4$ , both as regards magnitude and sign. This comparison shows, however, that the daily variation of electrical conductivity is at least as great as that indicated by the formula  $1 + \cos \omega$ , since if  $\alpha_1$  were less than unity the amplitudes of  $Q_2^1$  and  $Q_4^3$  would be still smaller in comparison with  $Q_3^2$ ; also it shows that the sign of  $\alpha_1$  must be positive, *i.e.*, that the conductivity must be great by day and small by night, since the observed phases of  $Q_2^1$  and  $Q_4^3$  are the same as that of  $Q_3^2$ . If  $\alpha_1$  were negative, their theoretical phases would be opposite to that of  $Q_3^2$ .

A more pronounced variation of the atmospheric conductivity can be represented by the law

$$(72) \quad 1 + \alpha_1 \cos \omega + \alpha_2 \cos^2 \omega.$$

In my first paper on the lunar diurnal magnetic variation I considered the following special case of this law\*

$$(73) \quad 1 + 3 \cos \omega + \frac{9}{4} \cos^2 \omega = \left(1 + \frac{3}{2} \cos \omega\right)^2,$$

which is never negative, and gives a much greater ratio of day to night conductivity than does (71). With the aid of Table O the following values of the relative

\* 'Phil. Trans.,' A, vol. 213. On p. 304 a graph of this expression is given.

theoretical equinoctial amplitudes of the magnetic variations are obtained.\* The ratios of these to the observed values of Table J are also given.

TABLE Q.

	$Q_2^1$ .	$Q_3^2$ .	$Q_4^3$ .	$Q_5^4$ .
Theoretical relative amplitudes . . . . .	$25.3k$	$6.5k$	$0.65k$	$0.021k$
Calculated	1.0	1.0	1.3	0.8
Observed				

The relative amplitudes of all four components now show very fair agreement. Clearly (72) is a great improvement on (71) as a representation of the law of variation of the electrical conductivity. Probably the true law is more complicated than (72), but we shall not trouble to seek for a closer approximation. The point gained is that, by taking a law which gives a general representation of the variation known to be probable on other physical grounds, we have been able to explain the presence and order of magnitude of magnetic variations of periods other than that of the primary atmospheric semi-diurnal oscillation.

The calculated amplitudes of the variations arising from  $p_2^{-1}$ ,  $p_3^{-2}$ , and so on, comparable with those in Table Q, are found to be

$$(74) \quad \begin{array}{cccc} Q_2^{-1} & Q_3^{-2} & Q_4^{-3} & Q_5^{-4} \\ -4.4 & 0.8 & 0 & 0 \end{array}$$

In the case of the lunar diurnal magnetic variations, however, these change their phases with great rapidity, and are not included in the "observed" amplitudes given in Table J.

We may proceed further to examine the seasonal changes in the relative amplitudes of the various components. The numbers in Table Q relate to the equinoctial variations, and are obtained by taking  $\delta$  to be zero in Table O. During the solstitial quarters, however,  $\delta$  is approximately 20 degrees. If this value is substituted, the following numbers, corresponding to those in Table Q, are obtained:—

$$(75) \quad \begin{array}{cccc} Q_2^1 & Q_3^2 & Q_4^3 & Q_5^4 \\ 24.0 & 6.5 & 0.61 & 0.018 \end{array}$$

\* The numbers given are  $60 \{(m+1)/(2m+1)\} p_m^n (R/r)^m$ , the factor 60 being inserted for convenience. The factor  $(R/r)^m$  allows for the fact that the magnetic variations are produced at some considerable height above the surface regions where observations are made;  $R/r$  is taken as 0.98 (*cf.* §§ 21, 22).

Formulae resembling those of Table O were given in my first memoir, but only carried as far as  $a_1^2$  and  $a_2$ ; in this paper some small corrections are made, and a further approximation is made by including the terms  $a_1^3$ ,  $a_1 a_2$ ,  $a_1^4$ ,  $a_1^2 a_2$ , and  $a_2^2$ . With the above values of  $a_1$  and  $a_2$  the results seem to show satisfactory numerical convergence.

From Table J it appears that the amplitudes of the three components  $Q_3^2$ ,  $Q_4^3$ ,  $Q_5^4$  are smaller at the solstices than at the equinoxes, while  $Q_2^1$  is approximately constant. If the lunar diurnal atmospheric oscillation resembles the corresponding solar diurnal variation, the amplitude is greater at the equinoxes than at the solstices; this probably explains most of the variation in  $Q_3^2$ ; our calculation just made would appear to indicate that, so far as the electrical conductivity is concerned,  $Q_3^2$  is constant throughout the year. Besides the variation in the amplitude of the atmospheric motion  $Q_2^2$ , which should affect equally all the magnetic variations  $Q_2^1$  to  $Q_5^4$ , it would appear that the non-semi-diurnal components should be further reduced at the solstices, because of the conductivity effect. Here the theory and observation are only in very rough agreement, since  $Q_2^1$  shows a relative increase at the solstices, while the observed decreases of  $Q_4^3$  and  $Q_5^4$  are much more than the theory would predict.

Similar discrepancies are met with when we examine the "seasonal" magnetic components  $Q_n^n$ . These are represented in Table O by the terms involving odd powers of  $\sin \delta$ , which vanish at the equinoxes and change sign between summer and winter. The following values of their relative amplitudes are calculated in the same way as the numbers in Table Q:—

	$Q_1^1$ .	$Q_1^{-1}$ .	$Q_2^2$ .	$Q_2^{-2}$ .	$Q_3^3$ .	$Q_3^{-3}$ .	$Q_4^4$ .	$Q_4^{-4}$ .
(76)	-4.2	-24.3	4.7	0	0.46	0	0.0012	0

The remarkable feature here is the excess of  $Q_1^{-1}$  over  $Q_1^1$ . The amplitude in Table J is that of  $Q_1^1$ . In any case, however, the above numbers, which should roughly agree with those given in Table J for the solstitial inequality (since the numbers in Table Q are approximately equal to the equinoctial data), are much smaller than the observed values.

Before considering this point further, we shall turn to the solar diurnal magnetic variation data of Table F. In this case we have no such certain means as before of determining the period or periods of the atmospheric oscillations to which the magnetic variations are due. We may notice, however, the similarity of phase ( $e_m^n$ ) between the four solar harmonics  $Q_{n+1}^n$  in Table F, which is at least as close as that shown in the lunar Table J. So far as this goes, there is a strong suggestion that the solar diurnal magnetic variations also arise from a single atmospheric oscillation.

For comparison of the amplitudes of the lunar and solar magnetic variations reference will be made to either the potentials derived from the horizontal force variations above (Tables C, G) or to those of the external fields  $\mathbf{E}_m^n$  (Tables F, J). The discussion in Part IV. has shown that the potentials from the vertical force variations lead to fairly similar sub-divisions of  $A_m^n$ ,  $B_m^n$  between the external and internal fields.

From Table C the amplitudes  $C_{n-1}^n$  may be calculated for the solar diurnal magnetic variation. The relative amplitudes are nearly the same in 1905 and 1902, as the following table indicates:—

TABLE R.—Ratios of  $C_{n+1}^n$  in 1905 and 1902.

	$C_2^1$ .	$C_3^2$ .	$C_4^3$ .	$C_5^4$ .
Equinox . . . . .	1.43	1.31	1.25	1.35
Solstice . . . . .	1.47	1.31	1.32	1.60

The increased amplitudes all round, in years of sunspot maximum, naturally point to a general increase in the electrical conductivity of the atmosphere, with little or no change in its functional dependence on the sun's zenith distance.

The lunar magnetic data refer to the quieter years of a solar cycle, and may be compared with the solar data for a mean of 1905 and 1902, giving double weight to the latter year. The comparison leads to the following results (the tenfold unit in Table F, as contrasted with Table J, should be remembered):—

TABLE S.—Ratios of Solar and Lunar  $E_{n+1}^n$ .

	$C_2^1$ .	$C_3^2$ .	$C_4^3$ .	$C_5^4$ .
Equinox . . . . .	21.8	10.4	10.0	7.6
Solstice . . . . .	18.5	10.2	10.0	7.3

The ratios for the last three harmonics are in moderate agreement, especially in view of the considerable seasonal variations in the amplitudes of the third and fourth harmonics. If the ratios for the first harmonic had also been about 10, little doubt could remain that all four are produced by a single semi-diurnal atmospheric oscillation, roughly of type  $Q_2^2$ , as in the case of the lunar diurnal magnetic variations.

Even as it is, the fact that the harmonic  $Q_2^{-1}$  will appear with  $Q_2^1$  in the solar, but not in the lunar data, leaves a possibility of explaining the above figures without introducing a further atmospheric oscillation into the theory. The agreement of phase, and the apparently more fundamental character of the 12-hour oscillation as compared with that of the 24-hour period (at the earth's surface) favour this solution.

It is worth while, however, to examine the magnetic effects of a 24-hour atmospheric oscillation. Considering the amplitudes of the magnetic components, on the



same relative scale as the results in Table Q, for 12-hour and 24-hour atmospheric movements of the same equatorial amplitudes, the following values are obtained (*cf.* Table I., p. 299, 'Phil. Trans.,' A 213):—

$$(77) \quad \begin{cases} 12\text{-hour wave} & . & . & . & Q_2^1 & Q_3^2 & Q_4^3 & Q_5^4 \\ & & & & 25 & 6\cdot5 & 0\cdot65 & 0\cdot021 \\ 24\text{-hour wave} & . & . & . & 23 & -3\cdot3 & 0\cdot24 & 0 \end{cases}$$

The ratios in Table S might be reproduced more closely if a 24-hour atmospheric wave of about one-third the amplitude of, and in phase with, the 12-hour wave is supposed present in the solar diurnal variations.

The seasonal changes in the amplitudes of the annual harmonics in the solar diurnal magnetic variations are similar to those in the lunar variations. The diminution at the solstices is partly explicable by the similar decrease in the semi-diurnal barometric variation (§ 19), which in each case takes place without appreciable change of phase. The further reductions in the higher magnetic harmonics, at the solstices, is to be referred to the effect of the dependence of conductivity on the solar zenith distance  $\omega$ , though the law (73) has been seen to be insufficient to account altogether for the observed changes. The necessary modification of (73) would seem to be in the direction of a more rapid diminution of  $\rho$  (the conductivity) as  $\omega$  increases from 0 degree to 90 degrees. This is probable on other grounds (§ 21), but the theoretical discussion of its consequences would be a very laborious task.

The same modification would also increase the *theoretical* values of the seasonal harmonics  $Q_n^n$ , which for the lunar diurnal magnetic variations were found to be three or four times too small, relatively to the annual harmonics, when compared with the observed data. But a more serious difficulty arises here. If we examine the solar diurnal seasonal harmonics it is found that they are in fair agreement with the theoretical values from (73), except in regard to phase. The seasonal harmonics in the lunar variation are, in fact, nearly thrice as great compared with the annual harmonics as in the solar variation. This is immediately evident in the initial data of this paper (*cf.* Tables III. ( $\alpha$ ) and III. ( $\gamma$ ) with VI. ( $c$ ) and VI. ( $d$ )), and the following ratios of the solar and lunar seasonal harmonics  $E_n^n$  show the same thing:—

$$\begin{array}{cccc} E_1^1 & E_2^2 & E_3^3 & E_4^4 \\ 7\cdot6 & 3\cdot4 & 4\cdot1 & (14\cdot7) \end{array}$$

These numbers are comparable with those of Table S; the same preponderance in the ratio for the diurnal harmonic is seen here, but the first three of these ratios are less than half as great as those for  $E_{n+1}^n$ .

If we suppose the electrical conductivity such that the seasonal harmonics due to an atmospheric oscillation  $Q_2^2$  have the relative magnitudes shown in the lunar

diurnal magnetic variations, the defect in the solar variations would seem to require us to assume some counter-balancing seasonal magnetic harmonics in the latter, due to atmospheric oscillations of type other than  $Q_2^2$ . These can hardly be present in the lunar diurnal atmospheric movements, though no observational evidence is available. As regards the solar diurnal motions, the semi-diurnal barometric oscillation is strikingly symmetrical about the equator throughout the whole year. The 24-hour surface variation, though less definite and well-determined, also seems free from unsymmetrical components of type such as  $Q_2^1$ . The symmetrical oscillation  $Q_1^1$ , which has been suggested as a co-factor with  $Q_2^2$  in the production of the annual magnetic harmonics, would also contribute seasonal harmonics. The amplitudes of the first two of these, comparable with (76) as are the two sets of numbers in (77), are approximately as follows:—

$Q_1^1$ .	$Q_2^2$ .
18	3

The first of these would tend to neutralize the corresponding harmonic due to  $Q_2^2$ , while in the second case there would be re-inforcement. The question of the exact origin of the seasonal variations must remain unsolved for the present, both their amplitudes and their phases (in view of the negative signs prefixed before the theoretical values of  $Q_1^1$ ) being difficult to explain. But as regards the presence of a 24-hour oscillation in the upper atmosphere, the calculations of § 26 indicate that there are possibilities of its local production by heating effects in the conducting layer, even if the surface variation of the same period does not persist into the upper atmosphere.

§ 24. *The Absolute Values of the Amplitudes and of the Electrical Conductivity in the Upper Atmosphere.*

We have provisionally concluded that both the solar and lunar diurnal magnetic variations are, in the main, due to semi-diurnal atmospheric oscillations, roughly of type  $Q_2^2$ , in conjunction with a variable electrical conductivity which may be approximately represented by the formula (73). We will therefore now confine ourselves to the principal magnetic harmonics,  $Q_3^2$ , in discussing the absolute magnitudes of the several variables involved in the theory.

It is clear that if, as we suppose, the solar and lunar magnetic variations are similarly produced, the ratio of the amplitudes of  $Q_3^2$  in the two cases will be equal to the ratio of the amplitudes of the corresponding semi-diurnal atmospheric oscillations. The former ratio was found in § 23 to be about 10. This is smaller than the ratio of the solar and lunar semi-diurnal barometric variations which, at Batavia for instance, is (1.00/0.063), or approximately, 16. It has already been noted, however, that (writing  $\delta p$  for the pressure variation at a height where the pressure is  $p$ )  $\delta p/p$  diminishes somewhat with height (§ 19); HANN has explained

such changes as due to the temperature variations in the lower regions of the atmosphere. As regards the lunar day, regular temperature variations should be almost or quite non-existent, and  $\delta\rho/\rho$  should not alter with height. The relative decrease of the solar as compared with the lunar semi-diurnal atmospheric oscillation, from a ratio of 16 to one of about 10, may possibly be explained in this way.

In order to obtain a numerical estimate of the electrical conductivity of the region in which the magnetic variations are produced, we will determine the constant  $K$  in the formula (40) by a comparison of the lunar diurnal atmospheric velocity potential (38) with the observed magnetic variation. Considering the equinoctial "annual" harmonic  $Q_3^2$ , from Table J, we find the amplitude (*cf.* 17) in C.G.S. units to be

$$(78) \quad 5.5 \cdot 10^{-7} R.$$

The theoretical value (§ 23) is

$$(79) \quad 4\pi \frac{m+1}{2m+1} \left(\frac{R}{r}\right)^m K_2^2 CK p_3^2$$

(where  $m = 3$ ), and, paying no attention to signs for the present,

$$(80) \quad C = \frac{2}{3}, \quad K_2^2 = 32.4R \cdot 0.010.$$

Substituting these values in (79), and equating the result to (78), we find that

$$(81) \quad K = 1.92 \cdot 10^{-6}.$$

Hence, approximately,

$$(82) \quad \rho e = 2 \cdot 10^{-6} (1 + 3 \cos \omega + \frac{9}{4} \cos^2 \omega).$$

At points directly beneath the sun ( $\omega = 0$ ) the value of  $\rho e$  thus given is  $12 \cdot 10^{-6}$ . This calculation applies to years of low solar activity. At times of solar maximum (*cf.* Table R, p. 60)  $\rho e$  would rise to  $17 \cdot 10^{-6}$  or  $20 \cdot 10^{-6}$ . Moreover, as we shall see when we come to take self-induction into account (§ 26), all these values must be increased by 30 or 40 per cent., and the probable maximum value of  $\rho e$  which has to be explained in any theory of the conducting layer must be, approximately,

$$(83) \quad 25 \cdot 10^{-6}.$$

SCHUSTER'S approximate determination of  $\rho e$  was  $3 \cdot 10^{-6}$ .\* The larger value here obtained accentuates the difficulties in the explanation of the conducting layer which have been mentioned in § 21; but there seems no reason to suppose that they are insuperable.

\* SCHUSTER, 'Phil. Trans.,' A, vol. 208, p. 181.

§ 25. *The Heating Effects of the Upper Air Currents.*

In his second memoir (p. 185) SCHUSTER remarked that a further consequence of the theory outlined for the magnetic variations would be the production of a sensible heating effect by the electric currents circulating in the low pressure conducting layer. This, it was suggested, might assist in the explanation of the isothermal layer of the atmosphere. The primary cause of the approximate constancy of temperature in the stratosphere is now well understood, and the suggested heating effect can have only a secondary influence on the phenomenon. For other reasons, however, it seems desirable to examine numerically this thermal consequence of the theory. The results prove to be of some interest, and may explain part of the difference between the solar and lunar diurnal magnetic variations.

If the conductivity of the upper atmosphere is small during the night hours, the electric currents in question will flow entirely or mainly in the sunlit hemisphere. The heating effect is proportional to the square of the current, so that all the harmonics in the current function, whatever their period, contribute to the heating of this one hemisphere. As the earth revolves, the temperature of a given portion of the conducting layer will begin to increase at sunrise, and the increase will continue till the time of sunset. During the night hours cooling, mainly by radiation, must take place in order that the average state may remain steady. The conducting layer will thus suffer a diurnal change of temperature in which the 24-hour term is of much greater magnitude than any sub-component. This variation, moreover, is purely solar diurnal, including even the part due to the currents which produce the lunar diurnal magnetic variations. The temperature variation will be confined mainly to the conducting layer so far as conduction and convection are concerned (the kinematic viscosity will be very high in regions of such low pressure). A corresponding variation of pressure and of motion, not confined to the conducting layer, will result, and this may possibly account for the diurnal oscillation suggested by the magnetic variations. The phase should be constant throughout the year, though the amplitude would be expected to show a seasonal change. The most important question regarding these effects is that of their absolute magnitude, however, and we proceed to a rough numerical calculation with this in view.

For simplicity the solar diurnal magnetic variations will alone be considered, though the lunar variations will slightly increase the heating effect, to a degree depending very little on lunar phase.

The principal terms in the solar diurnal magnetic variation potential at the equinoxes (mean of 1905 and 1902) are as follows (*cf.* Table F):—

$$(84) \quad 10^6 \cdot \frac{\psi}{R} = -38Q_2^1 \cos(t + 33^\circ) - 5.0Q_3^2 \cos(2t + 26^\circ) - 0.39Q_4^3 \cos(3t + 40^\circ).$$

Only the external variation field is considered here, of course. The corresponding terms in the current function  $\mathfrak{K}$  are consequently (*cf.* 68) given by

$$(85) \quad \frac{4\pi \cdot 10^6}{R} \mathfrak{K} = 63Q_2^1 \cos(t+33^\circ) + 8.7Q_3^2 \cos(2t+26^\circ) + 0.70Q_4^3 \cos(3t+40^\circ) \\ = 189 \sin \theta \cos \theta \cos(t+33^\circ) + 130 \sin^2 \theta \cos \theta \cos(2t+26^\circ) \\ + 74 \sin^3 \theta \cos \theta \cos(3t+40^\circ)$$

neglecting the factors  $(R/r)^m$ , for simplicity.

The energy expended per second in overcoming the resistance to current flow, in the conducting layer of thickness  $e$ , as given by

$$(86) \quad \iint \frac{1}{\rho e} \left\{ \left( \frac{\partial \mathfrak{K}}{R \partial \theta} \right)^2 + \left( \frac{\partial \mathfrak{K}}{R \sin \theta \partial \lambda} \right)^2 \right\} R^2 \sin \theta \, d\theta \, d\lambda.$$

In order to avoid excessive calculation, several approximations will be made. The current function (85) is such that the currents in the dark hemisphere are small, the various harmonics largely neutralizing one another there, and reinforcing one another in the sun-lit hemisphere. We shall imagine the three terms of (85) combined into one, however, which we shall suppose confined to one hemisphere. Since the sum of their squares is less than the square of their sum, we shall represent  $\mathfrak{K}$ , for this purpose, by the approximation

$$(87) \quad \frac{200R}{4\pi \cdot 10^6} \sin^2 \theta \cos \theta \cos 2t.$$

Also instead of the variable factor  $1/\rho e$  we shall use the constant approximation  $1/(\rho e)_m$ , where  $(\rho e)_m$  is an average value of (82) over the daylight hemisphere. The adopted value of  $(\rho e)_m$  will be\*  $8 \cdot 10^{-6}$  or, allowing for the correction due to self-induction, approximately  $10^{-5}$ .

When these values are substituted in (86), and the integration is taken over one hemisphere, the total expenditure of energy per second is found to be

$$(88) \quad \frac{3}{5} \pi \left( \frac{200R}{4\pi \cdot 10^6} \right)^2 \frac{1}{10^{-5}},$$

or, in watts,

$$(89) \quad \frac{3}{5} \pi \frac{10^{-7}}{10^{-5}} \left( \frac{200R}{4\pi \cdot 10^6} \right)^2.$$

The mean value over this hemisphere, per unit area, expressed in gramme-water-centigrade units, is consequently

$$(90) \quad \frac{1}{4.18} \frac{16}{35} \frac{10^{-7}}{10^{-5}} \left( \frac{200R}{4\pi \cdot 10^6} \right)^2 = 2.7 \cdot 10^{-13}.$$

\* *Cf.* the table of values of  $1 + 3 \cos \omega + \frac{9}{4} \cos^2 \omega$  on p. 303, 'Phil. Trans.,' A, vol. 213,

As the heating of any volume element proceeds continuously for twelve hours, the total thermal energy communicated during the daylight hours (and lost during the night time) is

$$(91) \quad 2.7 \cdot 10^{-13} \cdot 43,200 = 1.2 \cdot 10^{-8}.$$

This refers to one square centimetre of the conducting layer of thickness  $e$ , and it may be noticed that the calculation is independent of  $e$  and of the situation of the layer.

The pressure variation produced by this temperature change is much more uncertain, since the heating effect depends greatly on the density of the atmosphere of the conducting layer; also the variation of pressure will be less than that calculated from the equation  $\partial p/p = \partial T/T$ , on account of the yielding of the adjacent atmospheric layers. If we suppose that the conducting layer lies between 90 and 140 km. above the earth's surface, its mass per square centimetre column is

$$(92) \quad 760 \cdot 2 \cdot 10^{-6} \cdot 13.6 \text{ gm.},$$

13.6 being the density of mercury, and the difference of the pressures at top and bottom being approximately  $2 \cdot 10^{-6}$  atmosphere. The specific heat of air at the temperature of the atmosphere is about 0.24 (at constant pressure), while that of hydrogen is about 3.4. For the purpose of an approximate calculation we may take the specific heat as unity. In this case the total rise of temperature which would be produced by the amount of heat (91), in the above mass of gas, provided there were no loss, would be

$$6 \cdot 10^{-6}$$

in degrees centigrade. Hence  $\partial p/p$ , which must be less than  $\partial T/T$ , cannot be so great as  $3 \cdot 10^{-8}$ . This is negligible compared with the estimated amplitude of the pressure variation due to the atmospheric oscillation  $Q_2^2$ , which in the upper air is approximately 1/760 or  $1.3 \cdot 10^{-3}$  (assuming a surface amplitude of two millimetres of mercury, and a reduction in  $\partial p/p$  of about one-half, in the conducting layer, § 24).

In order that the pressure variation due to the electric heating of the conducting layer might be comparable with that due to the main atmospheric oscillation  $Q_2^2$ , the pressure of the region in which the conducting layer is situated would have to be of the order  $10^{-10}$  atmosphere. Assuming the existence of the hydrogen layers mentioned in § 21, this pressure would be attained only at a height of more than 800 km. The pressure is of the order required for the ionisation of the conducting layer by ultra-violet radiation, according to SWANN'S calculation; but it seems more probable that the conducting layer is at a lower level.

§ 26. *Discussion of the Phases of the Magnetic Variations.*

The explanation of the phases of the magnetic variations is, perhaps, the most difficult part of the present problem. The data to be reconciled are as follows. The various annual harmonics in the solar and lunar diurnal magnetic variations are approximately in agreement amongst themselves, the time factors being approximately as below, in the two cases

$$(98) \qquad \qquad \qquad (\text{Solar}) \qquad - \cos (nt + 25^\circ),$$

$$(99) \qquad \qquad \qquad (\text{Lunar}) \qquad - \cos (nt + 78^\circ).$$

Neglecting self-induction and the small terms  $p_m^{-n}$  (§ 22), the theory of § 22 indicates that the velocity potentials of the atmospheric oscillations responsible for these magnetic variations should have the *same* phase, the negative sign in (68) and the negative sign of C (*cf.* 47, 51, 68) neutralizing one another.

If the simple relation (31) holds good between the pressure variation and atmospheric velocity potential, the time factors in the pressure variations corresponding to (98) and (99) should be

$$(100) \qquad \qquad \qquad (\text{Solar}) \qquad \sin (2t - 155^\circ),$$

$$(101) \qquad \qquad \qquad (\text{Lunar}) \qquad \sin (2t - 102^\circ).$$

The factor  $n$  is here written as 2, since the fundamental pressure changes appear to be semi-diurnal.

The observed pressure variations at the earth's surface (§§ 19, 20) have the time factors

$$(102) \qquad \qquad \qquad (\text{Solar}) \qquad \sin (2t + 154^\circ) = \sin (2t - 206^\circ),$$

$$(103) \qquad \qquad \qquad (\text{Lunar}) \qquad \sin (2t + 65^\circ) = \sin (2t - 295^\circ).$$

There is consequently no kind of agreement between the observed and calculated pressure variations in the lunar diurnal case. In the solar case the two variations agree better, but it must be remembered that the observed phase diminishes with height to a considerable extent (90 degrees or possibly more—*cf.* (91)), so that the agreement between (100) and (102) would not hold good if the latter had represented the pressure variation as it is supposed to exist in the upper atmosphere, *viz.*, approximately

$$(104) \qquad \qquad \qquad (\text{Solar}) \qquad \sin (2t - 296^\circ).$$

The correction to the calculated magnetic variations produced by a given atmospheric motion, due to self-induction, may be considered at this stage. In place of a time factor  $\cos(nt + e_0)$ , as given by the method of § 22, the factor  $\cos(nt + e_0 - e_m^n)$  must be used, where\*

$$(105) \quad \tan e_m^n = \frac{2\pi}{86,400} \cdot \frac{4\pi R n \rho e}{2m+1},$$

$m$  being the degree of the harmonic with which the time factor is associated. If we take  $5 \cdot 10^{-6}$  as a mean value of  $\rho e$  throughout the day and night, the following values of  $e_m^n$  are yielded by the formula (105).

$$(106) \quad \left\{ \begin{array}{llll} e_2^1 = 30^\circ, & e_3^2 = 40^\circ, & e_4^3 = 44^\circ, & e_5^4 = 47^\circ, \\ e_1^1 = 44^\circ, & e_2^2 = 49^\circ, & e_3^3 = 51^\circ, & e_4^4 = 52^\circ. \end{array} \right.$$

These figures are only rough, since the non-uniform conductivity may considerably affect the theoretical formula (105). It may be noticed that the lag of phase, owing to self-induction, increases with the frequency of the harmonic, so that self-induction cannot explain the apparent *increase* of phase with frequency which is observed in the solar diurnal magnetic variation (Table F).

Self-induction will also diminish the amplitudes of the magnetic variations by a factor  $\cos e_m^n$ . This will not greatly affect the *relative* magnitudes of the various magnetic harmonics, but it will affect our estimate of the magnitude of  $\rho e$  in § 24, and of the heating effects in § 25. The calculated value of  $\rho e$  would appear to be increased on this account by 30 or 40 per cent., and this, again, would slightly increase the above values of  $e$ .

Taking into account the above phase changes due to self-induction, the calculated time factors in the pressure variations are modified as follows:—

$$(107) \quad \text{(Solar)} \quad \sin(2t - 115^\circ),$$

$$(108) \quad \text{(Lunar)} \quad \sin(2t - 62^\circ).$$

When these are compared with (104) and (103), the “calculated—observed” phase differences are found to be

$$(109) \quad \text{(Solar)} \quad +181^\circ, \quad \text{(Lunar)} \quad +233^\circ.$$

These values almost suggest that a mistake in sign has crept into the calculation of the magnetic from the pressure variations, but the signs have been carefully

\* Cf. MAXWELL'S ‘Electricity and Magnetism,’ II., § 672, or SCHUSTER, ‘Phil. Trans.,’ A, vol. 208, p. 172.



examined without detection of error, and they also agree with those in SCHUSTER'S investigation. We must conclude that the connection between the pressure and magnetic variations is decidedly less simple than our theory has so far assumed.

One way in which this can easily be demonstrated may be indicated. If the phase of the solar diurnal pressure variation diminishes with height through 90 degrees, its phase will agree with that of the lunar diurnal barometric variation at the earth's surface. The former change of phase is partly due to the solar semi-diurnal temperature variation in the successive layers of air, and this portion of the change will presumably have no counterpart in the lunar barometric variation. The remaining part, if any, may be ascribed to friction, and this may also affect the lunar variation to a similar extent. On this hypothesis, the solar semi-diurnal oscillation of the atmosphere should be ahead of its lunar counterpart, while the corresponding magnetic variation *lags behind* the lunar magnetic variation by about 43 degrees. It would appear, therefore, that the solar pressure variation must diminish in phase, relatively to the lunar variation, by  $(154^\circ - 65^\circ) + 43^\circ$ , *i.e.*, through 128 degrees approximately. Part of this may be ascribed to temperature, but if any considerable portion is due to friction the lunar variation must be likewise affected to some extent, so that the balance of the above 128 degrees, after the "temperature" portion of it is subtracted, must be a differential friction effect. Therefore either the diminution of phase due to temperature or that due to pressure, or both, must be larger than is generally imagined. It may be noted that the frictional effects usually referred to in this connection are those due to skin friction along the earth's surface, or the eddy friction which has recently been brought into prominence by Major G. I. TAYLOR.\* True viscosity is generally regarded as so small as to be negligible, but this will hardly be the case in regions where the density is extremely small.

The lunar diurnal pressure variation can hardly be other than of tidal origin. The difference of its observed phase from that which the equilibrium theory of the tides would predict ( $\sin(2t + 90^\circ)$  instead of the observed  $\sin(2t + 65^\circ)$ ) may, perhaps, be attributed to friction in the lower strata of the atmosphere. If the phase diminishes upwards to the value (108), the total actual retardation will be 127 degrees, or, measured from the theoretical tidal value, 152 degrees. It would be interesting to know whether there is any possibility of accounting for such large changes of phase by skin friction and viscosity. If not, there may be some hope of an explanation by a modification of the equation (31) connecting the pressure variation with the atmospheric motion.

Until the phases of the annual harmonics in the magnetic variations are explained, those of the seasonal harmonics are not likely to be accounted for, and they will therefore not be discussed here.

\* "Eddy Motion in the Atmosphere," G. I. TAYLOR, 'Phil. Trans.,' A, vol. 215, p. 1 (1915). *Cf.* also 'Roy. Soc. Proc.,' A, vol. 92, p. 196 (1916).

§ 27. *The Residual Variations, and the Terms not Dependent Solely on Local Time.*

Our discussion of the magnetic variations has so far related entirely to the simple analytical representation of the observed data which has been described in §§ 10, 13. In this representation the only terms considered were those dependent on local time. It remains, therefore, to discuss the residuals in Tables III. and VI., and to examine how far they are to be attributed to the presence of variations not depending solely on local time (*cf.* § 22).

In order to abbreviate this investigation, certain general features exhibited by the residuals will be described without setting out the detailed figures. In the first place, the mean residuals for any of the nine groups of observatories are generally similar for the years 1905 and 1902, and, in the case of the "annual" residuals in Tables III. ( $\alpha$ ) and III. ( $\beta$ ), for the equinoxes and solstices. They are, however, greater for 1905 than for 1902, and greater at the equinoxes than at the solstices. If all the nine group mean residuals from any Table are combined numerically (counting all signs positive), the ratio of the 1905 and 1902 sums, or of the equinoctial and solstitial sums, can readily be determined. The former ratio is rather less than those of Table R, being approximately 1.2, for the "annual" residuals. The increase, such as it is, confirms the view that the residuals are a real part of the phenomenon, and do not merely represent accidental errors of observations.

The ratio of the equinoctial to the solstitial "annual" residuals is greater, being about 1.4. This is shown in the case of all three magnetic elements, and all four periodic components, the separate mean ratios for these ( $n = 1, 2, 3, 4$ ) being 1.4, 1.2, 1.5 and 1.6. These increases roughly correspond to those shown by the  $Q_{n+1}^n$  harmonics already discussed.

The group-mean residuals, in the mean of equinox and solstice and of 1905 and 1902, taken from Tables III. ( $\alpha$ ) and ( $\beta$ ), are collected in Table T. The "seasonal" residuals from Tables III. ( $\gamma$ ) and ( $\delta$ ) will not be considered.

The largest residuals in Table T occur in the column relating to the 24-hour component variation of North force. The corresponding residuals for the West force are small and may well represent merely local peculiarities at the various observatories. If the variations indicated by the North force residuals have a potential of simple form, this must be of type  $Q_m^0$ , since this is the only type which yields North force terms without contributing also to the West force variations. In § 22 it was shown that the inclination of the magnet to the geographical axis of the earth could give rise in the current function to the variation

$$(110) \quad 6K_2^2CK \tan \phi \cdot r_m^0 Q_m^0 \sin (t - \lambda_0 - \alpha)$$

TABLE T.—Mean Residuals,  $\frac{1}{2}$  (Spring + Autumn) and  $\frac{1}{2}$  (Summer + Winter) combined, for the Two Years 1905 and 1902 taken together.

West.		North.		Radial.	
<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>
24-hour Component.					
- 4	- 19	- 18	6	- 42	- 28
1	- 17	- 62	- 1	- 24	1
17	- 2	- 42	1	- 7	8
6	11	- 102	42	- 25	- 11
- 18	12	- 52	56	16	10
- 6	12	27	21	28	2
8	- 36	8	- 12	- 57	11
- 2	- 17	- 10	15	- 56	- 20
14	36	- 16	- 22		
12-hour Component.					
- 5	- 5	11	- 4	- 2	6
- 6	- 11	- 4	- 8	3	3
3	- 4	- 20	5	1	3
15	2	- 36	42	- 4	- 8
0	0	- 2	52	2	11
12	- 7	5	12	6	- 21
11	- 32	- 22	3	- 14	- 14
20	- 24	- 32	- 10	24	- 3
18	21	16	- 16		
8-hour Component.					
- 1	1	2	2	1	2
- 1	2	2	6	4	4
10	- 1	17	14	4	4
2	- 9	0	24	- 2	0
- 4	- 3	7	30	- 1	2
10	- 10	1	1	- 1	- 15
6	- 15	- 3	7	- 15	- 9
16	- 20	26	- 14	24	4
17	- 14	- 16	4		
6-hour Component.					
- 1	4	1	0	4	3
0	4	2	2	3	2
4	1	9	6	2	1
0	- 7	7	5	- 2	- 1
0	- 6	7	6	- 1	1
0	- 9	- 2	0	- 4	- 5
- 1	- 5	- 2	9	- 5	- 2
10	- 7	4	- 8	7	4
4	- 14	- 8	4		

(among others), and this is of the above type. The chief coefficient  $r_m^0$  is  $r_2^0$  (*cf.* (67)), which is of the order  $-\frac{1}{12}\alpha_1$ . The longitude  $\lambda_0$  is measured from the meridian  $68^\circ$  West of Greenwich, while  $\tan \phi$  is approximately 0.2. Assigning to  $\alpha_1$  the value 3, and to  $\alpha$  and  $K_2^2CK$  the values 250 degrees and  $-33R \cdot 10^{-7}$ , deduced roughly from the mean solar semi-diurnal harmonic  $Q_3^2$ , (110) becomes

$$(111) \quad 10Q_2^0 \sin(t - \lambda_0 - 250^\circ) \cdot 10^{-7}R.$$

The corresponding term in the magnetic variation is

$$-6Q_2^0 \sin(t - \lambda_0 - 250^\circ) \cdot 10^{-7}R.$$

The North force variation deducible from this is

$$-9 \sin 2\theta \{ \sin(\lambda_0 + 250^\circ) \cos t - \cos(\lambda_0 + 250^\circ) \sin t \},$$

the unit being  $10^{-7}$  C.G.S. This is clearly far too small to account for the residuals referred to above, and, moreover, it is found that the signs do not agree at all consistently with those in the North force  $\alpha_1$  column of residuals. This is owing to the factors  $\sin(\lambda_0 + 250^\circ)$  and  $\cos(\lambda_0 + 250^\circ)$ , which vary considerably from group to group for the observatories here dealt with. The same difficulty is met with in regard to the 12-hour North force residuals; here also, moreover, the amplitude of the "longitude" harmonic (in this case the principal one is  $r_1^1Q_1^1 \sin(2t - \lambda_0 - \alpha)$ ) is too small to explain the observed residuals.

It may be noted that the magnetic variations depending on longitude would theoretically be smaller if, as suggested in § 23, the main oscillation responsible for the magnetic variations be semi-diurnal, than on the hypothesis considered by SCHUSTER; they are therefore less likely to serve as a check on the theory.

I have tried to represent the residuals of Table T by harmonics depending on the time of some standard meridian, but with little success, and I am inclined to think that they depend on local time so far as they are not merely irregularities peculiar to particular observatories. The latter can hardly be the case with regard, at any rate, to the 24-hour North force residuals; in other cases the position is much less clear. These North force residuals seem to present a difficult problem, since they apparently cannot be represented by any simple potential function. It may be recalled that the amplitude of the semi-diurnal pressure variation seems to vary with latitude according to the law  $\sin^3 \theta$ , instead of  $\sin^2 \theta$  (or  $Q_2^2$ ) as we have supposed; the true law could only be represented by the introduction of other harmonics besides  $Q_2^2$  into our theoretical calculations. Another fact worth noting is that the South component of the semi-diurnal variation of wind velocity (at St. Helena) is markedly larger than that calculated from GOLD'S theory\* of the wind, barometric and temperature variations, while the East component seems to be in agreement with theory. Such

\* *Loc. cit. ante* (§ 19).

meridional atmospheric motions would produce electromotive forces along circles of latitude, which, again, would give rise to North force variations. It is possible that the germ of a satisfactory account of the above residuals is to be found in these tentative suggestions. Before developing them further, however, it would be desirable to examine the magnetic data more closely. But in spite of the residuals of Table T, and the points left unsettled in the previous discussion, the present analysis has revealed some important and previously unsuspected regularities in the diurnal magnetic variations, and I hope that others will thereby be encouraged to contribute further to their elucidation.

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[*Note added December 9, 1918.*—In an interesting Dissertation (Utrecht, September 22, 1917: 'K. Nederland. Met. Inst.,' De Bilt, No. 102; also, in abstract, in 'K. Ak. van Wet.,' Amsterdam, 26, pp. 293–299, 1917), published since this paper was written, Miss VAN VLEUTEN has analyzed and discussed the solar diurnal magnetic variations, in order to test the theory developed by Prof. SCHUSTER in his two memoirs. The conclusions arrived at are (*a*) that "the forces causing the diurnal variation, taken as a whole, do *not* possess a potential, although it remains always possible to deduce part of these forces from a potential," and (*b*) that "the cause of the diurnal variation certainly cannot be ascribed to nothing else but a system of currents exterior to the earth and currents within the earth induced by the former system."

These conclusions appear to rest mainly on the non-correspondence of the observed North force variations with those calculated from the simple potential representation of the West force variations (*cf.* § 9). But their physical implication is that electric currents traversing the earth's surface have an important share in producing the diurnal magnetic variations. This seems extremely improbable, and, instead of (*a*) and (*b*), the interpretation of the above fact of observation seems rather to be merely that the diurnal variations are somewhat complicated, so that their potential cannot be represented exactly by any *simple* combination of spherical harmonics. There are physical grounds for such a conclusion; in a paper recently communicated to the Cambridge Philosophical Society I have given reasons for supposing that two distinct agencies and atmospheric layers are involved in the production of the diurnal magnetic variations.

While the magnetic variation field does not give simple results on the application of spherical harmonic analysis, the latter is still the only convenient means which mathematics affords for discussing the relation between the external and internal current systems, and between the former and the atmospheric circulations indicated by the barometer. I do not think that on these points the main results obtained in the present paper are likely to be modified seriously upon further investigation, but that, especially when the parts of the diurnal variations, due to the two agencies above mentioned, are separated and independently treated, the theory will be confirmed and brought more closely into accordance with observation.]



TABLE I. (b) (1).—Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Equinoxes.  
 (b) Sunspot Minimum, 1902.  
 (1) The 24-hour Component.

Group No.	Observatory No.	West.				North.				Radial.			
		$a_1$ .		$b_1$ .		$a_1$ .		$b_1$ .		$a_1$ .		$b_1$ .	
		Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.
I.	1	46	76	46	77	-70	-93	6	23	7	1	-14	-15
	2	52	64	107	97	-55	-60	46	63	-	5	-15	-9
	3	41	70	53	87	-47	-58	5	25	-	-	-	-
II.	4	57	84	46	74	-64	-100	-	19	31	29	-12	-7
	5	18	39	62	90	-52	-66	4	42	22	16	4	4
	6	47	64	48	73	-87	-117	4	28	24	32	-1	-13
III.	7	58	85	51	85	-19	-59	-18	5	45	36	-5	-12
	8	39	78	55	88	12	-33	-6	30	35	35	6	12
IV.	9	45	57	66	83	-71	-94	36	34	-	-	-	-
	10	43	56	68	95	-64	-97	18	33	32	26	-19	-16
V.	11	32	12	-10	25	13	50	57	84	72	58	14	1
	12	5	21	69	85	75	29	-3	11	-	-	-	-
VI.	13	-6	44	18	51	141	129	-40	-15	41	67	0	-6
	14	16	60	4	27	197	175	-19	-26	82	82	-36	-39
	15	-15	50	-82	-48	161	144	-46	-65	-67	-55	-27	-10
VII.	16	-52	-33	-114	-81	37	6	15	45	-164	-165	-26	-4
	17	-10	-13	-106	-71	-96	-45	0	-22	-6	-9	-1	6
	18	-10	-13	-106	-71	-96	-45	0	-22	-6	-9	-1	6





TABLE I. (b) (2).—Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Equinoxes.  
 (b) Sunspot Minimum, 1902.  
 (2) The 12-hour Component.

Group No.	Observatory No.	West.				North.				Radial.			
		$a_2$ .		$b_2$ .		$a_2$ .		$b_2$ .		$a_2$ .		$b_2$ .	
		Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.
I.	1	30	54	58	63	-32	-48	5	26	17	22	2	-1
	2	11	78	86	46	-49	-31	48	59	22	20	9	3
	3	24	52	62	67	-17	-24	22	40				
II.	4	48	72	59	70	-36	-46	-2	29	30	41	0	1
	5	5	49	65	69	-38	-36	38	63	12	16	14	1
	6	37	63	56	69	-46	-53	0	25	37	40	-5	-9
III.	7	48	78	66	82	-5	-13	-8	23	38	25	-1	0
	8	36	77	64	74	20	1	19	61	31	34	0	6
IV.	9	57	88	67	63	-49	-31	41	57				
	10	54	88	74	78	-54	-46	36	59	27	33	-10	-15
V.	11	7	5	31	65	31	81	73	65	37	43	13	3
	12	39	88	66	55	27	24	16	18				
VI.	13	19	82	24	33	76	72	-35	-7	27	53	-18	-42
	14	30	97	22	23	106	83	-27	-19	49	42	-17	-23
VII.	15												
	16	-19	53	-77	-77	71	60	-30	-32	-41	-36	-26	-24
VIII.	17												
	18	-46	-7	-136	-111	48	44	-20	14	10	7	-8	-14
	20	-1	13	-112	-85	-62	-49	5	-14	-2	-5	-8	-2

TABLE I. (a) (3).—Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Equinoxes.  
 (a) Sunspot Maximum, 1905.  
 (3) The 8-hour Component.

Group No.	Observatory No.	West.						North.						Radial.					
		$a_3$ .		$b_3$ .		$a_3$ .		$b_3$ .		$a_3$ .		$b_3$ .		$a_3$ .		$b_3$ .			
		Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.		
I.	1	20	30	47	32	-35	-18	22	38	10	11	2	1	17	-7	-14	-23		
	2	10	53	16	8	-24	-10	5	25	17	-7	-14	-23	21	18	5	2		
	3	19	36	55	31	-31	-19	24	41	26	27	1	1	26	27	1	1		
II.	4	39	49	56	38	-33	-8	22	40	36	30	0	-5	17	13	9	-1		
	5	7	38	75	41	-45	-22	30	44	34	6	24	3	23	27	-1	-1		
	6	31	48	49	34	-28	-8	15	26	42	12	12	12	36	30	0	-5		
III.	7	39	53	67	42	-10	12	12	42	36	6	24	69	34	32	0	-3		
	8	45	76	70	36	-7	6	24	69	34	6	24	69	34	32	0	-3		
	9	28	62	43	17	-29	19	30	57	26	31	-2	-16	26	31	-2	-16		
IV.	10	25	71	51	32	-32	-12	25	67	18	22	-6	-11	18	22	-6	-11		
	11	26	90	82	38	-9	12	21	46	37	24	2	-12	27	36	18	-17		
	12	24	82	55	12	15	27	15	15	27	36	18	-17	27	36	18	-17		
V.	13	48	94	34	-17	31	32	-37	-32	35	27	-30	-73	-4	-11	-5	-13		
	14	-28	55	48	14	2	19	4	-3	-4	-11	-5	-13	-4	-11	-5	-13		
	15	-28	55	48	14	2	19	4	-3	-4	-11	-5	-13	-4	-11	-5	-13		
VI.	16	-25	18	-33	-52	40	33	-24	-23	-38	-26	0	-11	-32	-26	0	-11		
	17	-32	-24	-41	17	17	10	-11	-25	-38	-26	0	-11	-32	-26	0	-11		
	18	-62	-3	-74	-82	24	5	5	-20	-38	-26	0	-11	-32	-26	0	-11		
VII.	19	-38	-11	-80	-79	30	32	-19	4	-38	-26	0	-11	-32	-26	0	-11		
	20	-38	-11	-80	-79	30	32	-19	4	-38	-26	0	-11	-32	-26	0	-11		
	21	-10	9	-50	-53	-50	-38	18	20	-38	-26	0	-11	-32	-26	0	-11		
VIII.	18	-62	-3	-74	-82	24	5	5	-20	-38	-26	0	-11	-32	-26	0	-11		
	19	-38	-11	-80	-79	30	32	-19	4	-38	-26	0	-11	-32	-26	0	-11		
	20	-38	-11	-80	-79	30	32	-19	4	-38	-26	0	-11	-32	-26	0	-11		
IX.	18	-62	-3	-74	-82	24	5	5	-20	-38	-26	0	-11	-32	-26	0	-11		
	19	-38	-11	-80	-79	30	32	-19	4	-38	-26	0	-11	-32	-26	0	-11		
	20	-38	-11	-80	-79	30	32	-19	4	-38	-26	0	-11	-32	-26	0	-11		
IX.	21	-10	9	-50	-53	-50	-38	18	20	-38	-26	0	-11	-32	-26	0	-11		
	21	-10	9	-50	-53	-50	-38	18	20	-38	-26	0	-11	-32	-26	0	-11		
	21	-10	9	-50	-53	-50	-38	18	20	-38	-26	0	-11	-32	-26	0	-11		

TABLE I. (b) (3).—Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Equinoxes.  
 (b) Sunspot Minimum, 1902.  
 (3) The 8-hour Component.

Group No.	Observatory No.	West.						North.						Radial.														
		$a_3$ .		$b_3$ .		$a_3$ .		$b_3$ .		$a_3$ .		$b_3$ .		$a_3$ .		$b_3$ .												
		Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.											
I.	1	22	33	26	29	-17	-19	19	28	7	8	-2	-3	II.	4	39	50	29	27	-18	-12	18	37	18	25	-2	-4	
	2	25	46	43	9	-5	1	31	30	18	17	3	-2		III.	5	13	33	49	36	-14	-14	32	37	11	11	4	-3
	3	25	35	32	27	-14	-13	25	27	23	24	-6	-6			IV.	6	34	46	27	28	-23	-8	15	25	23	24	-6
V.	7	44	60	36	32	-5	7	14	32	24	17	-11	-5	VI.	8		47	69	34	30	9	8	26	45	22	25	-6	-3
	9	38	58	26	14	-8	13	26	37	14	18	-8	-8		VII.	10	36	63	32	24	-20	0	26	42	14	18	-8	-8
VIII.	11	-11	5	21	42	36	35	64	66	23	20	-4	-11	IX.		12	30	69	33	-1	10	17	3	32	32	18	-8	-14
	13	16	80	43	5	26	30	-28	-20	24	33	-28	-52		X.	14	23	65	29	7	33	26	-23	32	18	-8	-14	
XI.	15	-23	17	-29	-48	26	28	-24	-20	-24	-21	-8	-13	XII.		16	-23	17	-29	-48	26	28	-24	-20	-24	-21	-8	-13
	17	-23	17	-29	-48	26	28	-24	-20	-24	-21	-8	-13		XIII.	18	-31	-6	-71	-67	24	27	-16	1	22	26	26	11
XIV.	19	-23	-6	-36	-46	-25	53	13	-3	-2	-2	-2	0	XV.		20	-23	-6	-36	-46	-25	53	13	-3	-2	-2	-2	0

TABLE I. ( $\alpha$ ) (4).—Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Equinoxes.  
 ( $\alpha$ ) Sunspot Maximum, 1905.  
 (4) The 6-hour Component.

Group No.	Observatory No.	West.						North.						Radial.					
		$a_4$ .		$b_4$ .		$a_4$ .		$b_4$ .		$a_4$ .		$b_4$ .		$a_4$ .		$b_4$ .			
		Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.		
I.	1	7	12	22	16	-14	-3	12	11	11	4	11	4	2	3				
	2	9	23	9	0	0	-6	-3	2	4	8	4	7	11					
	3	3	1	18	9	-7	3	14	10	7	8	7	5	3					
II.	4	16	18	26	11	-7	1	8	15	10	13	10	-1	0					
	5	8	8	21	4	-14	-3	11	13	3	5	3	5	-2					
	6	15	16	22	8	-6	4	6	10	13	13	10	0	0					
III.	7	18	22	26	8	-1	10	10	15	9	16	9	-4	-7					
	8	27	27	26	6	6	9	16	24	9	15	9	-2	-6					
IV.	9	17	25	11	-9	-2	23	12	14	6	6	4	-3	-10					
	10	13	24	12	0	-7	8	8	19	4	4	2	-5	-5					
V.	11	24	32	31	-2	-6	6	6	8	14	14	7	-1	-8					
	12	22	35	16	-20	3	14	6	1	16	11	11	0	-19					
VI.	13	28	24	5	-20	5	6	-12	-14	12	-6	-6	-21	-29					
	14	3	15	20	-20	-6	7	0	-2	0	-7	-4	7	7					
	15																		
VII.	16	-16	-9	-2	-20	8	3	-8	3	-14	-12	5	-4						
	17																		
VIII.	18	-26	-6	-19	-29	12	-1	-1	-9	-15	-10	6	-3						
	19	-11	-8	-18	-27	5	11	-9	-1	11	15	17	18						
	20																		
IX.	21	-7	4	-16	-18	-10	-14	8	8										

TABLE I. (b) (4).—Fourier Coefficients of the Solar Diurnal Magnetic Components at the Equinoxes.  
 (b) Sunspot Minimum, 1902.  
 (4) The 6-hour Component.

Group No.	Observatory No.	West.				North.				Radial.			
		$a_4$		$b_4$		$a_4$		$b_4$		$a_4$		$b_4$	
		Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.
I.	1	7	8	14	17	-2	-6	10	10	6	7	0	2
	2	4	13	14	1	2	1	15	11	7	7	2	3
	3	6	4	12	9	-6	-2	9	11	7	7	2	3
II.	4	16	20	16	13	-1	0	10	16	9	13	-2	-2
	5	8	6	14	6	-8	-4	14	11	6	2	3	0
	6	16	19	15	13	-2	2	7	13	9	10	-2	-5
III.	7	21	25	17	9	3	7	11	14	11	8	-6	-4
	8	25	27	12	7	3	10	17	16	10	8	-7	-6
IV.	9	17	21	3	-8	-1	15	10	10	2	4	-8	-6
	10	17	23	8	-5	-4	10	5	15	2	4	-8	-6
V.	11	-9	3	6	7	26	26	23	4	9	4	-3	-5
	12	20	25	6	-20	1	7	0	-2	9	4	-3	-5
VI.	13	2	26	25	-10	2	8	-14	-12	13	3	-18	-25
	14	12	12	12	-8	-1	0	-14	-15	12	3	-3	-5
	15	12	12	12	-8	-1	0	-14	-15	12	3	-3	-5
VII.	16	-15	-6	-2	-17	4	3	-6	-1	-12	-11	4	-3
	17	-15	-6	-2	-17	4	3	-6	-1	-12	-11	4	-3
VIII.	18	-10	1	-24	-23	5	8	-5	-3	5	5	17	15
	19	-11	4	-24	18	-3	-5	7	1	-1	0	1	0
	20	-11	4	-24	18	-3	-5	7	1	-1	0	1	0

TABLE II. ( $\alpha$ ) (1).---Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Solstices.  
 ( $\alpha$ ) Sunspot Maximum, 1905.  
 (1) The 24-hour Component.

Group No.	Observatory No.	West.						North.						Radial.					
		$a_1$ .		$b_1$ .		$a_1$ .		$b_1$ .		$a_1$ .		$b_1$ .		$a_1$ .		$b_1$ .			
		Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.		
I.	1	68	66	185	32	-155	-25	78	-	11	17	-	12	-	34	-	45		
	2	38	28	176	43	-89	-46	109	67	23	4	-	106	-	104	-	104		
	3	76	46	185	22	-135	-17	48	-	18	36	-	33	-	31	-	31		
II.	4	83	70	173	36	-149	-62	52	-	25	67	-	11	-	8	-	27		
	5	47	43	193	31	-118	-25	38	2	46	5	-	4	-	4	-	18		
	6	55	58	175	38	-153	-83	76	-	25	54	-	6	-	14	-	29		
III.	7	86	70	168	44	-71	-45	14	-	42	103	-	28	-	15	-	23		
	8	64	42	171	34	-44	1	38	-	41	62	-	20	-	14	-	9		
IV.	9	68	30	135	66	-24	-89	54	5	31	23	-	23	-	29	-	20		
	10	58	30	148	73	-45	-99	55	-	11	31	-	25	-	28	-	33		
V.	11	30	3	155	38	33	26	15	-	26	81	-	56	-	9	-	7		
	12	6	-19	126	55	68	79	-1	-	38	35	-	46	-	41	-	30		
VI.	13	61	-2	93	-2	200	160	-39	-	47	79	-	49	-	6	-	19		
	14	-1	-25	124	83	60	17	-34	-	76	7	-	41	-	23	-	7		
VII.	16	24	5	-13	-124	165	199	-69	-	35	-	-	75	-	37	-	16		
	17	10	-109	-3	-78	45	35	-97	-	198	-	-	-	-	-	-	-		
VIII.	18	-39	-133	-7	-95	50	184	-72	-	52	59	-	108	-	8	-	6		
	19	-32	-62	-33	-223	20	10	61	-	30	-	-	240	-	5	-	41		
IX.	20																		
	21	-34	-76	-14	-187	-15	-146	-31	-	23									

TABLE II. (b) (1).—Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Solstices.  
 (b) Sunspot Minimum, 1902.  
 (1) The 24-hour Component.

Group No.	Observatory No.	West.				North.				Radial.					
		$a_1$ .		$b_1$ .		$a_1$ .		$b_1$ .		$a_1$ .		$b_1$ .			
		Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.		
I.	1	67	49	127	3	-114	-	9	40	-6	28	-	3	-18	-19
	2	64	30	144	26	-79	-	13	62	24	62	-	2	-10	-17
	3	73	35	139	1	-85	-	8	32	-6	35	-	-	-	-
II.	4	71	52	117	5	-104	-	26	28	-12	56	-	5	-11	-16
	5	46	25	145	4	-74	-	2	31	0	25	-	12	3	-5
	6	41	45	125	7	-108	-	44	50	-10	62	-	-14	-12	-6
III.	7	69	56	120	7	-45	-	19	4	-20	69	-	22	-6	-29
	8	63	41	128	3	-17	-	17	23	-20	52	-	8	15	-8
IV.	9	60	27	107	27	-55	-	56	62	8	36	-	16	-17	-17
	10	68	23	107	31	-34	-	56	49	-6	36	-	-	-	-
V.	11	34	20	18	-17	43	-	3	118	-1	51	-	31	-5	12
	12	21	4	94	31	67	-	46	3	-13	3	-	-	-	-
VI.	13	41	-4	76	-28	137	109	-42	-33	-42	61	-	18	1	2
	14	48	-6	69	-28	163	154	-19	-35	-19	97	-	70	-25	-40
	15	18	-8	-1	-107	123	127	-42	-60	-42	-57	-	-56	15	-3
VII.	16	18	-8	-1	-107	123	127	-42	-60	-42	-57	-	-56	15	-3
	17	18	-8	-1	-107	123	127	-42	-60	-42	-57	-	-56	15	-3
	18	18	-8	-1	-107	123	127	-42	-60	-42	-57	-	-56	15	-3
VIII.	18	-16	-54	-16	-167	16	21	-7	64	-7	-101	-	-166	9	-44
	19	-17	-24	-20	-160	-26	-84	-17	-35	-17	-4	-	-9	4	-1
	20	-17	-24	-20	-160	-26	-84	-17	-35	-17	-4	-	-9	4	-1

TABLE II. (a) (2).—Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Solstices.  
 (a) Sunspot Maximum, 1905.  
 (2) The 12-hour Component.

Group No.	Observatory No.	West.				North.				Radial.			
		$a_2$ .		$b_2$ .		$a_2$ .		$b_2$ .		$a_2$ .		$b_2$ .	
		Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.
I.	1	80	- 14	109	42	- 96	- 28	35	- 1	35	21	12	7
	2	68	17	134	51	- 48	- 30	69	- 9	29	- 9	- 7	8
	3	61	- 10	126	37	- 82	- 22	44	- 2	42	17	- 1	13
II.	4	97	2	109	54	- 79	- 43	28	- 9	71	13	15	3
	5	67	- 13	136	27	- 77	- 19	41	7	43	11	0	6
	6	72	0	102	54	- 82	- 52	18	0	76	17	13	2
III.	7	100	7	131	63	- 10	23	- 15	- 15	79	19	8	- 5
	8	77	- 4	138	47	- 7	69	- 2	- 2	56	15	15	4
IV.	9	95	27	102	91	9	76	23	23	55	23	5	1
	10	98	20	127	99	- 40	83	13	13	42	24	- 4	- 13
V.	11	83	- 3	121	52	19	- 3	45	3	46	34	6	18
	12	67	8	77	73	43	22	23	7	40	27	9	33
VI.	13	97	- 18	51	20	101	53	- 27	- 36	63	21	- 43	2
	14	44	- 26	85	101	36	- 9	- 6	- 31	- 3	29	- 23	- 11
VII.	15												
	16	50	- 20	- 52	- 108	71	85	- 33	- 26	- 33	- 58	- 8	- 8
VIII.	17	- 27	- 108	50	- 75	23	19	- 53	- 105				
	18	- 10	- 136	- 45	- 52	9	88	- 39	53	- 38	- 55	4	23
IX.	19	20	- 70	- 76	- 219	36	61	40	- 56	- 37	34	- 16	1
	20												
	21	1	- 85	- 19	- 83	- 26	- 50	16	51				



TABLE II. (b) (2).—Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Solstices.  
 (b) Sunspot Minimum, 1902.  
 (2) The 12-hour Component.

Group No.	Observatory No.	West.				North.				Radial.			
		$a_2$		$b_2$		$a_2$		$b_2$		$a_2$		$b_2$	
		Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.
I.	1	69	2	80	27	-59	-15	24	0	28	6	0	2
	2	84	25	90	29	-32	-34	68	10	34	8	-2	2
	3	63	-1	92	20	-41	-3	42	3				
II.	4	86	13	77	34	-51	-29	19	-3	53	7	-1	-3
	5	65	-4	93	12	-56	-9	55	13	20	-1	1	7
	6	63	8	70	36	-59	-36	15	2	60	5	-6	-7
III.	7	88	16	91	36	1	-22	8	-9	47	16	2	-9
	8	69	8	97	28	12	-4	48	-7	38	8	7	-4
IV.	9	88	32	84	67	-14	-60	58	13	48	15	-16	-14
	10	100	24	86	67	-26	-62	67	11				
V.	11	14	4	48	24	84	-10	87	15	35	18	-2	7
	12	77	19	56	59	42	7	11	5				
VI.	13	73	-8	41	1	78	46	-21	-30	52	11	-29	-1
	14									50	31	-22	-4
	15	84	-4	34	1	82	74	-18	-21				
VII.	16	38	-17	-40	-84	55	56	-30	-30	-35	-38	-18	-9
	17												
VIII.	18												
	19	21	-56	-58	-166	41	49	46	32	-21	39	-17	3
	20	23	-18	-41	-133	-29	-68	-38	21	-2	-6	1	-4



TABLE II. (b) (3).—Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Solstices.

(b) Sunspot Minimum, 1902.

(3) The 8-hour Component.

Group No.	Observatory No.	West.				North.				Radial.			
		$a_3$ .		$b_3$ .		$a_3$ .		$b_3$ .		$a_3$ .		$b_3$ .	
		Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.
I.	1	24	9	33	10	-13	-12	22	12	7	1	2	-2
	2	34	10	13	10	-11	-10	14	0	16	4	6	-3
	3	11	12	31	7	-13	-7	30	9	22	17	5	-1
II.	4	42	21	24	11	-3	-15	22	17	22	22	5	-1
	5	18	9	31	17	-20	-14	36	14	5	4	3	-3
	6	34	17	18	14	-5	-13	12	16	26	7	-6	-3
III.	7	52	27	28	15	20	-14	21	12	21	10	-1	-12
	8	47	20	33	15	9	-10	47	6	18	6	1	-2
IV.	9	45	17	17	32	15	-27	42	5	24	10	-11	-10
	10	58	15	18	28	-5	-30	49	6	24	10	-11	-10
V.	11	5	-3	42	22	62	-2	30	22	14	-1	-12	-11
	12	55	9	3	49	13	0	3	2	14	-1	-12	-11
VI.	13	69	8	7	11	20	6	-16	-21	32	11	-39	-5
	14	56	-5	5	21	23	27	-11	-26	18	15	-14	7
VII.	16	29	-21	-23	-28	24	22	-18	-23	-14	-20	-8	0
	17												
VIII.	18	21	-47	-35	-72	23	29	29	-32	4	28	0	28
	19	13	-25	-25	-53	-17	-33	-27	25	0	-3	0	-1

TABLE II. (a) (4) Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Solstices.  
 (a) Sunspot Maximum, 1905.  
 (4) The 6-hour Component.

Group No.	Observatory No.	West.				North.				Radial.			
		$a_4$		$b_4$		$a_4$		$b_4$		$a_4$		$b_4$	
		Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.
I.	1	3	3	9	14	-7	-2	0	7	8	1	2	-4
	2	5	0	-7	3	10	-4	-5	1	2	-3	6	-4
	3	-8	6	1	13	6	-6	-5	7	5	8	1	2
II.	4	-1	16	3	14	2	-5	-2	6	8	4	0	-1
	5	-4	8	-4	16	8	-8	3	9	-2	3	2	1
	6	2	14	4	12	2	-2	1	9	5	3	-1	0
III.	7	3	19	0	19	16	-3	4	9	5	7	3	-1
	8	2	15	-1	14	4	1	16	13	0	9	1	0
IV.	9	-1	16	-15	14	17	-9	11	4	2	7	-2	-4
	10	8	17	-8	18	7	-14	19	5	-1	7	2	-6
V.	11	13	19	-15	28	10	-4	4	9	-2	10	-5	5
	12	11	16	-21	27	2	4	5	14	2	14	-14	6
VI.	13	7	20	-14	-2	-2	4	-3	-5	-3	5	-13	-17
	14	0	11	-14	29	2	-2	2	6	0	-1	5	-4
	15												
VII.	16	1	-6	-14	0	3	4	0	-7	-2	-8	-4	4
	17												
VIII.	18	-5	-16	-34	-1	-2	9	-7	-4	-14	1	-1	4
	19	16	-15	-25	-14	10	10	8	-19	11	3	15	6
	20												
IX.	21	1	0	-17	-16	-13	-9	7	11				

TABLE II. (b) (4).—Fourier Coefficients of the Solar Diurnal Magnetic Variation at the Solstices.  
 (b) Sunspot Minimum, 1902.  
 (4) The 6-hour Component.

Group No.	Observatory No.	West.						North.						Radial.					
		$a_4$		$b_4$		$a_4$		$b_4$		$a_4$		$b_4$		$a_4$		$b_4$			
		Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.		
I.	1	-1	4	9	3	-7	-2	5	6	4	2	-1	-1	4	2	-1	-1		
	2	-2	3	-5	4	0	0	1	-2	6	1	5	-1	6	1	5	-1		
	3	-4	6	6	5	4	-2	-6	1	8	3	2	-1	8	3	2	-1		
II.	4	4	8	5	5	1	-3	2	9	9	9	2	-1	8	3	2	-1		
	5	-6	7	-1	4	4	-7	7	8	-1	6	1	1	-1	6	1	1		
	6	5	9	3	2	2	-2	4	11	4	1	-4	-2	4	1	-4	-2		
III.	7	8	12	2	10	-3	5	9	9	2	5	2	5	2	5	2	5		
	8	5	15	-3	5	-3	8	6	6	0	4	0	-1	0	4	0	-1		
IV.	9	9	12	-13	14	-9	13	3	3	4	5	-4	-7	4	5	-4	-7		
	10	9	13	-6	9	-10	18	5	5	4	5	-4	-7	4	5	-4	-7		
V.	11	5	0	7	15	5	-12	14	14	-2	4	-2	0	-2	4	-2	0		
	12	14	9	-18	1	2	3	4	4	0	5	-16	-10	0	5	-16	-10		
VI.	13	15	13	-9	2	3	5	-6	-6	0	5	-16	-10	0	5	-16	-10		
	14	8	2	-15	-4	1	1	-11	-11	-4	8	-5	2	-4	8	-5	2		
	15	8	2	-15	-4	1	1	-11	-11	-4	8	-5	2	-4	8	-5	2		
VII.	16	5	-5	-11	7	3	2	-4	-4	0	-3	-11	3	0	-3	-11	3		
	17																		
VIII.	18	19	-10	-18	9	9	11	-12	-12	2	3	10	4	2	3	10	4		
	19	11	-10	-13	-2	-3	-14	9	9	-2	0	0	0	-2	0	0	0		
	20	11	-10	-13	-1	-2	-14	-1	-1	-2	0	0	0	-2	0	0	0		

TABLE III. (α) (α).—Fourier Coefficients (Group Means) of the Solar Diurnal Magnetic Variation, at Sunspot Maximum, 1905.

(α) The Mean Equinoctial Component,  $\frac{1}{2}$  (Spring + Autumn).

Group No.	West.			North.			Radial.			
	a.		b.	a.		b.	a.		b.	
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	
(1) The 24-hour Component.										
I.	61	66	102	138	-106	-71	48	34	-74	-19
II.	69	62	96	128	-138	-40	15	19	-20	-20
III.	76	54	108	112	-57	10	6	-5	-8	-21
IV.	65	49	115	102	-100	35	25	-17	-37	-21
V.	14	35	106	72	54	98	1	-47	36	-16
VI.	8	25	82	52	117	130	44	-63	-3	-12
VII.	-16	-14	-46	-28	133	152	-116	-73	42	4
VIII.	-62	-45	-103	-93	78	57	9	-27	-6	19
IX.	-43	-68	-106	-142	-118	-85	46	-41	-	-
(2) The 12-hour Component.										
I.	44	50	92	97	-55	-66	24	34	14	0
II.	49	54	96	105	-64	-58	24	30	6	0
III.	62	56	106	108	-7	-32	26	17	4	-1
IV.	62	55	102	106	-58	-15	60	8	-5	-1
V.	56	43	94	84	30	39	42	-20	16	-1
VI.	45	33	66	65	60	71	-18	-37	-26	0
VII.	-12	-19	-43	-37	60	95	-56	-49	-10	0
VIII.	-42	-52	-120	-100	53	1	9	1	-2	1
IX.	-10	-47	-80	-92	-58	-68	0	35	-	-

TABLE III. ( $\alpha$ ) ( $\alpha$ ) (continued).

Group No.	West.			North.			Radial.			
	$a$ .		$b$ .	$a$ .		$b$ .	$a$ .		$b$ .	
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.		
(3) The 8-hour Component.										
I.	28	30	32	33	-23	-24	26	22	12	-4
II.	36	37	49	41	-24	-26	30	23	17	2
III.	53	44	54	50	0	-21	37	19	33	2
IV.	46	47	36	52	-13	-16	45	14	24	9
V.	56	43	46	48	12	9	24	-8	31	2
VI.	42	35	20	39	21	24	-17	-22	12	-30
VII.	-16	-20	-28	-23	25	34	-21	-30	-32	-6
VIII.	-28	-47	-78	-52	22	-9	-8	8	-4	18
IX.	0	-26	-52	-29	-44	-22	19	20	-10	10
(4) The 6-hour Component.										
I.	9	10	12	6	-4	-5	8	7	7	6
II.	14	14	16	8	-4	-6	10	9	9	0
III.	23	20	16	12	6	-6	16	10	12	4
IV.	20	23	4	14	6	-5	13	9	4	6
V.	28	24	6	14	4	0	5	-1	12	7
VI.	18	21	-4	12	3	5	-7	-8	0	-12
VII.	-12	-8	-11	-5	6	11	-2	-18	-13	0
VIII.	-12	-24	-23	-14	-6	-4	-5	6	0	10
IX.	-2	-8	-17	-5	-12	-4	8	6	-10	5

TABLE III (a) (b).—Fourier Coefficients (Group Means) of the Solar Diurnal Magnetic Variation, at Sunspot Minimum, 1902.

(a) The Mean Equinoctial Component,  $\frac{1}{2}$  (Spring + Autumn).

Group No.	West.			North.			Radial.					
	a.		b.	a.		b.	a.		b.			
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.		
I.	58	62	78	87	-63	-45	28	32	2	45	-13	-5
II.	56	59	66	81	-81	-25	16	18	26	49	-4	-6
III.	65	51	70	70	-25	6	3	-4	38	51	0	-6
IV.	50	47	78	64	-82	22	30	-16	29	50	-18	-6
V.	17	33	42	45	-42	62	38	-45	65	45	8	-5
VI.	28	22	25	30	160	86	-25	-63	68	28	-20	-3
VII.	18	-8	-65	-11	152	101	-56	-73	-61	-10	-18	1
VIII.	-27	-49	-93	-67	-25	15	10	-11	-86	-50	-6	6
(1) The 24-hour Component.												
(2) The 12-hour Component.												
I.	42	48	64	69	-34	-47	34	33	20	19	4	-1
II.	46	52	64	74	-42	-41	26	28	29	24	0	-1
III.	60	53	72	77	1	-23	24	16	32	29	2	-1
IV.	72	52	70	75	-45	-11	48	7	30	31	-12	-1
V.	34	42	54	60	40	28	43	-19	40	31	8	-1
VI.	57	29	26	42	84	55	-22	-38	43	21	-26	-1
VII.	17	-11	-77	-16	66	74	-31	-51	38	-9	-25	0
VIII.	-10	-52	-111	-75	-4	-18	-4	13	0	-30	-8	-1



TABLE III (a) (b) (continued).

Group No.	West.			North.			Radial.					
	a.		b.	a.		b.	a.		b.			
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.			
I.	31	27	28	23	-11	-17	26	20	12	9	1	4
II.	36	35	32	29	-18	-18	28	22	18	14	2	6
III.	55	42	33	35	5	-15	29	18	22	20	6	8
IV.	48	44	24	37	-4	-11	33	13	16	22	8	9
V.	24	44	24	37	24	6	36	-7	22	24	8	-10
VI.	46	31	21	25	29	20	-26	-24	27	19	-26	8
VII.	-3	-12	-38	-10	27	30	-22	-36	-22	-8	-10	3
VIII.	-16	-43	-55	-36	20	-13	-2	15	11	-21	9	9
(3) The 8-hour Component.												
I.	7	7	11	4	-2	-3	11	6	6	2	2	2
II.	14	11	13	6	-2	-4	12	7	8	4	1	3
III.	24	16	11	8	6	-4	14	8	9	7	6	5
IV.	20	18	0	9	5	-4	10	7	3	8	7	6
V.	10	18	0	10	15	0	6	0	6	10	4	7
VI.	13	15	4	8	2	3	-14	-8	8	8	-12	6
VII.	-10	-6	-10	-3	4	7	-4	-14	-12	-4	0	3
VIII.	-6	-17	-13	-9	-2	-3	0	5	2	-8	8	5
(4) The 6-hour Component.												

TABLE III. ( $\beta$ ) ( $\alpha$ ).—Fourier Coefficients (Group Means) of the Solar Diurnal Magnetic Variation, at Sunspot Maximum, 1905.  
( $\beta$ ) The Mean Solstitial Component,  $\frac{1}{2}$  (Summer + Winter).

Group No.	West.			North.			Radial.					
	a.		b.	a.		b.	a.		b.			
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.				
(1) The 24-hour Component.												
I.	54	56	107	133	- 78	- 68	46	29	11	49	- 59	- 16
II.	60	53	108	123	- 98	- 39	20	16	32	53	- 17	- 18
III.	66	46	104	107	- 40	9	-	4	53	55	- 8	- 18
IV.	46	42	106	98	- 64	34	26	- 14	28	54	- 27	- 18
V.	5	29	93	69	52	94	- 12	- 40	54	43	22	- 14
VI.	8	21	79	50	109	126	- 49	- 53	44	33	- 4	- 11
VII.	- 18	- 12	54	- 27	111	146	- 100	- 62	66	- 11	26	4
VIII.	- 67	- 38	- 90	- 89	66	54	- 23	- 23	- 126	- 51	- 6	17
IX.	- 55	- 58	- 100	- 137	- 80	- 82	- 4	35	-	-	-	-
(2) The 12-hour Component.												
I.	34	42	83	86	- 51	- 59	22	29	22	26	5	2
II.	38	46	80	93	- 58	- 51	8	25	38	33	6	2
III.	45	47	94	96	- 16	- 29	19	14	42	40	6	3
IV.	60	46	104	94	- 48	- 13	49	7	36	42	- 3	3
V.	38	37	80	75	20	35	20	- 17	36	38	17	3
VI.	24	28	64	58	45	63	- 25	- 31	28	31	- 18	2
VII.	- 26	- 16	- 46	- 33	50	85	- 54	- 42	46	- 12	- 8	1
VIII.	- 49	- 44	- 98	- 89	48	1	- 1	1	- 24	- 42	- 6	3
IX.	- 42	- 40	- 51	- 81	- 38	- 60	34	30	-	-	-	-

TABLE III. ( $\beta$ ) ( $\alpha$ ) (continued).

Group No.	West.			North.			Radial.				
	a.		b.	a.		b.	a.		b.		
	Observed.	Calculated.	Observed.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.		
(3) The 8-hour Component.											
I.	17	21	24	17	18	13	16	8	8	0	1
II.	22	27	29	16	20	20	17	15	12	2	2
III.	38	32	35	2	16	29	14	22	17	2	3
IV.	33	34	36	16	12	36	10	20	19	3	3
V.	33	31	39	2	7	18	6	20	20	2	3
VI.	32	26	23	12	19	12	-16	13	18	-18	3
VII.	-16	-15	25	17	26	21	-22	20	-7	-5	1
VIII.	-32	-34	56	40	7	7	6	2	-20	11	3
IX.	-11	-19	26	22	17	25	15	-	-	-	-
(4) The 6-hour Component.											
I.	2	4	6	4	3	1	3	4	1	0	1
II.	6	6	8	6	4	4	4	4	2	0	1
III.	10	9	8	9	4	10	4	5	4	1	2
IV.	10	10	2	10	4	10	4	4	4	2	2
V.	15	11	5	10	0	8	0	6	5	2	3
VI.	10	9	0	9	3	0	-4	0	5	-7	3
VII.	-2	-4	7	3	8	4	-8	5	-2	0	1
VIII.	-5	-11	19	10	3	6	3	0	-5	6	3
IX.	0	-3	16	3	3	9	3	-	-	-	-

TABLE III. (β) (b).—Fourier Coefficients (Group Means) of the Solar Diurnal Magnetic Variation, at Sunspot Minimum, 1902.

(β) The Mean Solstitial Component,  $\frac{1}{2}$  (Summer + Winter).

Group No.	West.			North.			Radial.				
	a.		b.	a.		b.	a.		b.		
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	
I.	53	56	74	79	-41	24	29	16	40	-16	9
II.	47	53	67	74	-23	14	16	24	44	-8	-10
III.	57	46	64	64	6	-3	-4	38	46	-7	-10
IV.	44	42	68	59	21	28	-14	26	45	-17	-10
V.	20	29	32	41	56	27	-40	41	40	4	-9
VI.	20	19	22	27	78	-32	-55	62	25	-14	-6
VII.	5	-7	-54	-10	92	-51	-66	-56	-10	6	2
VIII.	-26	-43	-91	-61	14	10	-10	-70	-45	-8	10
(1) The 24-hour Component.											
(2) The 12-hour Component.											
I.	40	39	56	62	-42	24	26	19	20	0	2
II.	38	42	54	67	-37	17	23	24	25	-1	3
III.	45	43	63	69	-20	10	13	27	30	-1	3
IV.	61	42	76	67	-9	37	6	32	32	-15	3
V.	29	33	47	54	25	30	-16	26	32	2	3
VI.	36	24	20	38	49	-23	-31	36	22	-14	-2
VII.	10	-9	-62	-14	66	-30	-41	-36	-9	-14	1
VIII.	-8	-42	-100	-67	-16	-1	10	2	-31	-4	3

TABLE III. (β) (b) (continued).

Group No.	West.			North.			Radial.				
	a.		b.	a.		b.	a.		b.		
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	
(3) The 8-hour Component.											
I.	16	18	17	-11	-13	14	13	7	6	1	3
II.	24	23	22	-12	-14	20	14	12	9	2	4
III.	37	27	26	1	-11	22	12	14	13	-	-
IV.	34	29	28	-12	-8	26	9	17	15	-4	-6
V.	16	29	28	18	5	14	-5	6	16	-10	-7
VI.	32	20	19	19	15	-19	-15	19	12	-12	-8
VII.	4	-8	-8	23	23	-20	-23	-17	-5	-4	3
VIII.	-10	-28	-27	0	-10	-2	10	7	-14	7	7
(4) The 6-hour Component.											
I.	2	3	2	-1	-1	1	3	4	1	0	1
II.	4	5	3	-1	-2	6	3	4	2	0	1
III.	10	7	4	2	-2	7	3	2	3	1	2
IV.	10	8	4	1	-2	10	3	4	3	-	3
V.	7	8	5	6	0	2	0	1	4	-1	3
VI.	10	7	4	0	2	-2	-3	2	3	-7	3
VII.	0	-3	-2	5	3	-1	-6	-2	-1	-4	1
VIII.	2	-7	-5	4	-2	-2	3	1	-3	4	3

TABLE III. ( $\gamma$ ) ( $\alpha$ ).—Fourier Coefficients (Group Means) of the Solar Diurnal Magnetic Variation, at Sunspot Maximum, 1905.

( $\gamma$ ) The Solstitial Inequality,  $\frac{1}{2}$  (Summer - Winter).

Group No.	West.			North.			Radial.				
	a.		b.	a.		b.	a.		b.		
	Observed.	Calculated.	Observed.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.		
(1) The 24-hour Component.											
I.	7	4	75	-48	-32	32	19	14	30	1	7
II.	3	7	73	-42	-12	36	26	24	29	8	8
III.	10	12	66	-18	14	34	33	29	23	8	6
IV.	16	15	36	30	25	29	35	4	19	-1	5
V.	13	21	47	-1	36	20	32	4	3	4	1
VI.	22	24	34	21	33	12	27	-1	-7	-10	-1
VII.	34	27	46	-6	-22	17	-15	9	-16	10	-4
VIII.	31	17	70	-31	-31	18	-35	48	13	12	4
IX.	21	2	86	66	40	-27	-16				
(2) The 12-hour Component.											
I.	36	36	40	-24	-19	26	26	12	13	-4	1
II.	42	39	36	-20	-15	9	24	24	15	2	0
III.	43	43	40	8	-6	27	20	26	15	6	1
IV.	36	44	10	32	-1	31	17	12	14	3	2
V.	36	43	18	10	8	14	8	6	7	-9	5
VI.	46	43	4	23	11	9	4	2	-1	-14	8
VII.	38	42	46	-2	-7	12	-2	12	-5	0	-10
VIII.	54	44	38	-26	-3	1	-14	-14	12	-9	-3
IX.	43	34	32	12	20	-18	-26				

TABLE III. ( $\gamma$ ) ( $\alpha$ ) (continued).

Group No.	West.			North.			Radial.			
	a.		b.	a.		b.	a.		b.	
	Observed.	Calculated.	Observed.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	
(3) The 8-hour Component.										
I.	3	6	9	7	0	7	6	8	4	1
II.	8	9	10	7	1	6	1	7	3	2
III.	12	14	11	6	14	3	17	10	2	1
IV.	21	16	6	4	20	1	20	2	1	0
V.	23	24	-15	-2	6	-5	6	0	5	5
VI.	26	28	-13	-7	9	-6	8	-1	5	-9
VII.	18	31	27	-11	-5	5	9	14	4	-13
VIII.	38	19	8	2	-12	1	11	-10	-	-2
IX.	7	5	4	6	0	-7	-14	-	5	-
(4) The 6-hour Component.										
I.	-2	2	-4	-4	4	3	-4	2	0	1
II.	-7	3	-6	-6	4	4	4	0	0	1
III.	-8	4	-8	-9	6	6	0	3	-1	1
IV.	-6	4	-14	-11	12	6	6	-4	-1	1
V.	-3	4	-23	-16	3	5	-4	-6	-3	-1
VI.	-6	3	-14	-17	0	4	0	-2	-4	-3
VII.	4	-2	-7	-19	0	-1	4	3	-5	-5
VIII.	11	-4	-11	-12	-3	-6	6	-2	-1	0
IX.	0	-2	0	-3	-2	-3	-2	1	-	-

TABLE III. ( $\gamma$ ) ( $b$ ).—Fourier Coefficients (Group Means) of the Solar Diurnal Magnetic Variation at Sunspot Minimum, 1902.

( $\gamma$ ) The Solstitial Inequality,  $\frac{1}{2}$  (Summer—Winter).

Group No.	West.			North.			Radial.				
	a.		b.	a.		b.	a.		b.		
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.			
I.	15	8	64	72	-44	-32	20	16	21	2	7
II.	6	10	62	66	-36	-16	21	24	21	1	7
III.	9	12	60	56	-15	5	17	22	19	11	5
IV.	20	14	39	52	7	14	27	10	17	0	4
V.	8	17	24	40	17	25	34	10	12	-8	2
VI.	25	19	50	33	9	23	-2	12	3	4	3
VII.	13	20	53	28	-2	-9	-9	0	-1	9	5
VIII.	12	13	73	54	13	-10	5	13	17	14	4
(1) The 24-hour Component.											
(2) The 12-hour Component.											
I.	31	29	31	33	-14	-18	20	19	10	-2	1
II.	32	31	26	34	-16	-12	13	17	12	0	1
III.	33	33	31	31	10	0	18	12	13	5	0
IV.	33	33	9	29	20	7	25	9	13	1	1
V.	17	30	5	18	32	17	20	2	12	-4	4
VI.	42	28	18	11	10	18	3	-2	7	-12	8
VII.	28	27	21	3	0	-8	0	1	4	-4	-10
VIII.	30	32	50	29	8	-4	5	-10	13	-4	-1





TABLE III. ( $\delta$ ).—Fourier Coefficients of the Solar Diurnal Magnetic Variation, Combined Group Means for 1902 and 1905.

( $\delta$ ) The Unsymmetrical Seasonal Component,  $\frac{1}{2}$  (Spring—Autumn).

Group No.	West.			North.			Radial.				
	a.		b.	a.		b.	a.		b.		
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	
(1) The 24-hour Component.											
I.	-6	-7	-8	-11	5	10	-16	4	2	-2	3
II.	-9	-8	-11	-11	12	11	-19	2	2	-1	3
III.	-13	-10	-12	-12	24	11	-21	4	2	-1	2
IV.	-4	-11	-6	-12	10	11	-21	3	2	-3	1
V.	-11	-13	-13	-13	12	9	-15	2	1	6	0
VI.	-18	-14	-15	-13	17	6	-6	-3	0	4	2
VII.	-27	-15	-18	-14	5	-4	17	-10	-1	-8	3
VIII.	-12	-11	-20	-12	5	-11	-5	-11	1	-8	-1
IX.	-1	-6	-18	-11	-13	-11	1				
(2) The 12-hour Component.											
I.	-23	-21	4	1	-2	0	-16	-1	0	5	-1
II.	-23	-23	2	1	-2	0	-18	-2	0	2	0
III.	-25	-27	0	0	3	1	-24	1	-1	1	1
IV.	-26	-28	2	0	-13	1	-22	-3	-1	2	3
V.	-31	-30	0	-1	-5	2	-8	-3	-3	9	7
VI.	-37	-31	3	-1	4	2	-6	-3	-5	14	10
VII.	-32	-31	-7	-2	5	-1	6	-6	-6	0	12
VIII.	-18	-28	-11	0	4	-1	-3	2	-1	1	3
IX.	-16	-19	-10	2	-1	0	16	1	-1	1	

TABLE III. ( $\delta$ ) (continued).

Group No.	West.			North.			Radial.				
	a.		b.	a.		b.	a.		b.		
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.			
(3) The 8-hour Component.											
I.	-9	-7	7	4	-4	-3	-5	6	1	2	1
II.	-8	-9	7	6	-9	-4	-6	-8	1	2	1
III.	-10	-13	8	7	-6	-5	-14	-10	1	0	3
IV.	-16	-16	8	8	-14	-5	-12	-10	1	2	4
V.	-22	-22	12	11	-5	-4	-2	-10	1	8	6
VI.	-29	-25	18	11	-2	-3	-2	-8	0	10	8
VII.	-16	-27	0	10	1	2	0	5	-1	4	9
VIII.	-16	-16	1	13	-8	5	0	10	-1	6	4
IX.	-10	-6	2	8	-6	3	-1	5	-1	-	-
(4) The 6-hour Component.											
I.	-2	-1	3	2	-1	-1	0	-1	0	1	0
II.	-1	-2	5	3	-3	-3	2	-1	1	0	0
III.	-1	-3	6	5	-3	-4	-2	-2	1	0	1
IV.	-3	-3	7	6	-8	-5	-2	-1	1	1	1
V.	-5	-4	12	11	-4	-5	3	-1	2	4	2
VI.	-4	-5	15	14	-3	-5	0	-1	1	1	3
VII.	-4	-5	8	15	-2	2	-4	0	1	4	4
VIII.	-5	-4	-3	7	-1	5	0	2	1	1	1
IX.	-6	-1	1	2	-2	1	0	1	1	-	-

TABLE IV. (1) (a).\*—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to the Epoch of New Moon.

(1) Zi-Ka-Wei.

(a) West Declination (in Force Units).

Season.	Lunar phase.	$a'_1$ .	$b'_1$ .	$a_2$ .	$b_2$ .	$a'_3$ .	$b'_3$ .	$a'_4$ .	$b'_4$ .
Summer . . .	1	167	-34	283	-125	127	-113	14	-26
	2	153	-43	287	2	117	-30	2	-3
	3	125	37	235	35	112	3	5	-17
	4	93	-18	179	-9	114	-3	35	-21
	5	65	-30	209	-18	97	-44	4	-12
	6	181	55	270	-17	116	-32	11	-4
	7	86	-5	209	6	108	0	19	-3
	8	54	5	207	22	89	-13	-21	3
	Mean. .		116	-4	235	-13	110	-29	9
Equinox . . .	1	56	15	200	-17	101	-33	29	-37
	2	40	16	197	-7	103	-6	25	-1
	3	48	15	143	-34	61	-38	13	-16
	4	22	29	113	-4	98	-11	24	-28
	5	157	37	165	-46	78	-5	25	-9
	6	50	72	131	-2	84	-20	38	-16
	7	36	-9	211	-49	110	-63	23	-18
	8	81	-23	119	-16	57	5	26	0
	Mean. .		61	19	160	-22	86	-21	25
Winter . . .	1	21	-41	-13	-82	-22	-41	23	-12
	2	-34	49	-4	-14	-46	-15	-15	-2
	3	-8	31	-20	-50	-19	-21	8	-28
	4	-21	-16	-38	-39	-40	-21	-18	-2
	5	-49	11	-30	-55	-23	-36	8	-17
	6	44	-6	22	-103	-16	-55	-4	-22
	7	-16	-41	20	-54	-19	-27	10	10
	8	56	-24	65	-96	26	-44	-17	-36
	Mean. .		-1	-5	0	-62	-20	-32	-1

\* For an explanation of Tables IV., V., and VI., cf. § 12. The unit of force in these three tables is  $10^{-7}$  C.G.S.

TABLE IV. (1) (b).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to the Epoch of New Moon.

(1) Zi-Ka-Wei.

(b) Horizontal Force.

Season.	Lunar phase.	$a'_1$ .	$b'_1$ .	$a_2$ .	$b_2$ .	$a'_3$ .	$b'_3$ .	$a'_4$ .	$b'_4$ .
Summer . . .	1	40	33	112	- 24	43	- 6	- 8	- 20
	2	- 13	67	14	46	50	11	4	8
	3	- 13	- 20	38	- 55	36	27	- 13	- 2
	4	- 83	28	- 3	12	- 17	22	- 25	25
	5	41	54	- 35	- 31	- 6	- 18	- 1	1
	6	- 48	68	6	- 34	30	36	- 3	20
	7	6	53	30	15	2	9	1	21
	8	- 15	18	8	8	35	24	7	3
	Mean. . .	- 11	38	21	- 8	22	13	- 5	7
Equinox . . .	1	- 33	22	13	5	10	44	- 13	10
	2	68	27	38	61	38	31	- 4	34
	3	- 37	125	- 24	- 9	18	23	12	18
	4	- 42	4	- 19	- 35	50	1	23	32
	5	- 137	160	1	76	39	83	12	25
	6	151	5	40	54	0	38	5	23
	7	- 60	49	45	85	62	6	- 15	4
	8	- 116	- 83	2	- 20	- 24	3	- 19	9
	Mean. . .	- 26	39	12	27	24	29	0	19
Winter . . .	1	55	- 38	108	- 77	25	- 20	- 2	25
	2	- 74	- 89	15	- 154	3	- 42	2	- 13
	3	45	- 123	110	- 175	37	- 28	12	9
	4	94	- 182	119	- 139	40	- 52	23	- 9
	5	91	- 64	82	- 61	24	- 3	- 7	17
	6	95	- 9	85	- 100	68	- 19	44	4
	7	158	- 14	53	- 56	26	6	- 1	- 18
	8	105	- 13	74	- 101	- 1	- 32	3	16
	Mean. . .	71	- 66	81	- 108	28	- 24	9	4

TABLE IV. (1) (c).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to the Epoch of New Moon.

(1) Zi-Ka-Wei.

(c) Vertical Force (Upwards).

Season.	Lunar phase.	$a'_1$ .	$b'_1$ .	$a_2$ .	$b_2$ .	$a'_3$ .	$b'_3$ .	$a'_4$ .	$b'_4$ .
Summer . . .	1	41	- 39	87	- 15	- 34	- 45	- 18	- 9
	2	15	- 92	130	- 29	12	- 62	13	- 24
	3	47	- 37	116	- 1	14	- 29	8	1
	4	65	- 58	112	36	2	- 35	15	- 22
	5	- 12	- 27	80	11	- 3	- 17	- 4	6
	6	41	- 41	125	- 38	14	- 28	30	- 16
	7	- 5	20	118	- 4	14	- 48	- 8	- 17
	8	11	- 56	119	6	- 37	- 26	- 21	- 3
	Mean . .	26	- 41	111	- 4	- 2	- 36	2	- 11
Equinox . . .	1	14	23	98	28	- 5	- 4	- 6	3
	2	58	30	94	51	- 2	- 10	- 7	- 6
	3	28	- 12	119	31	- 1	- 20	- 12	- 17
	4	- 65	108	110	- 34	34	1	- 29	7
	5	32	- 160	190	135	- 1	- 70	38	40
	6	65	42	141	- 6	15	- 11	19	- 25
	7	32	- 21	99	- 11	- 19	- 37	4	- 14
	8	19	- 35	127	9	6	- 18	- 6	- 1
	Mean . .	23	- 3	122	25	4	- 21	0	- 2
Winter . . .	1	- 59	- 33	42	8	- 26	- 6	- 8	- 17
	2	- 60	- 68	43	- 23	7	- 34	23	- 10
	3	52	- 33	85	76	- 24	14	- 10	- 14
	4	- 98	65	65	- 47	43	2	- 27	8
	5	20	- 56	133	32	12	- 10	16	- 13
	6	51	- 92	50	2	- 10	- 8	- 5	1
	7	- 39	- 52	110	36	- 3	- 21	- 4	- 6
	8	- 89	- 8	114	64	28	4	20	- 34
	Mean . .	- 28	- 34	80	18	4	- 7	0	- 11

TABLE IV. (2) (a).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation.  
Reduced to the Epoch of New Moon.

(2) Manila.

(a) West Declination (in Force Units).

Season.	Lunar phase.	$a'_1$ .	$b'_1$ .	$a_2$ .	$b_2$ .	$a'_3$ .	$b'_3$ .	$a'_4$ .	$b'_4$ .
Summer . . .	1	92	-45	114	-146	42	-83	19	-10
	2	104	-71	145	-47	64	-28	-11	8
	3	127	36	162	9	100	0	-3	2
	4	71	-20	127	-17	93	-6	34	-12
	5	5	11	102	-30	59	-58	-3	-20
	6	156	7	181	-65	75	-61	-3	-23
	7	32	17	141	-3	80	-20	16	17
	8	36	19	133	-3	79	-23	6	-21
	Mean . .	78	-6	138	-38	74	-35	7	-7
Equinox . . .	1	82	-17	128	-70	67	-31	15	-9
	2	13	40	128	-21	115	-16	36	4
	3	44	27	116	-32	68	-43	18	-22
	4	56	29	86	-28	66	-38	23	-35
	5	77	37	88	-67	44	-19	25	-1
	6	37	39	57	-34	47	-14	22	-15
	7	17	-5	146	-53	85	-67	20	-11
	8	94	14	84	-54	36	-13	12	-17
	Mean . .	52	20	104	-45	66	-30	21	-13
Winter . . .	1	17	-74	-59	-90	-37	-31	20	-10
	2	-61	34	-83	-43	-70	-11	-30	-1
	3	-46	0	-108	-92	-54	-35	1	-17
	4	-38	-53	-120	-97	-75	-48	-26	-13
	5	-43	-76	-92	-118	-73	-52	-17	-5
	6	-60	-30	-102	-125	-53	-63	-6	-27
	7	4	-24	-54	-74	-46	-28	-4	15
	8	24	-39	-20	-134	-19	-60	10	-20
	Mean . .	-25	-33	-80	-97	-53	-41	-6	-10

TABLE IV. (2) (b).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to the Epoch of New Moon.

(2) Manila.

(b) Horizontal Force.

Season.	Lunar phase.	$a'_1$ .	$b'_1$ .	$a_2$ .	$b_2$ .	$a'_3$ .	$b'_3$ .	$a'_4$ .	$b'_4$ .
Summer . . .	1	- 57	-147	- 64	- 64	- 76	- 4	- 2	32
	2	-153	- 38	- 32	- 30	-10	-36	11	0
	3	- 12	- 24	- 39	-122	- 7	- 2	-14	1
	4	6	- 15	- 4	- 48	9	-27	-30	6
	5	-118	- 77	-123	- 23	-59	-12	9	22
	6	-146	- 58	24	- 70	-20	- 8	0	-10
	7	58	69	- 42	- 69	-45	-13	0	- 4
	8	79	- 54	- 6	- 51	3	-23	- 4	- 1
	Mean. .	- 43	- 43	- 36	- 60	-26	-16	- 4	6
Equinox . . .	1	- 14	-146	- 53	- 66	-34	0	-34	20
	2	- 80	- 61	55	- 56	6	-41	-12	11
	3	- 23	98	- 77	- 57	- 8	-25	2	25
	4	- 18	- 78	- 50	- 80	26	2	4	19
	5	-128	33	- 61	- 16	11	6	-10	- 4
	6	96	19	27	- 34	-12	-16	-22	-10
	7	24	68	- 47	- 63	0	-61	-33	-19
	8	28	-138	6	- 25	-13	-27	-28	- 9
	Mean. .	- 14	- 26	- 25	- 50	- 3	-20	-17	4
Winter . . .	1	- 44	-134	- 46	- 14	-86	-21	-46	11
	2	-183	-117	- 54	- 88	-55	- 4	-11	7
	3	17	- 40	- 19	-177	-32	-30	- 7	-15
	4	131	-252	- 30	-162	-24	-47	- 4	-19
	5	- 17	-174	- 4	-135	- 5	-52	-29	-14
	6	-161	-138	- 47	-168	-64	-32	-10	13
	7	73	- 1	- 74	-163	-26	-46	-32	-16
	8	53	-126	-137	-164	-92	-38	-25	- 2
	Mean. .	- 16	-123	- 51	-134	-48	-34	-20	- 4



TABLE IV. (2) (c).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to the Epoch of New Moon.

(2) Manila.

(c) Vertical Force (Upwards).

Season.	Lunar phase.	$a'_1$ .	$b'_1$ .	$a_2$ .	$b_2$ .	$a'_3$ .	$b'_3$ .	$a'_4$ .	$b'_4$ .
Summer . . .	1	- 4	- 58	- 38	- 80	- 26	- 33	11	- 2
	2	38	- 64	7	- 87	- 3	- 41	0	10
	3	63	- 58	42	- 79	10	- 36	4	4
	4	19	- 2	18	- 94	37	- 31	- 13	- 6
	5	9	- 20	- 14	- 47	- 27	- 38	- 13	- 3
	6	- 24	- 94	3	- 93	- 5	- 29	- 3	- 1
	7	15	- 15	15	- 77	9	- 43	2	- 5
	8	45	- 68	28	- 95	1	- 45	- 17	- 4
	Mean. .	20	- 47	8	- 81	0	- 37	- 4	- 1
Equinox . . .	1	38	- 42	11	- 123	- 9	- 70	- 12	- 17
	2	19	- 13	19	- 112	35	- 74	14	- 23
	3	50	- 42	16	- 122	7	- 70	3	- 11
	4	34	- 69	0	- 74	- 19	- 62	- 8	- 13
	5	- 2	- 64	- 15	- 122	5	- 56	6	- 23
	6	16	- 75	10	- 100	10	- 52	11	- 13
	7	- 20	- 43	5	- 69	- 2	- 55	0	- 19
	8	19	- 37	16	- 79	4	- 32	- 2	- 2
	Mean. .	19	- 48	8	- 100	4	- 59	2	- 15
Winter . . .	1	- 80	- 41	- 80	- 46	- 49	- 14	- 13	- 6
	2	- 55	- 16	- 93	- 32	- 49	- 13	- 10	- 10
	3	- 44	- 48	- 62	- 75	- 41	- 30	- 6	- 7
	4	66	12	- 63	- 45	- 32	- 7	- 19	1
	5	- 58	- 43	- 47	- 85	- 24	- 44	- 5	- 15
	6	- 25	- 58	- 74	- 109	- 40	- 61	- 14	- 16
	7	8	- 22	- 29	- 97	- 30	- 42	- 14	- 7
	8	- 21	- 124	- 75	- 112	- 50	- 47	- 9	- 13
	Mean. .	- 26	- 42	- 65	- 73	- 39	- 32	- 11	- 9

TABLE IV. (3) (a).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to the Epoch of New Moon.

(3) Batavia.

(a) West Declination (in Force Units).

Season.	Lunar phase.	$a'_1$ .	$b'_1$ .	$a_2$ .	$b_2$ .	$a'_3$ .	$b'_3$ .	$a'_4$ .	$b'_4$ .
Summer . . .	1	- 8	4	- 10	- 24	- 4	- 2	8	0
	2	10	- 3	35	- 56	2	- 50	- 9	- 21
	3	57	67	37	20	- 13	7	- 3	5
	4	- 6	2	6	- 32	19	3	3	- 3
	5	11	- 4	45	0	2	17	- 6	- 3
	6	38	55	34	- 10	- 2	- 3	- 24	- 15
	7	- 7	- 33	6	- 23	- 12	4	- 3	11
	8	- 17	55	29	2	14	7	- 9	- 15
	Mean . .	9	18	23	- 15	1	- 2	- 5	- 5
Equinox . . .	1	4	- 39	- 42	- 34	- 28	- 3	- 6	26
	2	- 55	- 50	- 153	- 2	- 37	- 2	- 25	24
	3	24	17	- 20	9	- 38	- 9	- 28	- 1
	4	- 28	51	- 102	38	- 18	6	- 42	3
	5	- 26	- 4	- 48	32	- 20	6	- 31	25
	6	- 41	- 27	- 95	- 13	- 55	- 15	- 37	- 21
	7	20	- 50	- 45	- 50	- 14	- 30	- 17	- 14
	8	- 7	- 12	- 21	- 44	- 10	- 6	- 31	- 18
	Mean . .	- 14	- 14	- 66	- 8	- 28	- 7	- 27	3
Winter . . .	1	- 109	- 70	- 262	59	- 113	112	- 21	56
	2	- 87	- 28	- 207	78	- 32	123	- 8	37
	3	- 119	- 52	- 246	- 63	- 126	55	- 38	42
	4	- 93	- 75	- 225	14	- 82	37	- 31	44
	5	- 60	- 46	- 256	15	- 118	30	- 4	33
	6	- 88	- 84	- 312	57	- 172	61	- 70	46
	7	- 56	- 69	- 301	18	- 157	55	- 80	32
	8	- 126	- 4	- 262	30	- 116	61	- 27	15
	Mean . .	- 92	- 54	- 259	26	- 114	67	- 35	38

TABLE IV. (3) (b).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation,  
Reduced to the Epoch of New Moon.

(3) Batavia.

(b) Horizontal Force.

Season.	Lunar phase.	$a'_1$ .	$b'_1$ .	$a_2$ .	$b_2$ .	$a'_3$ .	$b'_3$ .	$a'_4$ .	$b'_4$ .
Summer . . .	1	- 19	- 32	- 66	- 70	28	9	- 6	22
	2	- 83	- 114	- 54	- 78	- 22	- 42	20	10
	3	47	- 70	- 20	- 108	9	- 40	12	11
	4	- 50	- 54	7	- 37	- 1	- 27	- 7	- 5
	5	10	92	- 71	- 62	- 3	2	14	18
	6	38	- 41	- 64	- 88	1	16	3	12
	7	40	- 28	- 35	- 87	14	3	21	- 9
	8	- 8	- 68	- 42	- 64	9	- 18	- 21	11
	Mean. .	- 3	- 39	- 43	- 74	4	- 12	4	9
Equinox . . .	1	47	- 89	- 57	- 49	- 22	- 24	- 29	6
	2	30	8	- 93	- 64	- 10	- 2	- 23	3
	3	- 38	36	- 82	32	- 29	12	- 21	- 20
	4	- 103	22	- 42	- 71	20	- 29	21	0
	5	- 28	63	- 47	- 1	8	0	- 1	- 8
	6	96	- 108	- 17	- 87	- 9	- 17	- 22	- 9
	7	- 31	- 64	1	- 66	17	- 37	11	1
	8	- 102	- 137	- 154	- 53	- 42	- 7	- 11	23
	Mean. .	- 16	- 34	- 61	- 45	- 8	- 13	- 9	0
Winter . . .	1	- 59	- 57	- 64	- 128	- 32	- 27	- 12	- 8
	2	- 48	- 26	- 94	- 77	- 24	- 28	- 14	14
	3	59	- 2	- 87	- 118	- 31	- 39	5	- 6
	4	30	- 18	- 54	- 123	- 23	- 43	- 20	- 35
	5	- 7	30	- 90	- 93	- 24	- 4	- 17	- 20
	6	136	- 77	- 118	- 109	- 26	- 3	14	- 27
	7	78	- 23	- 88	- 123	- 22	- 8	- 40	4
	8	- 26	- 25	- 95	- 139	- 31	- 37	- 36	- 36
	Mean. .	20	- 22	- 86	- 112	- 27	- 38	- 15	- 14

TABLE IV. (3) (c).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to the Epoch of New Moon.

(3) Batavia.

(c) Vertical Force (Upwards).

Season.	Lunar phase.	$a'_1$ .	$b'_1$ .	$a_2$ .	$b_2$ .	$a'_3$ .	$b'_3$ .	$a'_4$ .	$b'_4$ .
Summer . . .	1	- 6	- 36	- 12	25	- 5	0	- 12	5
	2	- 21	- 4	18	49	15	11	15	5
	3	- 3	- 22	8	35	- 1	- 13	- 3	- 7
	4	- 8	- 16	33	73	- 13	- 5	8	- 5
	5	- 9	9	- 21	34	- 4	7	7	6
	6	- 13	- 47	- 3	26	- 8	- 1	5	- 2
	7	18	- 12	14	43	7	- 7	3	- 1
	8	- 21	- 20	- 3	23	8	- 8	7	1
	Mean. .	- 8	- 19	4	38	0	- 2	4	0
Equinox . . .	1	44	- 24	34	18	6	- 6	- 12	- 5
	2	42	- 11	19	- 10	25	- 11	- 2	- 7
	3	- 8	8	- 4	48	6	- 7	2	- 11
	4	8	6	10	19	4	8	3	6
	5	38	12	3	33	- 2	- 20	2	- 8
	6	16	- 41	27	23	20	- 4	16	- 9
	7	7	- 7	32	22	17	- 8	1	0
	8	- 16	- 53	14	58	0	7	21	- 6
	Mean. .	16	- 14	16	26	10	- 5	4	- 5
Winter . . .	1	23	- 47	8	- 69	- 20	- 55	- 25	- 15
	2	- 16	- 78	- 31	- 40	- 34	- 45	- 17	- 1
	3	64	- 21	33	- 19	- 18	- 31	- 7	- 22
	4	- 17	- 31	- 10	- 22	- 11	- 27	- 12	- 17
	5	12	22	22	- 19	18	- 8	- 8	- 10
	6	- 2	- 25	- 18	- 17	7	- 37	8	- 37
	7	49	- 42	18	- 21	7	- 38	- 5	- 9
	8	11	19	13	- 28	- 3	- 52	- 14	- 26
	Mean. .	16	- 25	5	- 29	- 7	- 37	- 10	- 17

TABLE V.—Fourier Coefficients (in the Formula  $\Sigma C_n \sin(nt + \theta_n)$ ) of the Lunar Diurnal Magnetic Variation, Reduced to the Epoch of New Moon, at Pavlovsk, Pola, Zi-Ka-Wei, Manila, and Bätavia.

Observatory.	Force component.	C <sub>1</sub> .	$\theta_1$ .	C <sub>2</sub> .	$\theta_2$ .	C <sub>3</sub> .	$\theta_3$ .	C <sub>4</sub> .	$\theta_4$ .
Summer.									
Pavlovsk .	West . . .	131	114	128	88	28	83	2	—
	North . . .	61	20	105	4	62	355	26	291
	Radial . . .	36	145	13	203	11	282	1	—
Pola . . . .	West . . .	113	124	161	78	80	86	4	269
	North . . .	111	12	133	25	86	41	20	46
	Radial . . .	15	126	62	129	30	131	6	126
Zi-Ka-Wei {	West . . .	117	81	236	83	117	94	14	130
	North . . .	42	328	14	112	23	40	10	316
	Radial . . .	50	138	111	82	37	173	12	159
Manila . . .	West . . .	80	85	144	97	84	107	11	128
	North . . .	61	216	69	201	30	228	7	318
	Radial . . .	52	149	82	166	38	172	4	248
Batavia . . .	West . . .	20	18	27	117	2	99	8	219
	North . . .	40	177	86	203	13	153	11	19
	Radial . . .	10	195	38	359	2	174	4	84
Equinox.									
Pavlovsk .	West . . .	79	116	82	84	13	96	15	115
	North . . .	42	345	48	359	63	1	27	338
	Radial . . .	13	46	17	15	2	—	5	229
Pola . . . .	West . . .	71	124	60	60	48	100	26	107
	North . . .	63	3	80	29	71	37	21	53
	Radial . . .	14	97	24	164	14	166	14	171
Zi-Ka-Wei {	West . . .	65	61	162	87	91	69	32	110
	North . . .	48	313	28	0	37	25	22	347
	Radial . . .	24	88	125	68	22	160	2	173
Manila . . .	West . . .	58	60	114	105	74	106	28	113
	North . . .	29	200	56	197	21	177	18	275
	Radial . . .	53	150	100	167	60	168	17	166
Batavia . . .	West . . .	20	216	66	256	29	249	30	269
	North . . .	38	198	76	226	16	205	10	266
	Radial . . .	22	123	31	25	11	111	7	134

TABLE V.—(continued).

Observatory.	Force component.	$C_1$ .	$\theta_1$ .	$C_2$ .	$\theta_2$ .	$C_3$ .	$\theta_3$ .	$C_4$ .	$\theta_4$ .
Winter.									
Pavlovsk . . .	West . . .	28	214	36	310	21	304	15	131
	North . . .	17	172	20	246	20	245	2	—
	Radial . . .	28	284	6	157	2	—	4	47
Pola . . . . .	West . . .	46	218	45	320	15	320	3	349
	North . . .	50	144	30	126	11	159	2	—
	Radial . . .	15	123	35	118	7	89	1	—
Zi-Ka-Wei {	West . . .	8	197	66	167	39	199	15	170
	North . . .	99	123	133	132	37	118	11	53
	Radial . . .	45	208	82	66	8	144	12	167
Manila . . .	West . . .	41	211	123	212	68	224	13	204
	North . . .	125	179	145	193	61	227	23	250
	Radial . . .	51	203	98	157	41	222	16	223
Batavia . . .	West . . .	109	233	260	268	135	293	67	310
	North . . .	31	130	141	210	48	208	23	219
	Radial . . .	30	142	30	164	38	183	33	202

TABLE VI. (a).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to New Moon, at the Solstices.

No. of observatory.	West.				North.				Radial.			
	a.		b.		a.		b.		a.		b.	
	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.
(1) The 24-hour Term.												
1	120	-16	-53	-23	20	2	57	-17	20	-27	-30	7
2	94	-29	-63	-36	24	30	108	-40	12	13	-9	-8
3	116	-3	19	8	-22	84	35	-53	33	-21	-37	-40
4	80	-21	6	-35	-36	1	-50	-125	27	-20	-45	-47
5	6	-86	19	-66	2	24	-40	-20	3	-19	10	24
(2) The 12-hour Term.												
1	128	-28	3	23	8	-18	105	-8	-5	2	-12	-6
2	157	-29	34	35	57	24	120	-18	48	31	-39	-17
3	234	15	30	64	13	98	-5	-89	110	75	16	33
4	143	-64	-17	-105	-25	-33	-64	-142	19	-54	-80	-81
5	24	-260	-12	8	-33	-71	-79	-122	1	-9	-38	-29
(3) The 8-hour Term.												
1	28	-17	3	12	-6	-18	62	-8	-11	-2	2	0
2	80	-10	5	11	57	4	65	-10	23	7	-20	0
3	116	-13	-8	37	15	33	18	-17	4	5	-37	7
4	80	-47	-24	-49	-22	-44	-20	-42	5	-28	-38	-30
5	2	-124	0	52	6	-23	-12	-42	0	2	2	38
(4) The 6-hour Term.												
1	2	11	1	-10	-24	0	9	2	1	3	1	-3
2	-4	0	0	3	14	1	14	-2	4	-1	-3	0
3	11	3	-9	15	-7	9	7	7	4	3	-11	-12
4	9	-4	-7	11	-5	-22	6	-8	-4	-11	-2	-12
5	-5	-52	-6	43	-4	-14	10	-18	-4	13	0	31

TABLE VI. (b).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to New Moon, at the Equinoxes.

No. of observa- tory.	West.			North.			Radial.					
	a.		b.	a.		b.	a.		b.			
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.		
(1) The 24-hour Term.												
1	71	88	-35	-1	-11	1	40	45	10	23	9	-12
2	59	72	-40	-1	3	0	63	0	14	26	-1	-14
3	57	53	32	-1	-35	-1	33	-42	23	23	1	-12
4	50	26	29	0	-10	-1	-28	-80	26	13	-46	7
5	-12	-11	-16	0	-12	-1	-36	-90	-18	-5	-12	3
(2) The 12-hour Term.												
1	81	118	9	9	-1	-7	48	84	4	27	16	5
2	52	135	30	10	39	-4	70	47	6	43	-23	8
3	162	120	8	9	0	2	28	22	115	47	48	9
4	110	66	-29	5	-16	8	-53	-106	22	29	-98	5
5	-64	-29	-16	-2	-55	10	-53	-130	-13	-13	-27	2
(3) The 8-hour Term.												
1	13	41	-1	2	1	-2	63	31	1	4	1	-10
2	47	66	-9	3	43	-2	56	31	3	8	-13	-23
3	85	71	33	4	15	0	33	3	7	11	-20	-30
4	71	44	-20	2	1	2	-21	-42	12	7	-59	-21
5	-27	-20	-10	-1	-7	3	-14	-58	-10	-3	4	10
(4) The 6-hour Term.												
1	14	13	-6	-4	-10	3	25	11	-4	0	3	3
2	25	30	-8	-9	17	5	13	16	2	2	-14	8
3	30	39	-11	-11	-5	2	21	6	0	2	2	-13
4	26	28	-11	-8	-18	-5	2	-19	4	2	-16	-11
5	-30	-13	-1	4	-10	-8	-1	-28	-5	-1	5	5



TABLE VI. (c).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to New Moon. Mean Solstitial Component,  $\frac{1}{2}$  (Summer + Winter).

No. of observatory.	West.			North.			Radial.					
	a.		b.	a.		b.	a.		b.			
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.				
(1) The 24-hour Component.												
1	52	74	-38	-25	11	13	20	42	-4	7	-12	-30
2	32	61	-50	-21	27	0	34	0	12	7	-8	-35
3	56	45	6	-15	31	-14	9	-	6	7	-38	-31
4	30	22	-14	7	-18	-26	-88	-	4	4	-46	-17
5	-40	-9	-24	3	13	-29	-30	-	8	-2	17	7
(2) The 12-hour Component.												
1	50	96	13	-5	-5	4	48	69	-2	20	9	-15
2	64	110	34	-6	40	2	51	39	40	32	-28	-24
3	110	98	-17	-5	56	1	47	-18	92	34	24	-26
4	40	54	-61	-3	-29	-5	-103	-87	-18	21	-80	-16
5	-118	-24	-10	1	-52	-6	-100	-107	4	-10	-4	7
(3) The 8-hour Component.												
1	6	29	8	-11	-12	9	27	22	-6	0	1	-9
2	35	46	8	-18	30	9	28	22	15	0	-10	-21
3	52	50	-22	-20	24	1	0	0	4	0	-22	-27
4	16	31	-36	-12	-33	-12	-31	-30	-12	0	-34	-19
5	-61	-14	26	6	-8	-16	-27	-41	1	0	20	9
(4) The 6-hour Component.												
1	6	4	-4	-4	-12	4	6	4	2	0	-1	-3
2	-2	10	2	-10	8	5	6	5	2	-1	-2	-8
3	7	13	-12	-13	1	2	7	2	4	-1	-12	-13
4	2	9	-9	-9	-14	-6	-1	-6	-8	-1	-7	-10
5	-28	-4	18	4	-5	-9	-4	9	4	1	16	5

TABLE VI. (d).—Fourier Coefficients of the Lunar Diurnal Magnetic Variation, Reduced to New Moon. The Solstitial Inequality,  $\frac{1}{2}$  (Summer — Winter).

No. of observatory.	West.		North.		Radial.							
	b.		a.		a.		b.					
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.				
(1) The 24-hour Component.												
1	67	57	-15	9	9	8	37	49	24	11	-18	3
2	62	57	-14	9	-3	6	74	40	0	15	0	4
3	60	57	14	9	-53	5	44	30	27	18	2	5
4	50	57	20	9	-18	2	38	14	24	21	1	5
5	46	57	42	9	-11	1	-20	-6	11	21	-7	5
(2) The 12-hour Component.												
1	78	67	-10	10	13	9	56	58	-4	5	-3	4
2	93	94	0	14	16	-10	69	67	8	9	-11	8
3	120	114	47	17	-42	9	42	59	18	14	-8	12
4	104	129	44	19	4	-5	39	32	36	17	0	15
5	142	132	-2	20	19	2	22	-14	5	18	-34	16
(3) The 8-hour Component.												
1	22	19	-4	-3	6	2	35	17	-4	1	1	2
2	45	38	-3	-5	26	4	38	27	8	2	-10	6
3	64	55	-14	-8	-9	4	18	29	0	4	-15	-10
4	64	71	12	-10	11	2	11	18	16	6	-4	-14
5	63	75	-26	-11	14	-1	15	-8	-1	6	-18	-15
(4) The 6-hour Component.												
1	-4	1	6	0	-12	0	4	1	-1	0	2	0
2	-2	3	2	-1	6	1	8	2	2	0	-2	1
3	4	6	3	-2	-8	1	0	3	0	-	0	-2
4	6	8	2	-3	8	1	7	2	4	-1	5	-4
5	24	9	-24	-4	9	0	14	-1	-8	-1	-16	-4

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THE SPECIFIC HEAT OF AQUEOUS SOLUTIONS, WITH SPECIAL  
REFERENCE TO SODIUM AND POTASSIUM CHLORIDES.

BY

W. R. BOUSFIELD, M.A., K.C., F.R.S., AND C. ELSPETH BOUSFIELD.

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## II. *The Specific Heat of Aqueous Solutions, with Special Reference to Sodium and Potassium Chlorides.*

By W. R. BOUSFIELD, M.A., K.C., F.R.S., and C. ELSPETH BOUSFIELD.

Received June 16,—Read June 28, 1917.

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1. *Introduction.*—When a solute is dissolved in water, some of the water usually enters into combination with the solute whilst the remaining free water undergoes certain changes in constitution. The total volume of the water is always diminished. This contraction of the water has in the past been correlated to various properties of solutions and light has in this way been thrown on the phenomena of solution. In this communication the matter is studied with reference to the specific heat of solutions by reference to the examples of potassium and sodium chlorides. THOMSEN

pointed out ('Thermochemische Untersuchungen,' I., 52, 1882) that there was a close relation between the volume changes and the specific heat changes which took place on the dilution of a solution, but he did not arrive at any definite quantitative relationship, nor was he immediately concerned with the bearing of his results on the elucidation of the theory of solutions. One object of the present investigation was to obtain the necessary data to bring out with sufficient accuracy the true relationship between volume changes and specific heat changes. The examples chosen possess the advantage that certain other physical data are already available which are of material assistance. Freezing-point and vapour-pressure determinations, and also densities, conductivities, and viscosities over the range of temperature and concentration to be studied all have a bearing on the elucidation of the results. In the case of sodium chloride solutions at 20° C. adequate data exist over a sufficient portion of the range to enable accurate deductions to be drawn. There are still but few substances for which a complete systematic investigation of the various physical properties exists of sufficient accuracy and over a sufficient range of temperature and concentration. The multiplication of such systematic data is essential for secure generalization. In the meantime, the two examples studied in this communication lead to useful results.

In the search for the true theoretical relation between specific heat changes and density changes four empirical linear relations presented themselves. One set of these relations pointed to the specific heat lowering of the *solution* as a linear function of the contraction; the other to the mean specific heat lowering of the *water* as a linear function of the contraction. Both are so close to the truth that it was difficult to decide between them, but upon the whole the latter is to be preferred, and it gives a rational interpretation to the phenomena. Upon this view the fundamental laws which result can be expressed as follows:—

- (1) *The specific heat of the solute may be taken as practically constant at all dilutions.*
- (2) *The solution of the solute lowers the mean specific heat of all the water (both free and combined) by an amount which is proportional to the mean specific contraction of the water.* This latter relation may be expressed by  $ds_M/dw_M = L$ , where  $s_M$  is the mean specific heat of the water and  $w_M$  is the mean specific volume of the water.

In a former paper (BOUSFIELD, 'Roy. Soc. Proc.,' A, vol. 88, 149, 1913) it was found that the heat evolution attributable to the reduction of internal energy brought about by the contraction which took place upon the combination of certain pairs of elements bore a constant ratio to the contraction, the ratio being independent of the nature of the combining substances. This principle appears to be connected with the present result, although the actual value of the ratio depends on the heat required for certain changes of state which take place with rise of temperature.



It follows that the calculation of the specific heat of a series of solutions at a given temperature from the densities requires the experimental determination of only two constants. (See Section 23, Table XVIII.) Given these constants, the specific heat of a solution of any concentration at the given temperature can be calculated with great accuracy from the densities and the known specific heat of water.

The change which takes place in the constitution of the free water of a solution through the agency of a solute is a matter of the greatest interest for the theory of solutions. The study of viscosities had already led to the hypothesis that certain changes in the constitution of the free water might be taken as proportional to the concentration of the solute. The examples studied in this communication lead to the conclusion that

- (1) The specific heat and specific volume of the combined water may be treated as approximately constant ;
- (2) The lowering of the specific heat and specific volume of the free water on the introduction of a solute are each proportional to the percentage concentration of the solute.

An important object of the present investigation was to compare the temperature-variations of the specific heats of solutions with those of pure water. For this purpose the range of temperature of about 0° C. to 40° C. has been taken divided into three intervals, the mean specific heat for each interval being found. As was to be expected, in dilute solutions the specific heat curve approximates to that of water, which has a minimum value in the neighbourhood of 25° C. In concentrated solutions the minimum disappears, and in the most concentrated solutions the variation of the specific heat with temperature appears to follow a nearly straight-line law. This behaviour is to be attributed to the simplification of the water by the considerable destruction of ice and steam molecules and is entirely analogous to the corresponding phenomenon noted in a former communication with respect to densities (BOUSFIELD and LOWRY, 'Phil. Trans.,' A, vol. 204, 283, 1905).

Incidentally a relation emerges between heat of solution and contraction which may be expressed as

$$\left(\frac{dQ}{d\theta}\right)_H = L\left(\frac{dX}{dH}\right)_\theta.$$

The method and apparatus, which were originally designed for their present use, have been described in a former communication (W. R. and W. ERIC BOUSFIELD, 'Phil. Trans.,' A, vol. 211, 199, 1911) relating to the variation of the specific heat of water with temperature and the value of the calorie. The perusal of the former communication will greatly facilitate the task of following the experimental portion of the present paper.

2. *Apparatus and Method.*—The two chief points of the method described in the

former paper were the use of a cylindrical Dewar vessel immersed in a water bath as the calorimeter, and of a new "mercury resistance thermometer" as an electrical heater. The open end of the Dewar vessel was closed by an obturator consisting of a well-fitting platinum box containing water, which was kept at a certain temperature above the contents of the calorimeter in order to prevent condensation of vapour. A stirrer and thermometers and the leads of the heater were passed through suitable channels in the obturator, and through these orifices and around the obturator there was a small unavoidable escape of vapour from the calorimeter. The heat loss due to this was the subject of a correction which, in the neighbourhood of  $80^{\circ}\text{C}$ ., became sufficiently uncertain to deprive the results of the great accuracy which was sought. The experiments were therefore not carried beyond  $80^{\circ}\text{C}$ . The experiments described in the present paper are only carried to  $40^{\circ}\text{C}$ ., within which range corrections can be applied of the same order of accuracy as that of the electrical measurements. In order to render the apparatus more easily workable by two observers only, certain changes of method have now been made which must be noted.

In the former experiments it was the business of one observer to keep the heating current as nearly as possible constant with the help of an ampere balance in the circuit and an auxiliary mercury thermometer resistance, the ends of which were shunted through a battery of standard cadmium cells and a galvanometer. It was the business of another observer, by means of electrical heaters and gas burners, to keep the temperature of the bath exactly equal to the rising temperature within the calorimeter so that there was no heat transfer through the Dewar vessel, and also to keep the temperature of the obturator exactly  $10^{\circ}\text{C}$ . above that of the calorimeter. At the same time constant notes of the temperatures had to be made. This process involved a good deal of strain and an amount of skill which could only be obtained by long practice. The following modifications were therefore made:—

(a) The ampere balance and standard cells have been abandoned and the heating regulated by observation of a watt balance in the circuit. Thus the electrical energy is now kept constant instead of the current. This involves some loss of accuracy, but gives some compensating advantages.

(b) Instead of endeavouring to keep the temperature of the bath exactly equal to that of the contents of the calorimeter, the bath heating is only adjusted every two or three minutes, so as to keep the temperature within  $\pm 0.5^{\circ}\text{C}$ . of that of the calorimeter contents. The bath temperatures are noted every minute and plotted (see fig. 1) and a suitable correction applied for the temperature differences.

(c) The obturator is at the beginning of every run filled with water at such a temperature that at the end of the run (which lasts about 15 minutes) its temperature will have sunk to one or two degrees above that of the calorimeter contents. The obturator temperatures are also noted every minute, and subsequently plotted in order to arrive at the proper correction.

With the above changes the observations can be easily carried out and the

necessary notes made by two observers, although the subsequent application of the corrections is more troublesome.

3. *Calibration of the Mercury Thermometer Resistance.*—The heater used for the observations for the former paper was broken and had to be mended and re-calibrated. The resistance measured was that of the actual heater, designated by  $M_2$ , together with the resistance of the primary circuit of the watt balance, other than the heater  $M_2$ , denoted by  $\rho$ . The necessary experimental data in bridge ohms are given in Table I. together with the differences on the values calculated from the formula

$$M_2 + \rho = 7.8039 + 0.0280m + 0.0002054m^2,$$

where  $m$  is the reading of the thermometer resistance graduated in centimetres.

TABLE I.—Calibration of Thermometer Resistance.  
Experiment 390.

Temperature.	$m$ .	$M_2 + \rho$ observed.	Difference from calculated values.
1.005	2.12	7.8640	+0.0002
13.87	5.16	7.9537	+0.0001
26.37	8.11	8.0448	-0.0003
39.05	11.05	8.1383	+0.0001

To reduce to international ohms the constant 7.8039 must be multiplied by the bridge factor which gives the final value of the constant as

$$7.8020.$$

The bridge factor in measuring with the 10,000/10 ratio is given by

$$f = 0.9995 + \frac{2}{3}(\theta - 8) \times 10^{-4}.$$

The bridge factor corrects for errors in coils as well as in the ratio arms.

The value of  $\rho$  was 0.0770.

4. *The Watt Balance.*—The Kelvin watt balance used was of an ordinary type. The use of this balance showed certain small defects which may be noted for future improvement.

(a) Accuracy depends on knowing the exact value of the shunt resistance (approximately 500 ohms). With the balance employed the temperature could only be ascertained by a thermometer inserted among the coils. Designing the resistance so that it could be placed in a well stirred oil-bath would remove this source of uncertainty.

(b) The oil in the dash-pot appears to creep over the edge of the pot so that the level of the oil is gradually lowered. This affects the flotation of the dash-pot piston

and consequently the zero of the scale. Possibly a pneumatic dash-pot would serve for accurate experiments or even a pair of light springs one on each side of the dash-pot piston.

(c) The pointer had a rather broad mark which made it difficult to see when the arm was exactly horizontal in order to obtain the zero correction. A finer mark or a fine pointer would probably obviate this.

The zero correction was always taken at the end of an experiment. The balance weight was always placed at the exact graduation 376 or 377 corresponding to about 5 amperes current and 188 watts. This exact graduation could be read with accuracy, but, owing to the breadth of the pointer mark, the zero corrections could only be read to within about  $\pm 0.1$ . The result of this was appreciable in comparing duplicate observations made under circumstances exactly similar except for the zero correction. Thus, for example, in Table III., comparing Experiments 490 and 498, where the weights of water employed were exactly the same, we see that the figures in the second set are lower throughout. This must be attributed to the zero error of the balance. The irregularities must mainly be attributed to the thermometer readings, as a difference of  $0.01$  C. on an interval of  $13^\circ$  C. would make a difference of 10 on the above figures. In the specific heat measurements to be described duplicate experiments were always made, and if these were not sufficiently concordant the experiment was again repeated.

The electrical arrangements were as shown in fig. 4 of the former paper (*loc. cit.*, p. 209), except that the auxiliary resistance  $M_1$  and its shunt circuit were omitted. The value of the ampere balance readings was known from the former experiments to within  $\pm 1$  in 5000 when passing a current of about 5 amperes. To calibrate the watt balance (Experiment 416) the calorimeter was charged with water, and a current of about 5 amperes was passed through the apparatus. At the same time a steady flow of water was passed through the calorimeter until a definite régime was obtained at a definite temperature. The watt balance graduation being fixed at 376 the current and the ampere balance were adjusted until the two balances were both in equilibrium together. The current was accurately known from the ampere balance and the resistance from the mercury thermometer heater, the shunt resistance  $R_0$  of the watt balance being also observed. The mean of a series of experiments showed that the watt balance graduation required at this point a correction on the reading equal to  $+0.5$ . The zero correction, to correct for alterations of the zero from time to time, had to be added to this. To correct for the portion of the energy expended, not in the calorimeter but in the leads and primary circuit of the watt balance, it was always necessary to multiply the total energy measured by the factor  $M_2/(M_2 + \rho)$ . This was practically constant, the values of the factor being

$0^\circ$ C. to $13^\circ$ C.	$13^\circ$ C. to $26^\circ$ C.	$26^\circ$ C. to $39^\circ$ C.
0.99032,	0.99043,	0.99054.

If  $x$  is the corrected graduation reading of the watt balance, the power in watts expended in the calorimeter through the heater  $M_2$  is therefore

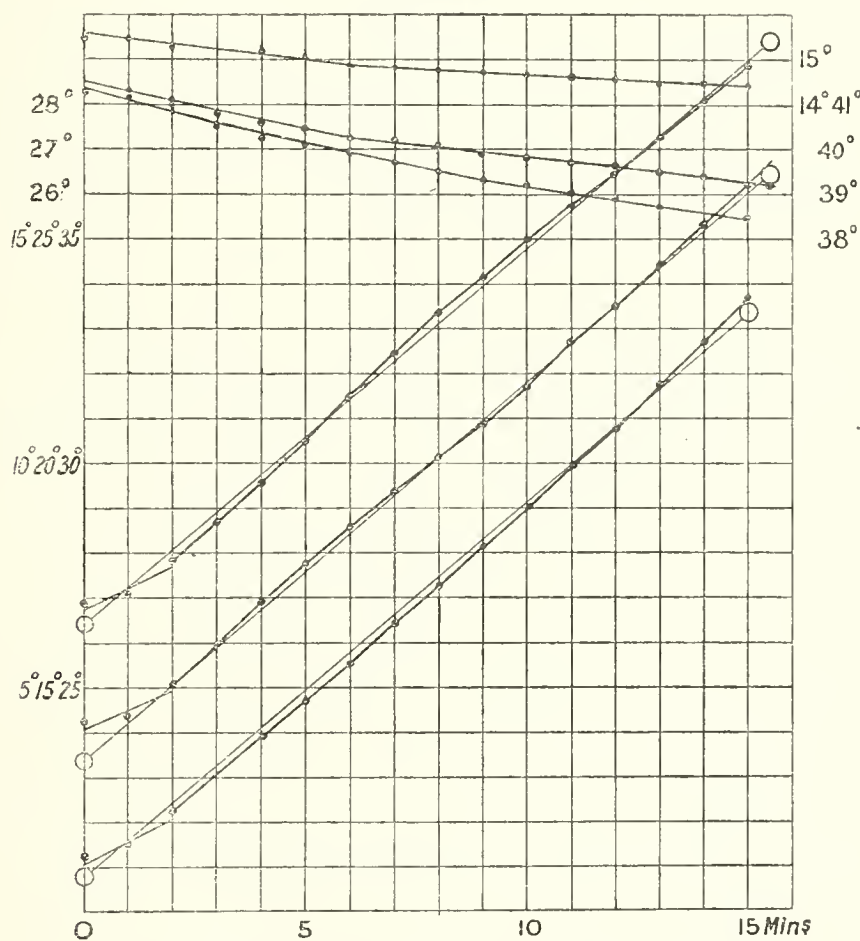
$$U = R_0 x \frac{M_2}{M_2 + \rho} \times 10^{-3}.$$

5. *Calorimeter Corrections.*—The formulæ for these corrections involved a series of experiments which may be briefly indicated. They are expressed in the following notation:—

- $Q$  = heat transferred to contents of calorimeter in joules,  
 $t$  = time in minutes,  
 $T_B$  = mean temperature of the bath during the short intervals,  
 $T_{OB}$  = mean temperature of obturator,  
 $T_D$  = mean temperature of liquid in Dewar vessel.

The plotting of the temperatures showed that the observations could be divided into short intervals of 2 to 10 minutes, during each of which a straight-line law held,

Fig. 1.



*Temperature Chart for Experiment No. 516.*

as will be observed from the specimen chart, fig. 1. (For details see Appendix.) The total of all corrections was less than 1 per cent. of the total energy applied.

6. *Correction for Stirring and Evaporation.*—These were estimated together. The temperature variations of viscosity and vapour pressure caused the correction to vary from a heat gain of about 55 joules per minute at 0° C. to a negative correction of about -30 joules at 40° C. Within this range the correction obeyed with sufficient approximation a straight-line law which for water is expressed by

$$dQ/dt = 55 - 2.2T_D.$$

This correction could also be taken for the KCl solutions, the viscosity of which is little different from that of water. But for the NaCl solutions the higher viscosities rendered it necessary to observe the value of this correction for each solution. For the strongest NaCl solution its value was

$$dQ/dt = 64 - 2.2T_D.$$

The observations for these corrections were made by observing the rise or fall of temperature in the calorimeter with stirring at the normal rate (350 revolutions per minute) at various temperatures between 0° C. and 40° C., keeping the temperature of the bath and obturator the same as that of the contents of the calorimeter.

7. *Obturator Heating.*—For this correction the rise of temperature was observed for various excess temperatures of the obturator whilst keeping the bath at the same temperature as that of the calorimeter contents. The rise due to stirring was calculated from the preceding formula. The balance due to obturator heating was simply

$$dQ/dt = 4.85 (T_{OB} - T_D).$$

8. *Radiation through Calorimeter Walls.*—For this correction various excess temperatures of the bath were maintained whilst the obturator was kept slightly above the temperature of the contents of the calorimeter, and the rise due to this and to the stirring was calculated from the preceding formulæ. The balance could be expressed as

$$dQ/dt = (32.7 + 0.36T_D)(T_B - T_D).$$

It will be noted that the formula shows that the Dewar vessel was more diathermanous at higher temperatures.

It may be observed that the above corrections are different from those given in the former paper. The Dewar vessel and mercury resistance thermometer formerly used had been broken. The fit of the obturator in the new Dewar vessel was not quite the same, which altered the correction for escape of vapour. The thickness of the walls of the Dewar vessel also turned out to be different and this necessitated the re-determination of its capacity. But as this has resulted in another series of experiments confirmatory of the former values of the specific heat of water between 0° C. and 40° C. it may be regarded as a fortunate accident.

9. *The Method of Calculation.*—Let

$U$  = watts developed in electrical heater,

$\Delta t$  = time of heating in minutes,

$\Delta Q$  = joules absorbed from obturator, radiation, stirring and evaporation,

$\Delta\theta$  = rise of temperature,

=  $b^\circ - a^\circ$ ,

$C_a^b$  = mean capacity of calorimeter in joules between  $a^\circ$  and  $b^\circ$ ,

$S_a^b$  = mean specific heat of liquid in joules from  $a^\circ$  to  $b^\circ$ ,

$W$  = weight of liquid in grammes.

Then

$$U \times 60 \Delta t + \Delta Q = WS_a^b \Delta\theta + C_a^b \Delta\theta.$$

Hence we have

$$WS_a^b + C_a^b = 60U \left/ \frac{d\theta}{dt} + \frac{dQ}{d\theta} \right.$$

From this expression we get the mean specific heat for the interval when the capacity is known, or the capacity when the specific heat is known. It will be observed that we are really dealing with the total heat for each interval. Hence whenever specific heat is spoken of in this paper, what is really meant is the mean specific heat for the interval under consideration, *i.e.*,  $\int_a^b s d\theta / (b-a)$ . Thus for the interval  $0^\circ.5$  C. to  $13^\circ.5$  C. the mean temperature is  $7^\circ$  C., and the total heat for the interval divided by 13 is spoken of for brevity as the specific heat at  $7^\circ$  C. Also  $d\theta/dt$  is the average rise of temperature per minute during the interval and  $dQ/d\theta$  is the total heating from obturator, radiation, &c., during the interval divided by  $(b-a)$ .

10. *The Specific Heat Observations.*—The experiments necessary to determine the capacity of the calorimeter and the specific heat of the solutions were conducted in the same way. A three-litre flask was filled with water or with the solution, weighed and left all night in a refrigerator packed in ice. The calorimeter and the bath were cooled with ice, and the empty flask was weighed after pouring the contents into the cooled calorimeter. The electrical heating was divided into three periods which were approximately  $0^\circ$  C. to  $13^\circ$  C.,  $13^\circ$  C. to  $26^\circ$  C., and  $26^\circ$  C. to  $39^\circ$  C. In actual working the initial temperature was usually from about  $0^\circ.5$  C. to  $1^\circ$  C. The ends of the intervals were determined by stopping at the nearest exact half-minute, which gave about  $13^\circ.5$  C.,  $26^\circ.5$  C., and  $39^\circ.5$  C.  $\pm 0^\circ.3$  C. for the end temperatures of the intervals. The mean temperatures for the intervals were thus almost exactly  $7^\circ$  C.,  $20^\circ$  C. and  $33^\circ$  C. A specimen set of observations (Experiment No. 516) which is given in the Appendix will serve to make the course of an experiment clear. These observations were plotted as shown in fig. 1, in order to arrive at approximate straight-line intervals for the corrections. Table II. gives all the experimental data from Experiment 516, including the mean temperatures  $T_B$  and  $T_{OB}$  of the bath and

TABLE II.—Experiment No. 516.

## Calculation of Results.

	1st period.				2nd period.				3rd period.		
Duration . . . . .	15 minutes.				15½ minutes.				15½ minutes.		
Temperature { start . . . . .	0·786				13·393				26·438		
{ end . . . . .	13·368				26·427				39·411		
Rise of temperature . . . . .	12·582				13·034				12·973		
$d\theta/dt$ . . . . .	0·8388				0·8409				0·8370		
Correction intervals . . . . .	2	2	4	7	2	3	5	5½	2	6	7½
$T_B$ . . . . .	1·72	3·17	5·64	10·50	14·50	16·45	19·74	24·26	27·25	30·61	36·40
$T_D$ . . . . .	1·62	3·30	5·82	10·43	14·23	16·34	19·70	24·11	27·27	30·61	36·26
$(T_B - T_D)\Delta t$ . . . . .	0·20	-0·26	-0·72	0·49	0·54	0·33	0·20	0·83	-0·04		1·05
Correction intervals . . . . .	6		9		6		9½		9		6½
$T_{OB}$ . . . . .	15·3		14·7		27·9		26·8		40·3		38·9
$T_D$ . . . . .	3·3		9·6		15·9		22·4		30·2		36·7
$(T_{OB} - T_D)\Delta t$ . . . . .	117·9				113·8				105·2		
$\Delta Q$ { bath . . . . .	-9·24				75·53				46·38		
{ obturator . . . . .	571·82				551·93				510·22		
{ stirring, &c. . . . .	591·75				173·60				-270·01		
Total $\Delta Q$ . . . . .	1154·3				801·1				286·6		
$dQ/d\theta$ . . . . .	92				61				22		
$R_0$ . . . . .	499·74				499·86				499·93		
$U$ . . . . .	186·58				186·64				186·69		
$60U \frac{d\theta}{dt}$ . . . . .	13346				13317				13383		
$60U \frac{d\theta}{dt} + \frac{dQ}{d\theta}$ . . . . .	13438				13378				13405		

the obturator as calculated from the observations for the straight-line intervals on the chart. The temperatures  $T_D$  of the contents of the Dewar vessel are calculated from the end values and the times of the short intervals. Table II, also sufficiently shows the method of calculation to obtain the result. Experiment No. 516 was one of those for determining the capacity, and the final figures are carried to Table III. The course of the experiments for the specific heats was precisely the same.

The whole procedure looks a little complicated, but in reality it is reduced to its simplest form. Practically each experiment, covering three periods, took one day for the observations and the plotting and calculation of the results.



11. *The Capacity of the Calorimeter.*—This was determined from the values of  $S_a^b$  for water, which it was the object of the former paper to determine. Since the date of that paper the results have been criticised by CALLENDAR (Bakerian Lecture, ‘Phil. Trans.,’ A, vol. 212, p. 1, 1912), and the question arose as to which values should be adopted. For the reasons given more fully in a “Note on the Specific Heat of Water,” which is communicated simultaneously with the present paper, (‘Roy. Soc. Proc.,’ A, vol. 93, 587, 1917), it has been thought that the values given in the former paper between  $0^\circ$  C. and  $40^\circ$  C. are preferable to those which result from the researches of CALLENDAR and BARNES. Moreover, if, as CALLENDAR suggests, the former values are affected by idiosyncrasies of the apparatus or method, there can be no doubt that the values now obtained for solutions will be similarly affected, and, therefore, for the purpose of comparing the specific heats of solutions with those for water, it will be best to work with the results for water given by the same method. For the intervals chosen for the present investigation the values of  $S_a^b$  for water derived from the former paper are (*loc. cit.*, p. 234)

$0^\circ$ C. to $13^\circ$ C.	$13^\circ$ C. to $26^\circ$ C.	$26^\circ$ C. to $39^\circ$ C.
4.193,	4.175,	4.175,

the equality for the second and third periods resulting from the position of the minimum at about  $25^\circ$  C., whilst those which result from the work of CALLENDAR and BARNES are

4.199,	4.189,	4.184.
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The results of two sets each of six experiments are set out below in Table III. The figures tabulated are the values of  $60U \left/ \frac{d\theta}{dt} + \frac{dQ}{d\theta} \right.$  (see Section 9), which result from the experiments of which the details of No. 516 have been given as an example.

Thus, applying the series of values of  $S_a^b$  derived from the former paper, we get the regular series of capacities

839,	857,	876,
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for the intervals. By applying the figures of CALLENDAR and BARNES we get the irregular series

824,	815,	849.
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Since the specific heat of glass steadily increases with temperature, it is clear that the first series of capacities is to be preferred, and they are adopted for the purposes of this paper.

TABLE III.

Reference No. of experiment.	Capacity experiments.			
	0° C. to 13° C.	13° C. to 26° C.	26° C. to 39° C.	Weight of water (W) in calorimeter.
FIRST SET.				
488	13,437	13,380	13,400	3000·4
490	13,443	13,383	13,410	2999·8
492	13,439	13,397	13,425	3000·2
494	13,415	13,398	13,411	3000·4
496	13,408	13,382	13,371	3000·4
498	13,398	13,371	13,386	2999·8
Means . . . .	13,423	13,385	13,401	3000·2
SECOND SET.				
504	13,424	13,373	13,386	2998·5
506	13,414	13,382	13,409	2999·7
508	13,417	13,378	13,418	2999·4
510	13,416	13,387	13,395	3000·0
514	13,409	13,380	13,397	3000·2
516	13,438	13,378	13,405	2999·5
Means . . . .	13,420	13,380	13,402	2999·6
Mean of all . .	13,421	13,382	13,401	2999·9
WS <sub>a</sub> <sup>b</sup> . . . .	12,582	12,525	12,525	
C <sub>a</sub> <sup>b</sup> . . . . .	839	857	876	

12. *The Specific Heat Measurements.*—The solutions were made up with “conductivity water” ( $\kappa = 1 \times 10^{-6}$ ) in the manner described in the next section. The KCl solutions were made from a pure salt re-crystallized and showing no trace of sodium in the flame test. The NaCl solutions were made from a pure salt precipitated by HCl and fused. The observations were made and plotted in the manner before described, the results being calculated from the expression given in Section 9. The experimental results are given in Tables IV. and V. where P indicates the percentage of the solution and  $h$  the number of molecules of water per gramme molecule of solute.

TABLE IV.—Mean Specific Heats of KCl Solutions for the Intervals, as Observed.

No. of experiment.	No. of solution.	h.	P.	Mean specific heat for the intervals.		
				7° C.	20° C.	33° C.
434	I.	16·362	20·188	3·210	3·224	3·245
436				3·206	3·225	3·245
440	II.	23·785	14·821	3·429	3·447	3·465
442				3·436	3·453	3·465
446	III.	35·296	10·495	3·634	3·640	3·648
448				3·627	3·644	3·659
452	IV.	53·743	7·150	3·796	3·799	3·807
470				3·792	3·789	3·806
472	V.	108·72	3·667	3·981	3·977	3·984
474				3·980	3·974	3·981
480	VI.	218·30	1·860 <sub>5</sub>	4·087	4·069	4·074
482				4·078	4·067	4·073
484	Water	$\infty$	0	4·076	4·065	4·066
				4·193	4·175	4·175

TABLE V.—Mean Specific Heats of NaCl Solutions for the Intervals, as Observed.

No. of experiment.	No. of solution.	h.	P.	Mean specific heat for the intervals.		
				7° C.	20° C.	33° C.
520	I.	9·7347	25·000	3·290	3·294	3·296
522				3·294	3·294	3·296
526	II.	13·883	18·945	3·426	3·437	3·444
528				3·430	3·438	3·441
532	III.	20·758	13·519	3·588	3·605	3·616
534				3·586	3·609	3·621
542	IV.	29·189	10·005	3·705	3·728	3·733
544				3·710	3·721	3·738
548	V.	54·442	5·625	3·896	3·903	3·916
550				3·883	3·896	3·908
552	VI.	109·94	2·8669	4·027	4·036	4·039
554				4·024	4·035	4·034
556	VII.	220·91	1·4476	4·106	4·099	4·104
558				4·102	4·097	4·096
	Water	$\infty$	0	4·193	4·175	4·175

13. *The Density Observations.*—In the case of the KCl solutions the density observations were made in duplicate with a pair of pycnometers of the kind described in a former paper (BOUSFIELD, 'Trans. Chem. Soc.,' vol. 93, 679, 1908). An accurate series of densities for KCl solutions was given in a former paper (BOUSFIELD, 'Zeit. für Phys. Chem.,' vol. 53, 312, 1905). For the purpose of the present paper it was

therefore sufficient to make up solutions of approximately the strength required and calculate the exact strength from the densities. To secure accuracy in the concentrations the densities were taken in duplicate, the means of the two determinations at 20° C. being used for the determination of the concentrations. The mean observed values of the densities are given in Table VI., together with the values of  $P$  and  $h$  calculated from the values of  $\rho_{20}$ .

TABLE VI.—Densities of KCl Solutions.

No. of solution.	$P$ .	$h$ .	$\rho_7$ .	$\rho_{20}$ .	$\rho_{33}$ .
I.	20.188	16.362	1.13907	1.13427	1.12878
II.	14.821	23.785	1.10034	1.09618	1.09111
III.	10.495	35.296	1.07030	1.066725	1.06205
IV.	7.150	53.743	1.04752	1.04445	1.04010
V.	3.667	108.72	1.02416	1.02172	1.01777
VI.	1.860 <sub>5</sub>	218.30	1.01219	1.01011	1.00636
Water	0.0	$\infty$	0.99993	0.99823	0.99473

The NaCl solutions were derived from a 25 per cent. solution very accurately made up, from which solutions II., III., and IV. were made up by weighing. Solution V. was made up by weighing to be as near normal as possible, and VI. and VII. were also made up by weighing to be as nearly as possible half and quarter normal. But no use is made of the volume concentrations in this paper, since they differ at the different temperatures. The quantity  $h$ , which represents the number of molecules of water per molecule of solute, is the more useful. The densities of NaCl solutions were not taken in duplicate. The observed values are given in Table VII.

TABLE VII.—Densities of NaCl Solutions.

No. of solution.	$P$ .	$h$ .	$\rho_7$ .	$\rho_{20}$ .	$\rho_{33}$ .
I.	25.000	9.7347	1.19538	1.18879	1.18188 <sub>5</sub>
II.	18.945	13.883	1.14531	1.13952	1.13323
III.	13.519	20.758	1.10238	1.09745	1.09178
IV.	10.005	29.189	1.07519	1.07094	1.06576
V.	5.625	54.442	1.04183	1.03857	1.03404
VI.	2.8669	109.94	1.02129	1.01873	1.01468
VII.	1.4476	220.91	1.01073 <sub>5</sub>	1.00858	1.00482
Water	0.0	$\infty$	0.99993	0.99823	0.99473

In Table VIII. are set out the values of the contraction function  $\chi$  which are calculated from the densities by means of either of the expressions

$$\chi = (E + he)(w - v),$$

or

$$\chi = 100E(w - v)/P,$$

where

$E$  = weight of a gramme molecule of the solute,

$e$  = weight of a gramme molecule of water,

$v = 1/\rho$  = the specific volume of the solution,

$w$  = the specific volume of pure water.

The values of  $E$  are taken as 74.56 for KCl and 58.46 for NaCl.

The properties of the contraction function  $\chi$  are explained in a former paper (BOUSFIELD, 'Trans. Chem. Soc.,' vol. 107, 1408, 1915) and will be referred to later.

TABLE VIII.—Values of  $\chi$ .

No. of solution.	$h$ .	$\chi_7$ .	$\chi_{20}$ .	$\chi_{33}$ .
KCl.				
I.	16.362	45.12	44.38	44.09
II.	23.785	45.91	45.03	44.67
III.	35.296	46.71	45.70	45.27
IV.	53.743	47.37	46.23	45.73
V.	108.72	48.11	46.83	46.28
VI.	218.30	48.53	47.21	46.57
	$\infty$	48.9	47.75	47.00
NaCl.				
I.	9.7347	38.24	37.55	37.22
II.	13.883	39.17	38.33	37.92
III.	20.758	40.19	39.17	38.64
IV.	29.189	40.90	39.74	39.15
V.	54.442	41.80	40.44	39.72
VI.	109.94	42.66	41.11	40.31
VII.	220.91	43.17	41.51	40.79
	$\infty$	44.06	42.23	41.44

14. *Final Specific Heat Values.*—On each interval of 13° C. there is a possible error of about 1 per 1000 on the thermometric reading of the interval and also of about 1 per 1000 on the reading of the watt balance. A glance at Table X. will show that the actual differences of calculated values from the observed mean values in that series are such as would result from casual adverse combinations of the

two errors. An approximate straight-line law was found to exist between  $h \Delta s$  and  $\chi$ ,  $\Delta s$  being the specific heat depression, *i.e.*, the difference between the specific heat of water and that of the solution.  $h \Delta s$  is proportional to the molecular specific heat depression. Though the relation turns out to be not strictly accurate, it enables closer final values to be obtained than by taking the mean values of two experiments in which the error might be in the same direction in both. The values of  $h \Delta s$  for all the solutions were plotted on the corresponding values of  $\chi$ , and the best straight line was drawn through all the points so plotted, the lines being expressible by

$$h \Delta s = A + B\chi.$$

For instance, in Table IX. are set out the experimental values for the specific heat of KCl solutions at 7° C., together with the values of  $\Delta s_7$  calculated from the expression

$$h \Delta s_7 = -92.14 + 2.4\chi_7.$$

The differences from the means of the experimental values are also set out.

TABLE IX.—Specific Heats of KCl Solutions at 7° C.

No. of solution.	$h$ .	$s_7$ , observed.	Mean values.	$\chi_7$ .	$\Delta s_7$ , calculated.	$s_7$ , calculated.	Difference from mean value.
I.	16.362	3.210	3.208	45.12	0.987	3.206	-2
II	23.785	3.206					
		3.429	3.433	45.91	0.758	3.435	+2
		3.436					
III.	35.296	3.634	3.630	46.71	0.566	3.627	-3
		3.627					
IV.	53.743	3.796	3.794	47.37	0.401	3.792	-2
		3.792					
V.	108.72	3.981	3.980	48.11	0.214	3.979	-1
		3.980					
VI.	218.30	4.087	4.080	48.53	0.111	4.082	+2
		4.078					
		4.076					

Furthermore in Table X. are set out similar figures for NaCl solutions at 20° C., which are of special importance, the relation in this case being

$$h \Delta s_{20} = -69.30 + 2.074\chi_{20}.$$

Each of the six series of results was plotted in the same way and the resulting line used as a guide in fixing the final values of the specific heats. The values of  $s_{20} - s_7$  and  $s_{33} - s_{20}$  were also plotted upon P, and the curves so obtained were also used to detect abnormal values and to help in fixing the final values more accurately. In the case of the NaCl series at 7° C., the  $h \Delta s, \chi$  line broke up into two straight lines

TABLE X.—Specific Heats of NaCl Solutions at 20° C.

No. of solution.	<i>h</i> .	$s_{20}$ , observed.	Mean values.	$X_{20}$ .	$\Delta s_{20}$ , calculated.	$s_{20}$ , calculated.	Difference from mean value.
I.	9.7347	3.294 3.294	3.294	37.55	0.881	3.294	±
II.	13.883	3.437 3.438	3.438	38.33	0.735	3.440	+2
III.	20.758	3.605 3.609	3.607	39.17	0.575	3.600	-7
IV.	29.189	3.728 3.721	3.725	39.74	0.449	3.726	+1
V.	54.442	3.903 3.896	3.900	40.44	0.268	3.907	+7
VI.	109.94	4.036 4.035	4.035	41.11	0.145	4.030	-5
VII.	220.91	4.099 4.097	4.098	41.51	0.076	4.099	+1
Water	∞	4.175					

inclined at a small angle and meeting at about  $P = 10$ . The divergence from the straight line appeared to be outside the limits of experimental error, and the values taken as final are within  $\pm 0.002$  of the mean observed values.

TABLE XI.—Final Values of Mean Specific Heats of KCl Solutions for Intervals of 13° C. and Mean Temperatures of 7° C., 20° C., and 33° C.

No. of solution.	<i>h</i> .	7° C.	20° C.	33° C.	$s_{20} - s_7$ .	$s_{33} - s_{20}$ .
I.	16.362	3.206	3.225	3.244	0.019	0.019
II.	23.785	3.435	3.451	3.469	0.016	0.018
III.	35.296	3.627	3.638	3.654	0.011	0.016
IV.	53.743	3.792	3.797	3.810	0.005	0.013
V.	108.72	3.979	3.974	3.981	-0.005	0.007
VI.	218.30	4.082	4.070	4.075	-0.012	0.005
Water	∞	4.193	4.175	4.175	-0.018	0.000

TABLE XII.—Final Values of Mean Specific Heats of NaCl Solutions for Intervals of 13° C. and Mean Temperatures of 7° C., 20° C., and 33° C.

No. of solution.	<i>h</i> .	7° C.	20° C.	33° C.	$s_{20} - s_7$ .	$s_{33} - s_{20}$ .
I.	9.7347	3.292	3.294	3.296	0.002	0.002
II.	13.883	3.430	3.440	3.449	0.010	0.009
III.	20.758	3.585	3.600	3.614	0.015	0.014
IV.	29.189	3.710	3.726	3.738	0.016	0.012
V.	54.442	3.892	3.907	3.918	0.015	0.011
VI.	109.94	4.025	4.030	4.036	0.005	0.006
VII.	220.91	4.104	4.099	4.101	-0.005	0.002
Water	∞	4.193	4.175	4.175	-0.018	0.000







temperature will be taken, because certain other data for NaCl at this temperature are available which are necessary for the complete explanation of the phenomena.

Let

$$\phi = (E + H) v - Hw,$$

$$\psi = (E + H) s - Hs_w,$$

where

$w$  = specific volume of pure water at the given temperature,

$s_w$  = specific heat of pure water at the same temperature, and

$H = he$ , the weight of water in which  $E$  grammes of the solute are dissolved. The symbol  $H$  is more convenient than  $he$  in some cases.

The quantities  $\phi$  and  $\psi$  correspond to those between which THOMSEN found a notable parallelism.  $\phi$  is sometimes called the "molecular volume" of the solute—a somewhat misleading term, especially when  $\phi$  happens to be a negative quantity. It is really the difference between the volume of the solution containing the gramme molecular weight  $E$  of the solute and the volume of the original water.  $\psi$  is the corresponding function substituting specific heat for specific volume, and is described by THOMSEN as the difference between the "caloric equivalent" of the solution and that of the water. It should be noted that

$$\phi = Ew - \chi,$$

and

$$\psi = Es - H \Delta s.$$

In Table XIII. are set out the values of  $\phi$  and  $\psi$  for NaCl solutions at 20° C. and also the values of  $H \Delta s$ . Fig. 4 shows the values of  $\psi$  plotted on the  $\phi$  values and also the values of  $H \Delta s$  plotted on the  $\phi$  values.

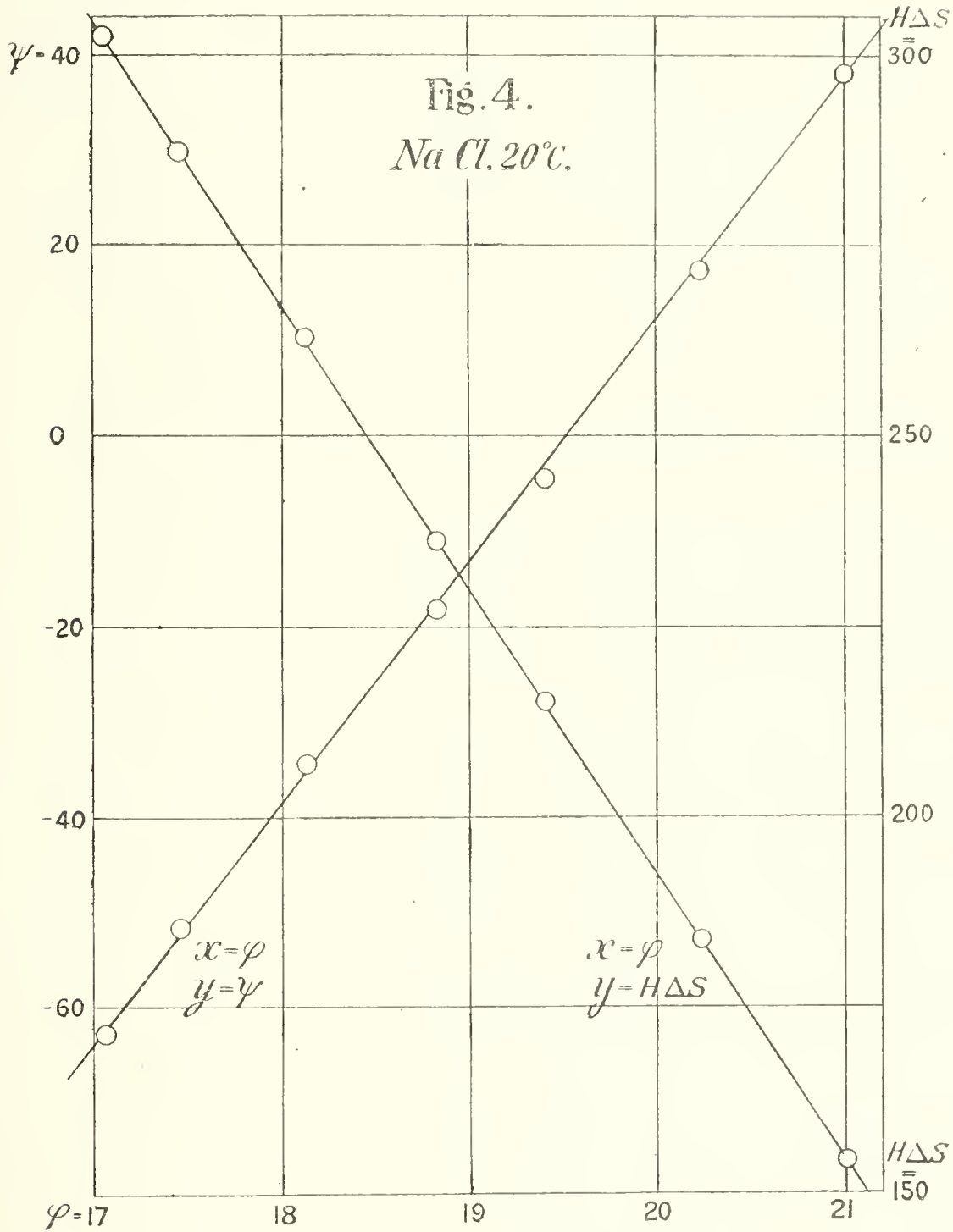
TABLE XIII.—NaCl Solutions at 20° C.

No. of solution.	P.	H.	$\psi$ .	$\phi$ .	$H \Delta s$ .
I.	25·000	175·38	38·06	21·01	154·5
II.	18·945	250·12	17·27	20·23	183·8
III.	13·519	373·98	- 4·59	19·40	215·1
IV.	10·005	525·87	- 18·30	18·82	236·1
V.	5·625	980·83	- 34·46	18·12	262·9
VI.	2·8669	1980·7	- 51·61	17·45	287·2
VII.	1·4476	3979·9	- 62·84	17·05	302·5

Both appear to be good straight lines, but they cannot both be absolutely straight unless there is a straight-line law between  $s$  and  $\chi$ . This is nearly but not quite the

case. The line which looks the best of the two is the  $H \Delta s, \phi$  line, but this is due to the linear relation having been used in another form to assist in adjusting the final values for  $s_{20}$ , as it is really equivalent to the relation

$$h \Delta s = A + B\chi.$$



It will be shown later that the linear relation between  $\phi$  and  $\psi$  is capable of a definite rational interpretation which appears to be fundamental for the relation between specific heat and specific volume.

16. *Volume Changes in the Solvent.*—When a solute is dissolved to form a concentrated solution, if the solute is a solid it assumes the liquid form with an accompanying change of volume owing to its liquefaction. We shall find good reason to suppose that dilution of the concentrated solution involves no further volume changes of the liquefied solute, and that the contraction which takes place on dilution is attributable to volume changes in the solvent. It is true that, owing to the compressibility of the atoms and molecules, the volume of the solute may be slightly diminished by dilution, owing to the molecular compression produced by further combination with the solvent. But this possible progressive volume change in the solute is too small to be traceable in the experimental results, and it will be seen later that both the specific heat and the specific volume of the solute, when once it has been reduced by solution to the liquid state, can be treated as constant for all isothermal dilutions. Thus for isothermal dilutions the contraction which takes place on dilution may be ascribed wholly to changes in the water, within the limits of experimental accuracy. These changes are due to

- (1) The disappearance of some of the bulkier molecules in the free water ;
- (2) The increased density of the combined water.

Assuming that water is a mixture chiefly of trihydrol or ice molecules  $(\text{H}_2\text{O})_3$ , dihydrol  $(\text{H}_2\text{O})_2$ , and hydrol or steam molecules  $(\text{H}_2\text{O})$ , it is probable that the addition of the solute reduces the proportion both of ice molecules and of steam molecules, both of which are comparatively bulky molecules (see BOUSFIELD and LOWRY, 'Phil. Trans.,' A, vol. 204, 283, 1905). At the same time both the freezing point and the vapour pressure of the solution are depressed. These depressions give us data from which, in conjunction with data as to conductivities and viscosities, the number of combined water molecules can be ascertained with some approach to accuracy. In the case of the most concentrated NaCl solutions all the necessary data, at temperatures of from  $18^\circ \text{C.}$  to  $20^\circ \text{C.}$ , exist, and in a former paper (BOUSFIELD, 'Trans. Chem. Soc.,' vol. 106, 1821, 1914) the water combination for three concentrated solutions of NaCl, which are nearly the same as solutions I., II., and III., was evaluated. By the help of these data we shall be able to arrive at the specific heat and the specific volume of the liquefied solute and thence at the volume changes in the solvent itself.

17. *The Specific Contraction of the Water of the Solution.*—It has been shown in a former paper (BOUSFIELD, 'Trans. Chem. Soc.,' vol. 107, 1409, 1915) in the case of a liquid solute that the contraction which takes place on the solution of a gramme molecular weight  $E$  of the liquid solute in  $H$  grammes of water is

$$\Delta\chi_0 = \chi - \chi_0,$$

where

$$\chi_0 = E(w - v_0)$$

is the value of  $\chi$  when  $H = 0$ ,  $v_0$  being the specific volume of the liquid solute. To apply this to the case of a solid solute the specific volume  $v_0$  of the liquefied solute as it exists in the solution must be deduced by the help of the data above-mentioned. It will be shown later that for NaCl solutions the value of  $E v_0$  (a gramme molecule of the liquefied solute) at  $20^\circ \text{C}$ . may be taken as  $25.053$  c.c.

If  $w_M$  is the mean specific volume of all the water in the solution, both free and combined, then

$$(E + H) v = E v_0 + H w_M,$$

and therefore

$$H w_M = H w + E (w - v_0) - (E + H) (w - v),$$

and since

$$\chi = (E + H) (w - v) \text{ and } \chi_0 = E (w - v_0),$$

we have

$$H (w - w_M) = \chi - \chi_0,$$

or writing  $w - w_M = \Delta w_M$ , the change in the mean specific volume of the water, we have

$$\Delta w_M = \Delta \chi_0 / H,$$

which also obviously follows from the mere fact that we treat  $E v_0$  as a constant, considering the whole contraction on dilution as due to changes in the density of the water.

Either of the quantities  $\Delta w_M$  or  $\Delta \chi_0 / H$  is the contraction per gramme (or the specific contraction) of the *water* of the solution.

18. *Relation of Specific Heat Lowering to Specific Contraction of the Water.*—In the search for the true relation between specific heat and specific volume changes the values of  $\Delta s_{20}$  were plotted on the specific contraction of the water. The values of  $\Delta \chi_0$  at  $20^\circ \text{C}$ ., taking  $E v_0 = 25.053$ , are set out in Table XIV. together with the values of  $\Delta s_{20}$  and of the specific contraction. They are plotted in fig. 5.

TABLE XIV.—NaCl Solutions at  $20^\circ \text{C}$ .

No. of solution.	$\Delta s_{20}$ .	$\Delta \chi_0$ .	$\Delta \chi_0 / H$ .	$\Delta s_{20}$ , calculated.	Difference.
I.	0.881	4.04	0.02304	0.880	-1
II.	0.735	4.82	0.01927	0.736	+1
III.	0.575	5.66	0.01513	0.578	+3
IV.	0.449	6.23	0.01185	0.453	+4
V.	0.268	6.93	0.00707	0.270	+2
VI.	0.145	7.60	0.00384	0.147	+2
VII.	0.076	8.00	0.00201	0.077	+1

The graph shown in fig. 5 looks an excellent straight line which may be represented by

$$\Delta s_{20} = 38.2 \Delta \chi_0 / H.$$

This relation would indicate that the specific heat lowering of the *solution* is proportional to the specific contraction of the water. We may compare it with the before obtained relation

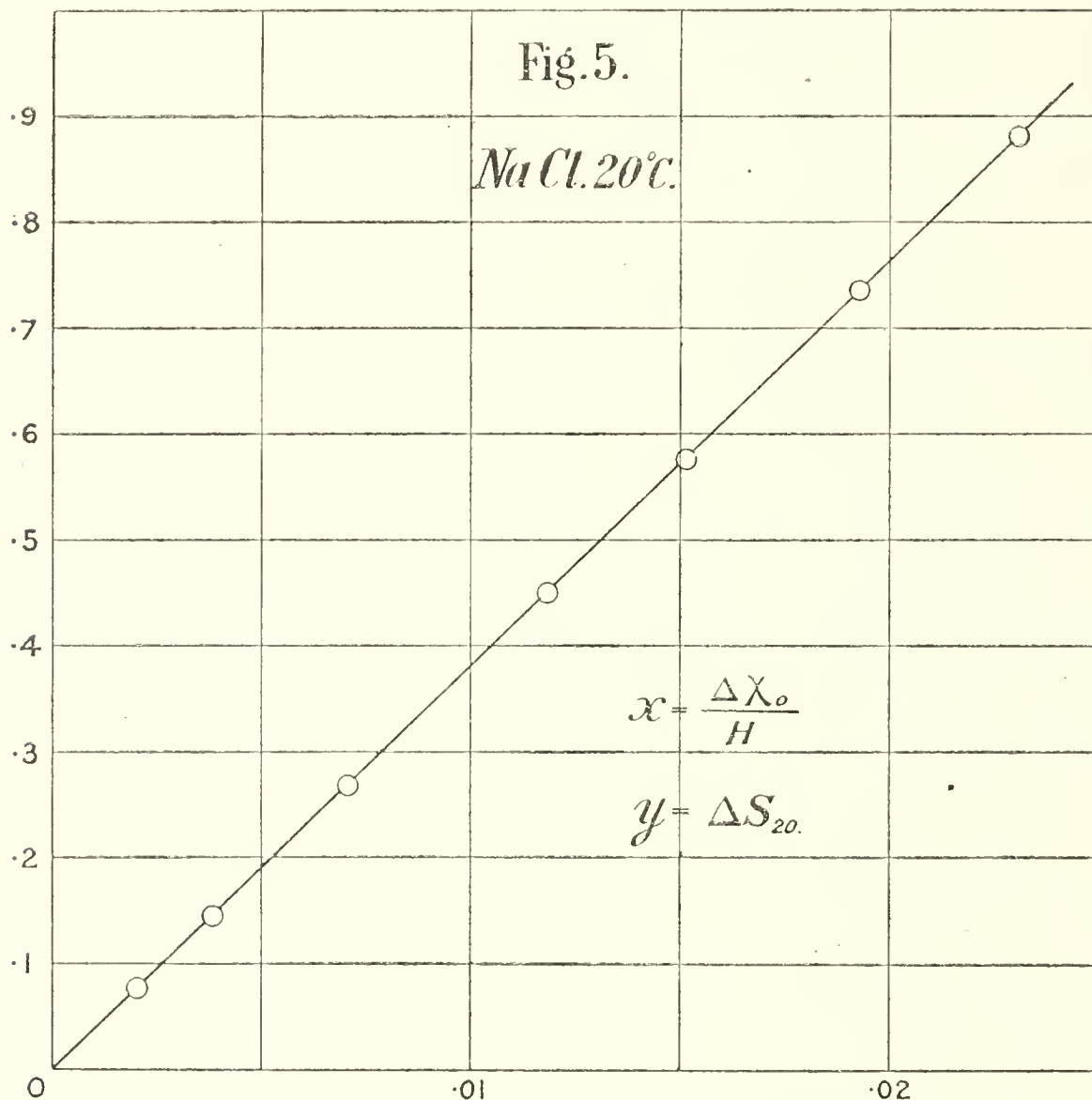
$$h \Delta s_{20} = -69.30 + 2.074\chi,$$

which may be written

$$\Delta s_{20} = 37.37 (\chi - 33.40)/H,$$

whilst the new relation may be written

$$\Delta s_{20} = 38.2 (\chi - 33.51)/H.$$



These are obviously the same relations, though the different paths by which they are obtained bring out slightly different values for the constants. In Table XIV. are given the calculated values for  $\Delta s_{20}$  from the above relation, with the differences. Though these are within the range of experimental errors yet the course of their variation indicates that the straight line may still be only a close approximation, and one is therefore led to look still further.

19. *Change in the Mean Specific Heat of the Water.*—There appeared good reason to suppose that the specific heat of the liquid solute might be treated as practically constant for all dilutions, and that the change in the mean specific heat of the water itself was that which was fundamentally related to the contraction. This hypothesis was tested in the following manner:—

Let

$s_M$  = the mean specific heat of the total water both free and combined,

$s_S$  = the specific heat of the liquid solute, taken as constant for all isothermal dilutions.

Then we have

$$s(E+H) = Es_S + Hs_M,$$

or

$$s_M = s + E(s-s_S)/H.$$

Hence for the lowering of the mean specific heat of the water we have

$$\Delta s_M = s_W - s_M = s_W - s - E(s-s_S)/H.$$

Now if  $\Delta s_M$  is proportional to  $\Delta\chi_0/H$ , we must have  $\Delta s_M = L\Delta\chi_0/H$  where  $L$  is a constant, and therefore

$$L\Delta\chi_0 = (s_W - s)H - Es + Es_S,$$

or since

$$\psi = Es - H\Delta s$$

we must have

$$L\Delta\chi_0 = -\psi + Es_S.$$

Hence if we plot the values of  $\psi$  upon the values of  $\Delta\chi_0$  we must get a straight line if the suggested relation holds.

In Table XV. are set out for NaCl solutions at 20° C. the values of  $\Delta\chi_0$  and the values of  $\psi$  calculated from the experimental data, and in fig. 6 the values of  $\psi$  are shown plotted upon the values of  $\Delta\chi_0$ .

TABLE XV.—NaCl Solutions at 20° C.

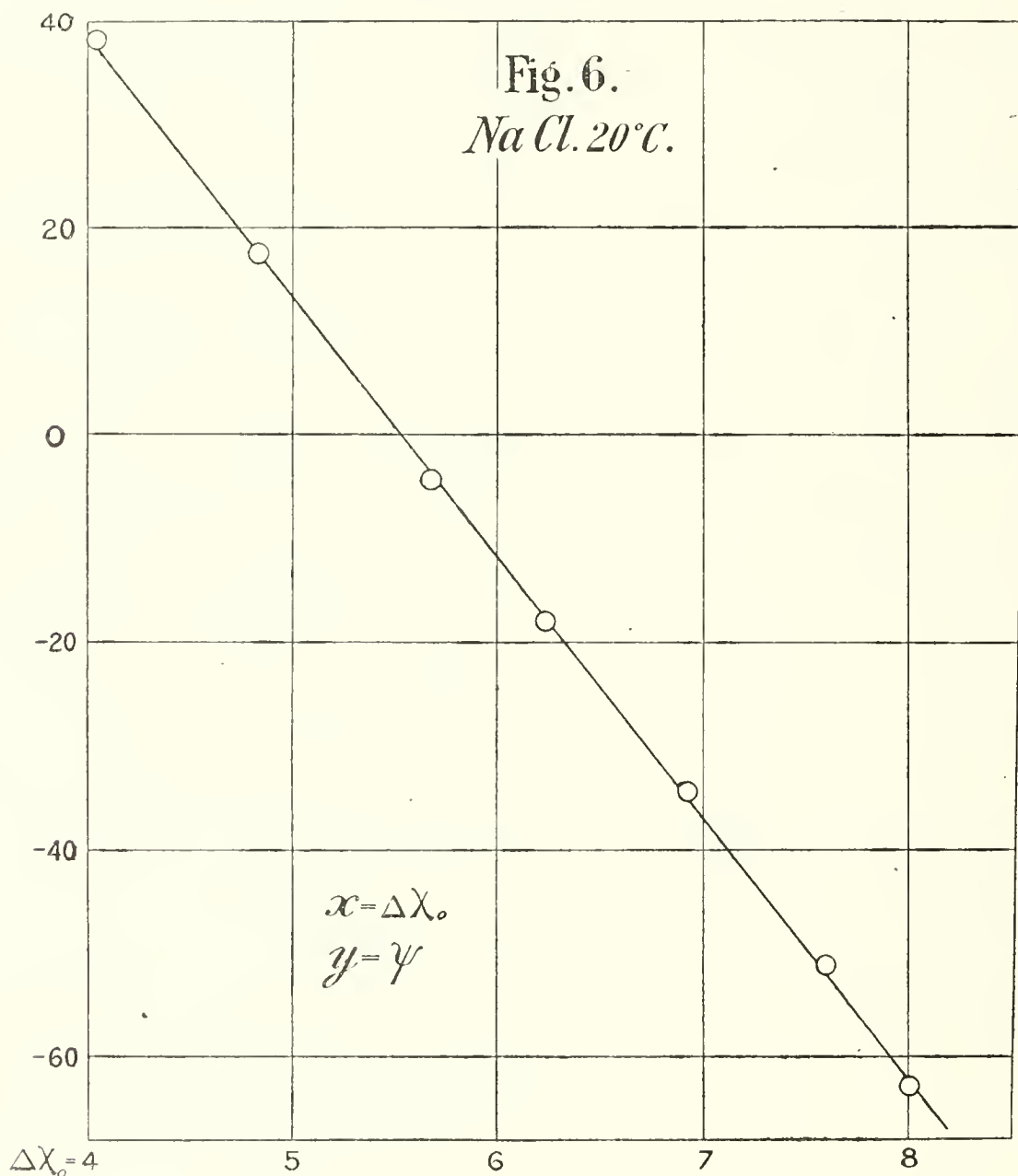
No. of solution.	$\Delta\chi_0$ .	$\psi$ .
I.	4.04	38.06
II.	4.82	17.27
III.	5.66	- 4.59
IV.	6.23	- 18.30
V.	6.93	- 34.46
VI.	7.60	- 51.61
VII.	8.00	- 62.84

It will be seen that a good straight line is obtained, the relation given being

$$25.73 \Delta\chi_0 = -\psi + 142.25,$$

which shows that  $E_{s_s} = 142.25$ , and that *the specific heat of the liquid solute may be taken as constant for all dilutions and has the value*

$$s_s = 142.25/58.46 = 2.433,$$



and also that the suggested relation holds, giving

$$\Delta s_M = s_W - s_M = 25.73 \Delta\chi_0 / H = 25.73 \Delta w_M,$$

or

$$\Delta s_M / \Delta w_M = 25.73.$$

We are now able to interpret the experimental results accurately and quantitatively on the hypothesis that the specific heat of the solute remains constant for isothermal



dilutions, whilst the *lowering of the mean specific heat of the water is proportional to the mean specific contraction of the water*. A glance at Table XVIII., which is given in Section 23, will show that this relation brings out the calculated results with an accuracy greater than that indicated by the differences set out in Table XVI., of Section 18. Another reason for regarding this as the fundamental relation is that this result seems to come into line with certain theoretical considerations which were developed in a former paper (BOUSFIELD, 'Roy. Soc. Proc.,' A, vol. 88, 149, 1913). It was shown for a large group of substances in the solid or liquid state that the heat of combination of pairs of the substances could be expressed by the sum of three components, two of which were constants belonging to the respective substances and the third of which was  $\frac{7}{8} \delta V$ ,  $\delta V$  being the contraction of the atomic volumes taking place on combination. Contraction in a solid or liquid means a limitation of the vibratory movements which involves a certain loss of kinetic energy per unit of mass. In that case it appeared that *the heat development due to the contraction was proportional to the contraction*. Moreover, within the area investigated, the ratio was independent of the kind of matter.

In the case of the specific heat of a solution we now find a lowering of the mean specific heat of the water which is proportional to the mean specific contraction of the water. The ratio differs from the former ratio in that the specific heat involves the additional element of changes of state with temperature, which may differ for different solutes. For instance in the case of the series of NaCl solutions at 7° C. the graph corresponding to fig. 6 breaks up into two straight lines inclined at a small angle to one another and involving two slightly different values of L above and below 10 per cent. strength. As both portions of the line are straight one can hardly attribute this result to experimental errors. It may be that the fundamental hydrate of NaCl in solution changes at the lower temperature in the neighbourhood of a 10 per cent. solution. Any such change of state might affect the ratio L.

The value for KCl worked out in the same way by calculating  $Ev_0$  with the aid of the known vapour pressures and conductivities in the neighbourhood of 20° C. comes out as  $L = 24.83$  as against 25.73 for NaCl. Experimental errors in any of the numerous data required for the calculation might account for the difference, and the area covered by research is not extensive enough for a generalization as to the variation of L with different solutes, but the value of L will probably come out nearly the same for a series of similar salts.

It remains to show that the relation  $\Delta s_M / \Delta w_M = L$  necessarily implies (at the same time as it interprets) the linear relation between  $\phi$  and  $\psi$  to which reference has been made in Section 15.

Since

$$\psi = Es_s - L(\chi - \chi_0)$$

and as can easily be shown

$$\phi = Ev_0 - (\chi - \chi_0)$$

by eliminating  $\chi - \chi_0$  we get

$$\psi = E(s_s - Lv_0) + L\phi.$$

Thus the result of this section involves a linear relationship between  $\phi$  and  $\psi$ . Furthermore this relation now gives us a new way of obtaining the important constant  $L$ , which is independent of the necessity of ascertaining  $s_s$  and  $v_0$ . It now turns out that  $L = d\psi/d\phi$ .

We can get its value at once from the series of values of  $\psi$  and  $\phi$  in Table XIII. Deducing it from the values of  $\psi$  and  $\phi$  for the two end solutions at 20° C. we get for NaCl,  $L = 25.48$ ; and similarly for KCl,  $L = 24.79$ .

From the above linear relation between  $\psi$  and  $\chi$  it follows that  $d\psi/d\chi = -L$ , a relation which will be of use later. Hence we get for  $L$  three forms of expression:—

$$L = \frac{ds_M}{dw_M} = \frac{d\psi}{d\phi} = -\frac{d\psi}{d\chi}$$

20. *Relation of Heat of Dilution to Specific Heat and Contraction.*—A certain relation comes to light in the course of this enquiry, which it may be well to put on record, though no figures are available for testing it practically. Let the heat of dilution at temperature  $t$  of 1 gr. molecule of the solute from a solution whose specific heat is  $s_1$  containing  $H_1$  grammes of water to a solution whose specific heat is  $s_2$  containing  $H_2$  grammes of water be denoted by  $q_t$ . To compare  $q_t$  with  $q_T$ , the corresponding heat of dilution at the higher temperature  $T$ , we proceed in the usual manner (as in THOMSEN, I., 66) on the principle that the heat required to pass from separate masses at temperature  $t$  to mixed masses at temperature  $T$  is independent of the order of mixing and heating. Hence we get

$$(E + H_2) \int_t^T s_2 dt - q_t = (E + H_1) \int_t^T s_1 dt + (H_2 - H_1) \int_t^T s_w dt - q_T.$$

Now the quantity  $s$  which is tabulated in this paper is really

$$s = \int_t^T s dt / (T - t),$$

and therefore we get

$$\begin{aligned} \frac{q_T - q_t}{T - t} &= (E + H_1)s_1 + (H_2 - H_1)s_w - (E + H_2)s_2 \\ &= (E + H_1)s_1 - H_1s_w - [(E + H_2)s_2 - H_2s_w] \\ &= \psi_1 - \psi_2 \end{aligned}$$

If we take  $Q$  as the mean heat of dilution per gramme of added water we have

$$Q(H_2 - H_1) = q,$$

and therefore

$$\frac{Q_T - Q_t}{T - t} = \frac{\psi_1 - \psi_2}{H_2 - H_1},$$

whence

$$\left(\frac{dQ}{dt}\right)_H = -\left(\frac{d\psi}{dH}\right)_t.$$

From the preceding section it follows that

$$\frac{d\psi}{dH} = -L \frac{d\chi}{dH},$$

and hence we get the result

$$\left(\frac{dQ}{dt}\right)_H = L \left(\frac{d\chi}{dH}\right)_t.$$

Since  $d\chi/dH$  is the contraction which takes place when 1 gr. of water is added to an infinite quantity of the solution we get a direct relation between heat of dilution and contraction which has been arrived at indirectly through the law developed for the specific heats.

21. *Specific Heat in Relation to Free and Combined Water.*—In Section 18 the specific heat of the solution was considered in relation to the mean specific heat of all the water both free and combined. It may now be considered in relation to the separate specific heats of the free and combined water, for which purpose we must have recourse to the number of molecules of combined water at different dilutions as determined in a former paper (BOUSFIELD, 'Trans. Chem. Soc.' vol. 105, p. 1821, Table X., 1914).

Let us examine the matter on the hypothesis:—

- (1) That the specific heat of the combined water is constant for all dilutions, and
- (2) That the specific heat of the free water is lowered by an amount which is proportional to the percentage of the solute.

The first assumption is probably sufficiently accurate for concentrated solutions, where the combined water molecules are few. The second suggested itself as the result of an enquiry into the changes which take place in the free water in relation to viscosity changes.

Let

$n$  = molecules of combined water per molecule of solute,

$h - n$  = molecules of free water per molecule of solute,

$s_C$  = specific heat of combined water (assumed a constant),

$s_F$  = specific heat of uncombined or free water for which we assume

$s_F = s_W - CP$ , where  $C$  is a constant.

Then we must have

$$(he + E)s = Es_s + nes_C + (h - n)es_F,$$

or substituting the assumed value of  $s_F$  and deducting  $hes_W$  from each side we get

$$\psi = Es_S - ne(s_W - s_C) - C(h - n)eP.$$

The values of  $n$  derived from the former paper are

$$\begin{array}{lll} h = 9\cdot10, & 14\cdot79, & 21\cdot95, \\ n = 3\cdot18, & 4\cdot41, & 5\cdot10. \end{array}$$

From these values we get the interpolation formula,

$$n = 0\cdot042 + 0\cdot4389h - 0\cdot009323h^2,$$

whence the values of  $n$  required for the first three NaCl solutions are

$$\begin{array}{lll} \text{I.} & \text{II.} & \text{III.} \\ n = 3\cdot348 & 4\cdot254 & 5\cdot052 \end{array}$$

Using these values of  $n$  for these first three solutions with the corresponding known values of  $\psi$  and  $s_W$ , taking  $E = 58\cdot46$  and  $e = 18\cdot016$ , we have three simultaneous equations to determine the three unknown constants, and we thus obtain the values

$$Es_S = 142\cdot09, \quad s_C = 3\cdot404, \quad C = 0\cdot02.$$

The value of  $Es_S$  deduced in Section 19 depended on taking  $Ev_0 = 25\cdot053$  in order to calculate the values of  $\chi_0$ .

In the present section the value of  $Es_S$  is deduced *without reference to the value of  $Ev_0$* . In Section 19 we obtained the value  $Es_S = 142\cdot25$  giving  $s_S = 2\cdot433$ . The value now deduced gives  $s_S = 142\cdot09/58\cdot46 = 2\cdot431$ . So far then the present method of treatment gives consistent results. Using the above values of the constants we may proceed to calculate the values of  $n$  from the formula,

$$n = \frac{Es_S - heCP - \psi}{(s_W - s_C - CP)e},$$

which is derived from the equation given above.

In Table XVI. are set out the data for this calculation and the results.

TABLE XVI.—Calculated values of  $n$  for NaCl Solutions at 20° C.

No. of solution.	$h$ .	$\psi$ .	CP.	$n$ .
I.	9·7347	38·1	0·5000	3·35
II.	13·883	17·3	0·3789	4·25
III.	20·758	— 4·5	0·2704	5·05
IV.	29·189	— 18·3	0·2001	5·36
V.	54·442	— 34·5	0·1125	5·58
VI.	109·94	— 51·6	0·05734	6·23
VII.	220·91	— 62·9	0·02895	6·71

In the next section these values of  $n$  will be compared with those given in Table XVII. which are calculated from the specific volumes, with a view to consider how far further support is given to the hypothesis as to the variation of the specific heat of the free water.

22. *Derivation of the Value of  $Ev_0$ .*—It remains to deduce the value of  $Ev_0$  which has been used in preceding sections. This may be obtained, by a process similar to that used in the last section for  $Es_s$ , from the volume data for solutions I., II. and III., and with the aid of the values of  $n$  deduced from the interpolation formula above given, making also a similar assumption as to the change in the specific volume of the free water. Let

$$\begin{aligned} v &= \text{specific volume of solution,} \\ v_0 &= \text{specific volume of liquid solute,} \\ w &= \text{specific volume of pure water,} \\ w_c &= \text{specific volume of combined water.} \\ w_f &= \text{specific volume of uncombined water.} \end{aligned}$$

Then we must have

$$(he + E)v = Ev_0 + new_c + (h - n)ew_f,$$

and assuming that  $w_c$  is constant and that  $w_f = w - BP$ , where  $B$  is a constant, and introducing this value of  $w_f$  into the above relation, we get

$$(he + E)v - (h - n)ew = Ev_0 + new_c + B(h - n)eP.$$

As before using the values of  $n$  for solutions I., II. and III., we get three simultaneous equations to evaluate the three unknown constants, and obtain

$$Ev_0 = 25.053, \quad w_c = 0.97551, \quad B = 0.0008536.$$

With these values of the constants we may calculate the values of  $n$  for the more dilute solutions from the expression

$$n = \frac{hew + Ev_0 - (he + E)v - heBP}{(w - w_c - BP)e}.$$

The results are set out in Table XVII.

TABLE XVII.—Calculated Values of  $n$  for NaCl Solutions at 20° C.

No. of solution.	$h$ .	$P$ .	$v$ .	$BP$ .	$n$ .
I.	9.7347	25.000	0.84119	0.02134	3.35
II.	13.883	18.945	0.87756	0.01617	4.26
III.	20.758	13.519	0.91120	0.01154	5.07
IV.	29.189	10.005	0.93376	0.00854	5.45
V.	54.442	5.625	0.96286	0.004802	5.75
VI.	109.94	2.8669	0.98161	0.002447	6.41
VII.	220.91	1.4476	0.99149	0.001236	6.83

Comparing the values of  $n$  in Table XVII. with those in Table XVI., the values for solutions I., II. and III., are of course those from which the respective constants were derived. The values of  $n$  for solutions IV., V., VI. and VII. agree well with one another considering that for solution VII. we are in both cases extrapolating to a dilution ten times as great as that of solution III. The values of  $n$  for the four last solutions are also in fair agreement with the values calculated in the former paper ('Trans. Chem. Soc.,' vol. 105, p. 1821, 1914) from freezing points and vapour pressures. The value of  $n$  for  $h = 236$  derived in the former paper from the freezing point value came out as 6.86. The present values for  $h = 221$  at  $20^\circ \text{C}$ . are, as they should be, a little lower.

These concordant results appear to justify the hypothesis that the specific heat lowering and the specific volume lowering of the free water may without serious error be taken as proportional to the percentage concentration, with the corollary that the specific heat and the specific volume of the liquid solute may be treated as constant for all dilutions, and also the specific heat and specific volume of the combined water with perhaps somewhat less accuracy. One is inclined to think that the slight divergence in the values of  $n$  in Tables XVI. and XVII. may be due to the diminished accuracy of the latter hypothesis. It may be noted that the ratio of the constant C for the specific heat lowering of the free water to the constant B for the specific volume lowering of the free water is  $C/B = 0.02/0.0008536 = 23.4$ , which is nearly equal to L.

In a previous paper ('Roy. Soc. Proc.,' A, vol. 88, p. 167, 1913) the value of  $Ev_0$  for NaCl came out as about 21 c.c. instead of 25 c.c. But at that time no method had been devised for treating the variation of the constitution of the free water with concentration, and the calculation was made on the assumption that the specific volume of the free water was the same as that of pure water, or in other words the constant B was taken as zero. To obtain a closer approximation it was necessary to make some allowance for the variation of the specific volume of the free water with the varying concentration of the solute, as has been done above.

The values of the various constants have been worked out for KCl as well as for NaCl, and although the vapour pressure data and the resulting values of  $n$  for KCl are not as accurate as those for NaCl it may be well to note the comparative results.\*

\* Too much stress must not be laid on these figures, since there still exists some uncertainty as to the exact values of  $n$  both for NaCl and for KCl. This would affect the values of all the constants except L. The value of L does not in any way depend on the value of  $Ev_0$ , nor the L relations at the end of Section 19. More exact vapour pressure data are required to settle the values of  $n$ .

<i>Values of Constants.</i>		
	KCl.	NaCl.
B =	0·001132	0·000854
$w_c =$	0·98592	0·97551
$Ev_0 =$	36·804	25·053
L =	24·83	25·73
$Es_s =$	123·4	142·1
$s_s =$	1·655	2·433

The molecular heat  $Es_s$  of the liquid solute comes out curiously high in both cases. Expressed in calories the molecular heats given above are

KCl.	NaCl.
29·5	34·0

According to the law of DULONG and PETIT as supplemented by KOPP the molecular heats for the solids are both about 13 cal. Thus the molecular heats for the liquefied solutes are more than double those of the solids. The same phenomenon is to be noted in the case of ice, the molecular heat of which is 8·6, whilst that of liquefied ice is 18, again more than double. In both cases there are no doubt changes of state with rise of temperature which account for the difference. The figures seem to point to the fact that the liquefied solutes have like water a complex molecular structure which is altered by rise of temperature.

23. *Analysis of the Specific Heat of the Solutions.*—The relations at which we have arrived enable us to analyse in a simple manner the isothermal changes in specific heat which take place on dilution of a solution.

If we put E grammes of solute into H grammes of water then in one gramme of the solution we have present  $\frac{E}{E+H}$  grammes of solute and  $\frac{H}{E+H}$  grammes of water.

Since

$$s(E+H) = s_s E + s_M H$$

we can write  $\Delta s$  in the form

$$\Delta s = \frac{E(s_w - s_s)}{E+H} + \frac{H(s_w - s_M)}{E+H}.$$

That is to say, the specific heat lowering by the introduction of E grammes of solute into H grammes of water may be regarded as the sum of two components.

- (1) The specific heat lowering due to the mere substitution of  $\frac{E}{E+H}$  grammes of solute for the same weight of water;
- (2) The reduction of the mean specific heat of the water from  $s_w$  to  $s_M$ .

The result developed in Section 19 gives for NaCl

$$s_w - s_M = 25·73 \Delta\chi_0/H.$$

Taking the constant value  $s_s = 2.433$  for the specific heat of the liquid solute and  $s_w = 4.175$  for the specific heat of pure water, we can then at once calculate the specific heat of the solution by means of the relation

$$s = \frac{Es_s + Hs_w - 25.73 \Delta\chi_0}{E + H}.$$

In Table XVIII. are set out the necessary data, together with the observed and calculated values and the differences, the values of the constant terms being

$$E = 58.46, \quad Es_s = 142.25, \quad s_w = 4.175.$$

TABLE XVIII.—Specific Heat of NaCl Solutions at 20° C.

No. of solution.	H.	$\Delta\chi_0$ .	$s_{20}$ , observed.	$s_{20}$ , calculated.	Difference.
I.	175.38	4.04	3.294	3.295	+1
II.	250.12	4.82	3.440	3.443	+3
III.	373.98	5.67	3.600	3.602	+2
IV.	525.87	6.23	3.726	3.726	±
V.	980.83	6.93	3.907	3.905	-2
VI.	1980.68	7.60	4.030	4.029	-1
VII.	3979.91	8.00	4.099	4.099	±

Thus, upon the simple assumptions that

- (1) The specific heat  $s_s$  of liquid NaCl has a constant value 2.433; and
- (2) That the mean specific heat lowering of the water in the solution is proportional to the mean specific contraction of the water;

we are able to calculate the specific heat of the solution for isothermal dilutions with errors less than those shown in Table XIV., thus confirming the conclusion that of the various very nearly linear empirical laws which have been examined the relation

$$\Delta s_M = L \Delta w_M$$

is the true law.

Furthermore, with the aid of the osmotic data, which furnish the number  $n$  of combined water molecules, the analysis can, as has been shown, be carried still further and the specific heats can be separated into three components instead of two:—

- (1) The specific heat of the liquid solute which by this method of treatment again shows the same constant value;
- (2) The specific heat of the combined water, which can be treated as a constant within the limits of experimental error, at all events for the more concentrated solutions;
- (3) The specific heat of the free water which is expressible as

$$s_F = s_w - CP.$$



24. *Changes in the Free Water of a Solution.*—To discover the true law governing the changes in the free water of a solution is an essential problem for the foundation of a rational theory of aqueous solutions. One is constantly brought face to face with this problem in considering the physical properties of an aqueous solution. In considering the densities of sodium hydroxide in a former paper (BOUSFIELD and LOWRY, 'Phil. Trans.,' A, vol. 204, pp. 280–283, 1905) it appeared that the simplification in certain phenomena of concentrated solutions must be attributed to a simplification of the solvent by the action of the solute. In a later paper (BOUSFIELD, 'Phil. Trans.,' A, vol. 206, pp. 129–142, 1906) the matter had to be considered in relation to the viscosity of aqueous solutions of sodium and potassium chlorides. It was there stated (*loc. cit.*, p. 136) that

“There is good reason for believing that the introduction of a solute into water somewhat lowers the radion of water, since the process of abstraction of water molecules by the solute breaks up some of the molecular complexes of the uncombined water, and therefore lowers the average molecular size of the uncombined water. The investigation of the amount of this lowering is a complex matter, and we shall neglect it, as it does not seriously affect the general character of our results, though it involves a slight loss of accuracy.”

Later investigation showed that improved results in the calculation of the viscosities of aqueous solutions could be obtained by treating the change in the radion of the free water as being proportional to the concentration of the solute.

Generally it may be said with regard to the physical properties of aqueous solutions that no relation can be formulated which is accurate over the whole range from great dilution to saturation which does not take into account the progressive change in the constitution of the free water. Certain properties of very dilute solutions can be accurately formulated over a range in which the concentration is so small that the constitution of the water may be considered as constant and practically unchanged. Certain properties can be accurately formulated over a range in which the concentration of the solute is so great that the constitution of the water is again practically unchanged, being mainly dihydrol. But to fill the gap between dilute and concentrated solutions the consideration of the changes taking place in the free water over the whole range seems to be essential.

A study of the ionisation law of LiCl in relation to the law of mass action over the whole range of concentration in a former paper (BOUSFIELD, 'Trans. Chem. Soc.,' vol. 105, pp. 1823–1828, 1914) well illustrates the point at which the constitution of the free water becomes a necessary element in the completion solution. It was shown that the application of the law of mass action to the ionisation of a solution involved the application to the dissociation constant of a factor dependent upon the progressive change which takes place in the free water as dilution proceeds.

The foregoing treatment of the matter in the consideration of the specific heats and specific volumes of aqueous solutions appears to throw further light on the problem.

Following up the hint given by a consideration of viscosities the present investigation shows that good results can in fact be attained by treating the changes in both the specific heat and the specific volume of the free water as being simply proportional to the percentage of the solute present, *i.e.*,

$$s_w - s_f = P \times \text{constant},$$

$$w - w_f = P \times \text{constant}.$$

P is proportional to  $1/(E+H)$ . The constants were also calculated on the hypothesis that the changes were proportional to  $1/H$  instead of P. The results were not very different but not quite so concordant, and the hypothesis that certain changes in the free water of a solution which depend on diminution of molecular complexity are simply proportional to the percentage concentration of the solute appears to be a step in the right direction in the solution of the problem.

## APPENDIX.

## EXPERIMENT No. 516.

Time.	Temperatures.			
	Bath.	Obturator.	Calorimeter.	R <sub>0</sub> .
Zero 10.30	1.24	15.5	0.786	17.0
1	1.63	15.5		
2	2.39	15.3		
4	3.95	15.2		
5	4.80	15.1		
6	5.61	14.9		
7	6.56	14.8		
8	7.33	14.8		
9	8.20	14.7		
10	9.06	14.7		
11	9.95	14.6		
12	10.81	14.6		
13	11.75	14.5		
14	12.72	14.5		
15	13.67	14.5	[13.368]	stop
16	13.96	—	13.373	18.1
17	14.0	—	13.378	
Zero 11.50	14.29	—	13.393	18.3
1	14.34	28.3		
2	15.09	28.1		
3	15.96	27.8		
4	16.87	27.6		
5	17.78	27.5		
6	18.58	27.3		
7	19.35	27.2		
8	20.12	27.1		
9	20.87	26.9		
10	21.70	26.8		
11	22.63	26.7		
12	23.50	26.6		
13	24.42	26.5		
14	25.31	26.4		
15	26.18	—		
15 $\frac{1}{2}$	—	26.3	[26.427]	stop
16 $\frac{1}{2}$	26.81	—	26.430	19.2
17 $\frac{1}{2}$	26.87	—	26.433	

## APPENDIX (continued).

## Experiment No. 516 (continued).

Time.	Temperatures.			
	Bath.	Obturator.	Calorimeter.	R <sub>0</sub> .
Zero 12.10	26.92	41.3	26.438	19.4
1	27.11	41.2		
2	27.86	41.0		
3	28.75	40.6		
4	29.64	40.3		
5	30.57	40.1		
6	31.54	39.9		
7	32.47	39.7		
8	33.39	39.5		
9	34.19	39.3		
10	34.99	39.2		
11	35.75	39.0		
12	36.53	—		
13	37.30	38.7		
14	38.11	—		
15	38.89	38.5		
15½	—	—	[39.411]	stop
16½	39.54	—	39.409	20.1
17½	39.57	—	39.407	

Laboratory Temperature 16° C.	
Flask and water . . . . .	3407.0
Flask . . . . .	410.7
	<u>2996.3</u>
Air . . . . .	3.2
	<u>2999.5</u>
Water in calorimeter . . . . .	2999.5
Watt balance . . . . .	377.0
Zero correction . . . . .	- 0.5
	<u>376.5</u>

N.B.—Observed temperatures are corrected.

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BAKERIAN LECTURE, 1917.

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THE CONFIGURATIONS OF ROTATING COMPRESSIBLE  
MASSES.

BY

J. H. JEANS, M.A., F.R.S.

PRINTED AND PUBLISHED FOR THE ROYAL SOCIETY BY  
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III. BAKERIAN LECTURE, 1917.—*The Configurations of Rotating Compressible Masses.*

By J. H. JEANS, M.A., F.R.S.

Received May 14,—Lecture delivered May 17, 1917.

1. ON the supposition that astronomical matter may be treated as incompressible and homogeneous, a single star rotating freely in stable equilibrium can be spheroidal or ellipsoidal, but of no other shape, while DARWIN has shown that both components of a binary star must be very approximately of the ellipsoidal shape.

Both for the interpretation of astronomical observations and for the more general purposes of cosmogony, it becomes of importance to examine how the sequence of figures assumed by an ideal homogeneous mass will be modified by the compressibility and non-homogeneity of actual astronomical matter.

The general mathematical problem of determining the configurations of stable equilibrium of the most general compressible mass is one of great complexity, but some important simplifications can be introduced by the use of general considerations. These are discussed in §§ 2–5 of the present paper. In § 10 we abandon the general problem and turn to a detailed study of the configurations possible when the compressibility is such that pressure and density are connected by the law

$$p = \kappa\rho^\gamma - \text{const.},$$

where  $\kappa$  and  $\gamma$  are constants, this of course including the important case of a gas in convective equilibrium. The results obtained are summarised, and their astronomical bearings discussed, in §§ 45–58. The paper is arranged so that these last sections contain the main results of the paper in a form which is free from mathematical technicalities; it is hoped that they will prove intelligible to readers who have omitted the more mathematical sections.

2. For a mass of matter of the most general kind, rotating with angular velocity  $\omega$  about the axis of  $z$ , the equations of relative equilibrium are three of the type

$$\frac{\partial p}{\partial x} = \rho \frac{\partial \Omega}{\partial x}, \text{ \&c., . . . . . } (1)$$

where

$$\Omega = V + \frac{1}{2}\omega^2(x^2 + y^2). \text{ . . . . . } (2)$$

Here  $V$  is the total gravitational potential, including that of tidal forces from neighbouring stars, if any are present. From equation (1) it follows that the surfaces  $p = \text{cons.}$ ,  $\Omega = \text{cons.}$ , and  $\rho = \text{cons.}$ , all coincide, so that the free surface, being a surface of constant pressure, must also be a surface of constant density, say  $\rho = \sigma$ , and must also be one of the equipotentials  $\Omega = \text{cons.}$ , say  $\Omega = C$ . The value of the gravitational potential over the surface must accordingly be

$$V = C - \frac{1}{2}\omega^2(x^2 + y^2),$$

this being the potential of the rotating mass itself and of certain tide-generating masses outside. We may suppose the positions and structure of these tide-generating masses to be given, so that  $\nabla^2 V$  is given at all points outside the surface of the rotating mass, while  $V$  is given at all points on the surface by the above equation, and vanishes at infinity. By a fundamental theorem in potential theory, it follows that  $V$  is determined uniquely at every point outside the mass in terms of  $\omega$ ,  $C$  and the shape of the boundary, whence  $\partial V/\partial n$  must be determined uniquely in terms of these quantities at every point of the boundary.

If  $M$  is the total mass of the rotating body,

$$4\pi M = \iint \frac{\partial V}{\partial n} dS,$$

where the integral is taken over the surface of the body, and on substituting the value of  $\partial V/\partial n$ , this becomes a linear equation, which may be regarded as determining  $C$  uniquely in terms of  $M$ .

Thus when  $M$ ,  $\omega$  and the equation of the boundary are given, it appears that  $V$  and  $\partial V/\partial n$  are uniquely determined over the boundary. If the value of  $\rho$  at the boundary, say  $\sigma$ , is given, and if we also know the law of compressibility at the boundary, then  $\rho$  and  $d\rho/dn$  are uniquely determined over the boundary. Thus not one, but two, surfaces of constant density are fixed, namely the boundary  $S$  and the surface just inside it, say  $S'$ .

The mass, say  $M'$ , inside  $S'$  is in equilibrium under the rotation  $\omega$  and gravitational forces which originate from the external tide-generating masses and also from the layer of matter between  $S$  and  $S'$ . It now follows from the preceding argument that the surface of constant density next inside  $S'$ , say  $S''$ , is also determined. There are now three surfaces of constant density fixed, and by a continual repetition of the foregoing process, we can fix all such surfaces in turn.\* Thus when the external boundary is given, and also  $M$ ,  $\omega$  and the tide-generating masses, which may be

\* This cannot be defended as a piece of rigorous mathematical reasoning, but there can, I think, be no doubt that it is true for practical purposes. I have discussed the mathematical complications elsewhere ('Roy. Soc. Proc.,' A, vol. 98, p. 413). A more formal proof of the theorem will be found in the 'Monthly Notices of the R.A.S.,' vol. 77, p. 187.

regarded as the data of the problem, the interior arrangement of the matter is uniquely determined.

3. The first consequence of the foregoing theorem is that when the boundary of a mass is fixed, all the internal vibrations are necessarily stable. For the change from stability to instability can only occur through a vibration of zero-frequency, and this would require that there should be two contiguous equilibrium arrangements of the interior matter, a possibility which is excluded by the result just obtained.

The only possible configuration for a mass at rest and under no tidal forces will clearly be one in which the boundary is spherical and the surfaces of constant density are also spherical and concentric with the boundary.\* If the mass is set into slow rotation, this system of concentric spheres will give place to a system of concentric spheroids. As the rotation increases further, the surfaces of equal density will no longer be strictly spheroidal, but it is clear that there must always be a linear series of configurations of equilibrium in which the boundary has the shape of a figure of revolution. This series of course reduces to the series of Maclaurin spheroids when the matter is incompressible.

Excluding for the present the case in which  $\sigma$  (the density at the boundary), vanishes, it can be shown† that there must be an infinite number of points of bifurcation on this series of figures of revolution, these corresponding to the different sectorial harmonics of the figure. The first point of bifurcation corresponds to the second sectorial harmonic: when this is reached the circular cross-section gives place to a slightly elliptic cross-section, and this leads to a series of figures having three planes of symmetry and three unequal axes, these figures reducing to the Jacobian ellipsoids when the matter is homogeneous and incompressible. It is convenient to refer to these two series as the series of pseudo-spheroids and pseudo-ellipsoids respectively. The first point of bifurcation on the series of pseudo-ellipsoids corresponds to a third harmonic displacement and leads to a series of pear-shaped figures.

It seems almost certain, although it has not been rigorously proved, that this last series of figures ends by fission into two detached masses revolving round one another as in the ordinary binary star formation. Assuming this, we may regard the passing of the first point of bifurcation on the series of pseudo-ellipsoids as the beginning of the process of fission. Until this stage is reached we have seen that the only possible figures of equilibrium for a rotating mass are pseudo-spheroids and pseudo-ellipsoids. For an incompressible mass the pear-shaped figures are unstable, so that spheroids and ellipsoids are the only possible figures of stable equilibrium. If the pear-shaped

\* The special application of this to the figure of the Earth has been discussed in a separate paper ('Roy. Soc. Proc.,' A, vol. 98, p. 413).

† 'Monthly Notices of the R.A.S.,' vol. 77, p. 189. In this paper I was mistaken in thinking that  $\sigma = 0$  presents a true exception to the general theory. The general argument there given failed to prove the result in the special case of  $\sigma = 0$ , but the result is true nevertheless, as will appear from the present paper.

figure proves to be unstable also for all compressible masses, then the only possible figures of stable equilibrium for a compressible mass will be pseudo-spheroids and pseudo-ellipsoids.

4. When the mass is compressible a complication can occur which, as it happens, does not arise in the incompressible problem. The resultant normal force at any point on the surface of rotating mass is  $-\partial\Omega/\partial n$ , this being the resultant of gravity and centrifugal force. In the incompressible problem,  $\partial\Omega/\partial n$  does not vanish, except in the unstable configurations at the far ends of the spheroidal and ellipsoidal series, but this is not necessarily the case in the compressible problem. We shall find that  $\partial\Omega/\partial n$  can vanish either on the series of pseudo-spheroids or on the series of pseudo-ellipsoids, and when this happens matter will necessarily be thrown off at the points at which  $\partial\Omega/\partial n$  vanishes. The series of figures of equilibrium may accordingly be abruptly terminated at any stage by the vanishing of  $\partial\Omega/\partial n$ .

5. Thus it appears that the series of figures of equilibrium for a compressible mass, until the stage at which fission begins, will consist of pseudo-spheroids and pseudo-ellipsoids, these series possibly being abruptly terminated by the vanishing of  $\partial\Omega/\partial n$  at any point. Our problem is to study these series of configurations; our method will be as follows:—

For an incompressible mass the density at the centre, which we shall denote by  $\rho_0$ , is identical with the density at the boundary, which we denote by  $\sigma$ . For a compressible mass,  $\rho_0$  will be different from  $\sigma$ , and a rough measure of the extent to which the density differs from uniformity will be given by a quantity  $\epsilon$  defined by

$$\epsilon = \frac{\rho_0 - \sigma}{\rho_0} \dots \dots \dots (3)$$

We know the solution of the problem when  $\epsilon = 0$ ; we require to obtain it for all values of  $\epsilon$ . Our method is to adopt the known solution when  $\epsilon = 0$  as generating solution and to obtain, by what amounts to a method of successive approximations, an expansion for  $\Omega$  in powers of  $\epsilon$ . The success of the method will depend on the extent to which the series so obtained is convergent.

The value of  $\Omega$  obtained in this way will be a function of  $x, y, z, \epsilon$  and of the constants which enter into the law of compressibility. When  $x, y, z$  are small the value of  $\Omega$  will be found to be convergent for all values of  $\epsilon$ , but as  $x, y, z$  increase, the range of convergence of the series contracts. But in the most important case we shall consider, it is found that the series is convergent, even for points furthest removed from the origin, for values of  $\epsilon$  up to some value between two and three. The largest value of  $\epsilon$  which is of physical interest is  $\epsilon = 1$ , corresponding to  $\sigma = 0$ , and for this value of  $\epsilon$  the series converges with considerable rapidity, so that the first few terms will give a fair approximation to the truth.

Our method, then, is to obtain the series of pseudo-spheroids and pseudo-ellipsoids as deformations of the already known series of spheroids and ellipsoids, expanding in

powers of the parameter  $\epsilon$ . The boundaries may accordingly be regarded as distorted ellipsoids.

In a previous paper\* I showed how to obtain the potential of a homogeneous mass, expanded in powers of a parameter which measured its divergence from the ellipsoidal shape. As a preliminary to the present investigation, we must examine the corresponding problem when the mass is not homogeneous.

*Potential of a Non-homogeneous Distorted Ellipsoid.*

6. We shall assume, as being adequate for the present problem, that it is possible to expand the density in the form

$$\rho = \rho_0 - \rho_2 - \rho_3 - \rho_4 - \dots \quad (4)$$

where  $\rho_0$  is the density at the origin, which is taken to be the point of maximum density, and  $\rho_2, \rho_3, \rho_4, \dots$ , are functions of  $x, y, z$  of degrees 2, 3, 4 ... respectively. No terms of degree unity occur because, from our choice of origin, the first differential coefficients of  $\rho$  vanish at the origin. The value of  $\rho_2$  is

$$\rho_2 = -\frac{1}{2} \left( x^2 \frac{\partial^2 \rho}{\partial x^2} + 2xy \frac{\partial^2 \rho}{\partial x \partial y} + \dots \right),$$

the differential coefficients all being evaluated at the origin. Our choice of origin has been such that  $\rho_2$  is necessarily positive for all values of  $x, y$  and  $z$ , so that by a suitable choice of direction of axes, it must be possible to express  $\rho_2$  in the form

$$\rho_2 = (\rho_0 - \sigma) \left( \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} \right).$$

Let us further put

$$\rho_3 + \rho_4 + \dots = (\rho_0 - \sigma) \epsilon P_0,$$

where  $\epsilon$  is a numerical quantity which may for the present be left undefined, but will ultimately be taken to be the parameter defined by equation (3), and  $P_0$  is a function of  $x, y$  and  $z$ . Then the general value of  $\rho$ , as given by equation (4), becomes

$$\rho = \rho_0 - (\rho_0 - \sigma) \left( \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} + \epsilon P_0 \right), \quad (5)$$

and the boundary, defined by  $\rho = \sigma$ , has for its equation

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} + \epsilon P_0 = 1. \quad (6)$$

When  $\epsilon$  is not too great this is a distorted ellipsoid. In the paper already referred to, I showed how to write down the potential of a homogeneous mass whose

\* 'Phil. Trans.,' A, vol. 215, p. 27.

boundary was given by an equation of the type of (6), the solution occurring as a series of powers of  $\epsilon$ . It is now necessary to extend the method so as to be able to write down the potential when the internal density is variable and given by equation (5).

As a matter of convenience, of which the advantage will appear later, we shall permit  $P_0$  to include terms of degree 2 as well as terms of degree 3 and higher. This is equivalent to regarding the mass under discussion as being arrived at by distortion from an ellipsoid of density,

$$\rho = \rho_0 - (\rho_0 - \sigma) \left( \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} \right) \dots \dots \dots (7)$$

the only restriction on the distortion being that the point of maximum density must remain the origin, and that the density at this point must remain equal to  $\rho_0$ . But distortions which are themselves ellipsoidal are not prohibited, as they would be if second-degree terms were excluded from  $P_0$ .

7. Let  $q$  be a function of the density  $\rho$ , defined by

$$q^2 = \frac{\rho_0 - \rho}{\rho_0 - \sigma} \dots \dots \dots (8)$$

so that, as we pass from the centre to the boundary,  $q$  varies continuously from 0 to 1. The surface of constant density  $\rho$  has for its equation

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} + \epsilon P_0 = q^2, \dots \dots \dots (9)$$

which may be regarded as a distorted ellipsoid of semi-axes  $qa, qb, qc$ . The boundary now figures as the special case of  $q = 1$ .

Let the potential of a homogeneous mass of unit density bounded by the surface (9) be denoted by  $V_0(q)$  when evaluated at a point outside the surface, and by  $V_i(q)$  when evaluated at a point inside the surface.

The whole heterogeneous mass of density given by equation (5) may be regarded as split up into shells of constant density, and the potential of the whole will be found to be given by the formulæ :

$$V_0 = \sigma V_0(1) + \int_{\sigma}^{\rho_0} V_0(q) d\rho \dots \dots \dots (10)$$

$$V_i = \sigma V_i(1) + \int_{\sigma}^{\rho} V_i(q) d\rho + \int_{\rho}^{\rho_0} V_0(q) d\rho, \dots \dots \dots (11)$$

the first formula giving the potential at a point entirely outside the mass, and the second formula giving the potential at a point inside the mass at which the density is  $\rho$ .

8. Suppose that  $P_0$  is expressed in the form

$$P_0 = F\left(\frac{x}{a^2}, \frac{y}{b^2}, \frac{z}{c^2}\right)$$

and let  $P$  be a function of  $x, y, z$  and a new variable  $\mu$ , given by

$$P = F\left(\frac{q^2x}{q^2a^2 + \mu}, \frac{q^2y}{q^2b^2 + \mu}, \frac{q^2z}{q^2c^2 + \mu}\right)$$

so that  $P_0$  is the value of  $P$  when  $\mu = 0$ . Further introduce  $\xi', \eta', \zeta'$  defined by

$$\xi' = x/(q^2a^2 + \mu), \text{ \&c.,}$$

so that

$$P = F(q^2\xi', q^2\eta', q^2\zeta')$$

and  $f$  and  $D$  (an operator) defined by

$$f = \frac{x^2}{q^2a^2 + \mu} + \frac{y^2}{q^2b^2 + \mu} + \frac{z^2}{q^2c^2 + \mu} - 1 = (q^2a^2 + \mu) \xi'^2 + \dots - 1,$$

$$D = \left(\frac{1}{q^2a^2} - \frac{1}{q^2a^2 + \mu}\right) \frac{\partial^2}{\partial \xi'^2} + \left(\frac{1}{q^2b^2} - \frac{1}{q^2b^2 + \mu}\right) \frac{\partial^2}{\partial \eta'^2} + \left(\frac{1}{q^2c^2} - \frac{1}{q^2c^2 + \mu}\right) \frac{\partial^2}{\partial \zeta'^2}.$$

Let  $\phi(q)$ , a function of  $\xi', \eta', \zeta', \mu$  and  $q$ , be given by

$$\begin{aligned} \phi(q) = \epsilon \left[ P - \frac{1}{4} f DP + \frac{1}{2^2} \left(\frac{1}{4} f\right)^2 D^2 P - \frac{1}{2^2 \cdot 3^2} \left(\frac{1}{4} f\right)^3 D^3 P + \dots \right] \\ - \frac{1}{8} \epsilon^2 \left[ DP^2 - \frac{1}{8} f D^2 P^2 + \frac{1}{192} f^2 D^3 P^2 - \frac{1}{9216} f^3 D^4 P^2 + \dots \right] \\ + \frac{1}{192} \epsilon^3 [D^2 P^3 - \dots], \text{ \&c. . . . . } \end{aligned} \quad (12)$$

When  $\mu = 0, D = 0$  and  $P = P_0$ , so that  $\phi(q)$  reduces to  $\epsilon P_0$ , and

$$f + \frac{\phi(q)}{q^2} = \frac{1}{q^2} \left( \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} + \epsilon P_0 - q^2 \right).$$

Thus the surface of constant density  $\rho$  is the surface  $\mu = 0$  in the family of surfaces

$$f + \phi(q)/q^2 = 0. \quad (13)$$

From the previous investigation\* it now follows that the value of  $V_0(q)$  is

$$V_0(q) = -\pi \int_{\mu'}^{\infty} \left( f + \frac{\phi(q)}{q^2} \right) \frac{q^3 abc d\mu}{[(q^2 a^2 + \mu)(q^2 b^2 + \mu)(q^2 c^2 + \mu)]^{\frac{1}{2}}}, \dots \dots (14)$$

in which the lower limit of integration  $\mu'$  is the root of equation (13) at the external point  $x, y, z$  at which the potential is being evaluated. The same formula (14) with  $\mu'$  put equal to zero will give the value of  $V_i(q)$ , the potential at an internal point.

To transform these expressions into a form suitable for use in the present problem, introduce new variables  $\lambda, \xi, \eta, \zeta$  to replace  $\mu, \xi', \eta', \zeta'$ , these being defined by

$$\lambda = \mu/q^2, \quad \xi = q^2 \xi' = x/(a^2 + \lambda), \text{ \&c.} \dots \dots (15)$$

We now have

$$P = F(\xi, \eta, \zeta),$$

$$q^2 f = \frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} + \frac{z^2}{c^2 + \lambda} - q^2,$$

$$\frac{D}{q^2} = \left( \frac{1}{a^2} - \frac{1}{a^2 + \lambda} \right) \frac{\partial^2}{\partial \xi^2} + \left( \frac{1}{b^2} - \frac{1}{b^2 + \lambda} \right) \frac{\partial^2}{\partial \eta^2} + \left( \frac{1}{c^2} - \frac{1}{c^2 + \lambda} \right) \frac{\partial^2}{\partial \zeta^2},$$

while formula (14) becomes

$$V_0(q) = -\pi \int_{\lambda'}^{\infty} [q^2 f + \phi(q)] \frac{abc d\lambda}{\Delta}, \dots \dots (16)$$

in which  $\Delta$  stands for  $[(a^2 + \lambda)(b^2 + \lambda)(c^2 + \lambda)]^{\frac{1}{2}}$ , and  $\lambda'$  is the root of

$$\frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} + \frac{z^2}{c^2 + \lambda} + \phi(q) = q^2. \dots \dots (17)$$

The same formula (16) in which  $\lambda'$  is put equal to zero will of course give the value of  $V_i(q)$ .

9. Attacking equations (10) and (11), we now have

$$\int_{\sigma}^{\rho_0} V_0(q) d\rho = (\rho_0 - \sigma) \int_0^1 V_0(q) dq^2$$

$$= (\rho_0 - \sigma) \left[ V_0(1) - \int_0^1 q^2 \frac{dV_0(q)}{dq^2} dq^2 \right],$$

so that equation (10) becomes

$$V_0 = \rho_0 V_0(1) - (\rho_0 - \sigma) E_0, \dots \dots (18)$$

\* 'Phil. Trans.,' A, vol. 215, p. 27.



where

$$E_0 = \int_0^1 q^2 \frac{dV_0(q)}{dq^2} dq^2. \quad \dots \quad (19)$$

This expresses that  $V_0$  is equal to the potential of a homogeneous solid of density  $\rho_0$  minus  $(\rho_0 - \sigma)$  times the potential  $E_0$ , this last term accordingly representing the effect of the falling off of density from the maximum value  $\rho_0$ .

Similarly equation (11) becomes

$$V_i = \rho_0 V_i(1) - (\rho_0 - \sigma) E_i. \quad \dots \quad (20)$$

where

$$E_i = \int_0^q q^2 \frac{dV_0(q)}{dq^2} dq^2 + \int_q^1 q^2 \frac{dV_i(q)}{dq^2} dq^2, \quad \dots \quad (21)$$

in which the limit of integration is the value of  $q$  at the internal point at which the potential is being evaluated.

The value of  $V_0(q)$ , as given by formula (16), is a function of  $q^2$  and  $\lambda'$ , the two being connected by equation (17). Thus we have

$$\frac{dV_0(q)}{dq^2} = \frac{\partial V_0(q)}{\partial q^2} + \frac{\partial V_0(q)}{\partial \lambda'} \frac{\partial \lambda'}{\partial q^2},$$

and the last term vanishes since  $\partial V_0(q)/\partial \lambda'$  contains  $[q^2 f + \phi(q)]$  as a factor. Thus we have

$$\frac{dV_0(q)}{dq^2} = \frac{\partial V_0(q)}{\partial q^2} = \pi abc \int_{\lambda'}^{\infty} \left(1 - \frac{\partial \phi(q)}{\partial q^2}\right) \frac{\partial \lambda}{\Delta} \quad \dots \quad (22)$$

and the value of  $dV_i(q)/dq^2$  is given by the same formula with  $\lambda'$  put equal to zero.

Using these values we find

$$E_0 = \pi abc \int_0^1 q^2 \left[ \int_{\lambda'}^{\infty} \left(1 - \frac{\partial \phi(q)}{\partial q^2}\right) \frac{d\lambda}{\Delta} \right] dq^2, \quad \dots \quad (23)$$

$$E_i = \pi abc \int_0^q q^2 \left[ \int_{\lambda'}^{\infty} \left(1 - \frac{\partial \phi(q)}{\partial q^2}\right) \frac{d\lambda}{\Delta} \right] dq^2 + \pi abc \int_q^1 q^2 \left[ \int_0^{\infty} \left(1 - \frac{\partial \phi(q)}{\partial q^2}\right) \frac{d\lambda}{\Delta} \right] dq^2. \quad \dots \quad (24)$$

Both values of  $E$  may be regarded as given by a double integration in a plane in which  $\lambda$  and  $q$  are rectangular co-ordinates. Let us first consider  $E_0$ .

In fig. 1, let PQ represent the curve whose equation is

$$\frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} + \frac{z^2}{c^2 + \lambda} + \phi(q) = q^2. \quad \dots \quad (25)$$

Clearly, when  $q = 0$ , the value of  $\lambda$  is  $\infty$ , while when  $q = 1$ ,  $\lambda$  has some value  $\lambda''$ , which is the root of

$$\frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} + \frac{z^2}{c^2 + \lambda} + \phi(1) = 1. \dots \dots \dots (26)$$

The value of  $E_0$  is obtained by integrating over the area shaded in fig. 1. Changing the order of integration, we find

$$E_0 = \pi abc \int_{\lambda''}^{\infty} \left[ \int_q^1 \left( 1 - \frac{\partial \phi(q)}{\partial q^2} \right) dq^2 \right] \frac{d\lambda}{\Delta}, \dots \dots \dots (27)$$

in which the lower limit  $q$  is the root of equation (25), while the lower limit  $\lambda''$  is the root of equation (26).

The value of  $E_i$  is obtained by a double integration in the same plane over an area such as that shaded in fig. 2, the different directions of shading distinguishing the

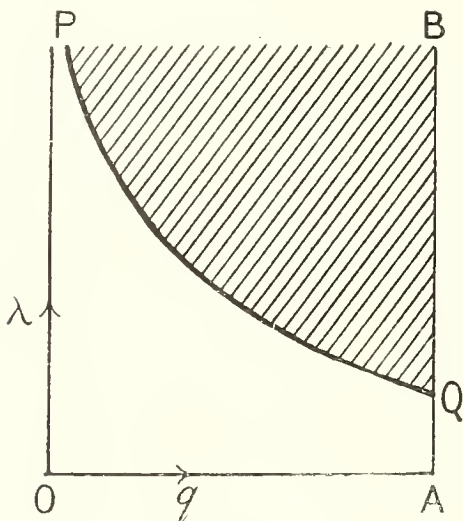


Fig. 1.

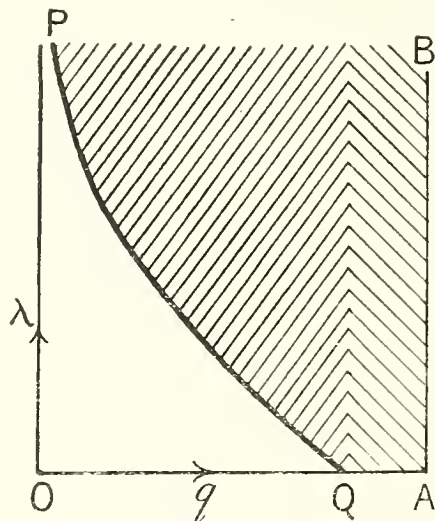


Fig. 2.

areas covered by the two separate integrals in equation (24). Again changing the order of integration, we obtain

$$E_i = \pi abc \int_0^{\infty} \left[ \int_q^1 q^2 \left( 1 - \frac{\partial \phi(q)}{\partial q^2} \right) dq^2 \right] \frac{d\lambda}{\Delta}, \dots \dots \dots (28)$$

in which the lower limit  $q$  is again the root of equation (25).

This completes the solution of the potential problem; we now attack the main problem of determining configurations of equilibrium.

*General Equations of Equilibrium.*

10. We can only find configurations of equilibrium by assuming a definite law to connect pressure with density. We shall accordingly assume the relation

$$p = \kappa \rho^\gamma - \text{const.} \dots \dots \dots (29)$$

The equations of equilibrium (1) now assume the form

$$\kappa\gamma\rho^{\gamma-2}\frac{\partial\rho}{\partial x} = \frac{\partial\Omega}{\partial x}, \text{ \&c.,}$$

and these have the common integral

$$\frac{\kappa\gamma}{\gamma-1}\rho^{\gamma-1} = \Omega + \text{cons.} \quad \dots \quad (30)$$

We have already (equations (3) and (5)) assumed the value of  $\rho$  to be

$$\rho = \rho_0 \left[ 1 - \epsilon \Sigma \frac{x^2}{a^2} - \epsilon^2 P_0 \right], \quad \dots \quad (31)$$

and on expanding  $\rho^{\gamma-1}$  by the binomial theorem, equation (30) becomes

$$\begin{aligned} \Omega = \text{cons.} + \kappa\gamma\rho_0^{\gamma-1} & \left[ - \left( \epsilon \Sigma \frac{x^2}{a^2} + \epsilon^2 P_0 \right) + \frac{1}{2} (\gamma-2) \left( \epsilon \Sigma \frac{x^2}{a^2} + \epsilon^2 P_0 \right)^2 \right. \\ & \left. - \frac{1}{6} (\gamma-2) (\gamma-3) \left( \epsilon \Sigma \frac{x^2}{a^2} + \epsilon^2 P_0 \right)^3 + \dots \right]. \quad \dots \quad (32) \end{aligned}$$

Let the figure of density given by equation (31) be supposed to be a figure of equilibrium under a rotation  $\omega$  and tidal forces of potential  $V_T$  where

$$V_T = \tau_1 x^2 + \tau_2 y^2 + \tau_3 z^2, \quad \dots \quad (33)$$

in which of course  $\tau_1 + \tau_2 + \tau_3 = 0$ . We then have at any point inside the mass

$$\begin{aligned} \Omega &= V_i + V_T + \frac{1}{2}\omega^2(x^2 + y^2) \\ &= \rho_0 [V_i(1) - \epsilon E_i] + (\tau_1 x^2 + \tau_2 y^2 + \tau_3 z^2) + \frac{1}{2}\omega^2(x^2 + y^2), \quad \dots \quad (34) \end{aligned}$$

and on equating the right-hand members of equations (32) and (34) we obtain a solution of the problem.

11. The simplest solution occurs when the variations of density are small, so that  $\epsilon$  is small; in this case  $\kappa\gamma$  is large. We must not simply put  $\epsilon = 0$  in equation (32), for otherwise  $\Omega$  would reduce to a pure constant. We accordingly suppose  $\kappa\gamma\epsilon$  to remain finite, and put  $\epsilon = 0$  in all remaining terms. Thus the equation to be solved is

$$\rho_0 V_i(1) + (\tau_1 x^2 + \tau_2 y^2 + \tau_3 z^2) + \frac{1}{2}\omega^2(x^2 + y^2) = \text{cons.} - \kappa\gamma\epsilon\rho_0^{\gamma-1} \left( \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} \right). \quad \dots \quad (35)$$

The boundary reduces to the ellipsoid

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1,$$

and the value of  $V_i(1)$ , which is the potential of this ellipsoid filled with matter of unit density, is

$$V_i(1) = -\pi abc (J_A x^2 + J_B y^2 + J_C z^2 - J), \quad \dots \dots \dots (36)$$

where the notation is that I have previously used\* in which

$$J_{AB\dots} = \int_0^x \frac{d\lambda}{\Delta (a^2 + \lambda) (b^2 + \lambda) \dots} \dots \dots \dots (37)$$

On substituting this value for  $V_i(1)$  into equation (35) and equating coefficients of  $x^2, y^2, z^2$ , we obtain, as the conditions for equilibrium,

$$J_A - \frac{\tau_1}{\pi \rho_0 abc} - \frac{\omega^2}{2\pi \rho_0 abc} = \frac{\theta}{a^2}, \quad \dots \dots \dots (38)$$

$$J_B - \frac{\tau_2}{\pi \rho_0 abc} - \frac{\omega^2}{2\pi \rho_0 abc} = \frac{\theta}{b^2}, \quad \dots \dots \dots (39)$$

$$J_C - \frac{\tau_3}{\pi \rho_0 abc} = \frac{\theta}{c^2}, \quad \dots \dots \dots (40)$$

in which

$$\theta = \frac{\kappa \gamma \epsilon \rho_0^{\gamma-2}}{\pi abc} \dots \dots \dots (41)$$

By addition of the corresponding sides of the three equations (36) to (38), we obtain

$$\frac{2}{abc} - \frac{\omega^3}{\pi \rho_0 abc} = \theta \left( \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \right) \dots \dots \dots (42)$$

It is now clear that equations (38) to (40) together with (41) are simply the equations which determine  $a, b, c$ , the semi-axes of the ellipsoid which is a figure of equilibrium for an incompressible mass. We have, however, found that as far as this first approximation the value of  $\rho$  is not necessarily constant throughout the ellipsoid; it is given by

$$\rho = \rho_0 - (\rho_0 - \sigma) \left( \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} \right) \dots \dots \dots (43)$$

We have further found the relation connecting  $\theta$  with the constants  $\kappa$  and  $\gamma$ . Substituting the value for  $\theta$  from equation (41) into equation (32), and equating the

\* 'Phil. Trans.,' A, vol. 215, p. 50.

value of  $\Omega$  so obtained to the value given by equation (34), the general equation of equilibrium is obtained in the form

$$\begin{aligned} &\rho_0 [V_i(1) - \epsilon E_i] + (\tau_1 x^2 + \tau_2 y^2 + \tau_3 z^2) + \frac{1}{2} \omega^2 (x^2 + y^2) \\ &= \text{cons.} - \pi \rho_0 abc \theta \left[ \left( \sum \frac{x^2}{a^2} + \epsilon P_0 \right) - \frac{1}{2} \epsilon (\gamma - 2) \left( \sum \frac{x^2}{a^2} + \epsilon P_0 \right)^2 \right. \\ &\quad \left. + \frac{1}{6} \epsilon^2 (\gamma - 2) (\gamma - 3) \left( \sum \frac{x^2}{a^2} + \epsilon P_0 \right)^3 - \dots \right]. \quad (44) \end{aligned}$$

12. The first approximation has been obtained by putting  $\epsilon = 0$  in this equation; we now proceed to higher approximations. A second approximation will be obtained by omitting all power of  $\epsilon$  beyond the first; a third approximation by not going beyond  $\epsilon^2$ , and so on.

On replacing  $\epsilon P_0$  by  $\epsilon P_0 + \epsilon^2 Q_0 + \epsilon^3 R_0 + \dots$ , we may suppose that the density expanded in powers of  $\epsilon$  is

$$\rho = \rho_0 \left[ 1 - \epsilon \left( \sum \frac{x^2}{a^2} + \epsilon P_0 + \epsilon^2 Q_0 + \epsilon^3 R_0 + \dots \right) \right], \quad (45)$$

so that the boundary,  $\rho = \sigma$ , is

$$\sum \frac{x^2}{a^2} + \epsilon P_0 + \epsilon^2 Q_0 + \epsilon^3 R_0 + \dots = 1. \quad (46)$$

The general equation of equilibrium will be obtained from equation (44) on replacing  $\epsilon P_0$  by

$$\epsilon P_0 + \epsilon^2 Q_0 + \epsilon^3 R_0 + \dots \quad (47)$$

The value of  $V_i(1)$  to be used in equation (42) will no longer be that given by equation (36); let us suppose the whole value to be

$$V_i(1) + \epsilon \Delta V_i(1) + \epsilon^2 \delta V_i(1) + \dots, \quad (48)$$

this being the internal potential of a homogeneous solid of unit density whose boundary is determined by equation (46). Similarly, let the whole value of  $E_i$  be supposed expanded in the form

$$E_i + \epsilon \Delta E_i + \epsilon^2 \delta E_i + \dots$$

Finally, let the value of  $\omega^2$  in the complete solution be supposed given by

$$\frac{\omega^2}{2\pi\rho_0 abc} = n + \epsilon \Delta n + \epsilon^2 \delta n + \dots \quad (49)$$

Then the complete equation (44) becomes, on dividing throughout by  $\pi\rho_0abc$ ,

$$\begin{aligned} & \frac{1}{\pi abc} [V_i(1) + \epsilon \Delta V_i(1) + \epsilon^2 \delta V_i(1) + \dots - \epsilon (E_i + \epsilon \Delta E_i + \dots)] \\ & \quad + \frac{\tau_1 x^2 + \tau_2 y^2 + \tau_3 z^2}{\pi \rho_0 abc} + (n + \epsilon \Delta n + \epsilon^2 \delta n + \dots)(x^2 + y^2) \\ & = \text{cons.} - \theta \left[ \left( \sum \frac{x^2}{a^2} + \epsilon P_0 + \epsilon^2 Q_0 + \epsilon^3 R_0 + \dots \right) - \frac{1}{2} \epsilon (\gamma - 2) \left( \sum \frac{x^2}{a^2} + \epsilon P_0 + \epsilon^2 Q_0 + \dots \right)^2 \right. \\ & \quad \left. + \frac{1}{6} \epsilon^2 (\gamma - 2)(\gamma - 3) \left( \sum \frac{x^2}{a^2} + \epsilon P_0 + \dots \right)^3 - \dots \right], \quad \dots \quad (50) \end{aligned}$$

an equation in which each side is equal to  $\Omega/\pi\rho_0abc$ .

13. On equating terms which are independent of  $\epsilon$ , we of course arrive merely at equations (38) to (40); these determine  $a, b, c$  when the data of the problem are given.

On equating terms in  $\epsilon$ , we obtain

$$\frac{1}{\pi abc} (\Delta V_i(1) - E_i) + \Delta n (x^2 + y^2) = -\theta \left[ P_0 - \frac{1}{2} (\gamma - 2) \left( \sum \frac{x^2}{a^2} \right)^2 \right]. \quad \dots \quad (51)$$

In evaluating  $E_i$  we put  $\epsilon = 0$ , and so may neglect  $\phi(q)$ . Thus, from equation (28),

$$E_i = \pi abc \int_0^x \frac{1}{2} (1 - q^4) \frac{d\lambda}{\Delta}, \quad \dots \quad (52)$$

in which, from equation (25),  $q$  is given by

$$q^2 = \frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} + \frac{z^2}{c^2 + \lambda}. \quad \dots \quad (53)$$

Thus, in the notation defined by equation (37),

$$E_i = -\frac{1}{2} \pi abc (J_{AA} x^4 + J_{BB} y^4 + J_{CC} z^4 + 2J_{BC} y^2 z^2 + \dots - J). \quad \dots \quad (54)$$

Using this value for  $E_i$ , it appears that all terms in equation (51) are of degrees 4 and 2 except  $P_0$  and  $\Delta V_i(1)$ . The value of  $\Delta V_i(1)$  depends on that of  $P_0$ , and terms of degree  $n$  in  $P_0$  give rise to terms of degrees  $n, n-2, \dots$  in  $\Delta V_i(1)$ . It is accordingly clear that the solution of equation (51) must be such that  $P_0$  consists of terms of degrees 4 and 2; the value of  $\Delta V_i(1)$  is then also of degrees 4 and 2, and, on equating coefficients, we can determine the coefficients in  $P_0$ .

Following closely the notation previously used,\* let us assume for  $P_0$  the value

$$P_0 = \frac{Lx^4}{a^8} + \frac{My^4}{b^8} + \frac{Nz^4}{c^8} + \frac{2ly^2z^2}{b^4c^4} + \frac{2mz^2x^2}{c^4a^4} + \frac{2nx^2y^2}{a^4b^4} + \frac{2px^2}{a^4} + \frac{2qy^2}{b^4} + \frac{2rz^2}{c^4}, \quad \dots \quad (55)$$

\* 'Phil. Trans.,' A, vol. 215, p. 54. The small quantity  $\frac{1}{2}\epsilon^2$  of that paper is replaced by  $\epsilon$  in this paper, otherwise the figure of that paper reduces to the present figure on taking  $\alpha, \beta, \gamma$  and  $s$  all zero.

so that (*cf.* § 8)

$$P = L\xi^4 + M\eta^4 + N\zeta^4 + 2l\eta^2\xi^2 + 2m\xi^2\zeta^2 + 2n\xi^2\eta^2 + 2p\xi^2 + 2q\eta^2 + 2r\zeta^2. \quad (56)$$

As far as terms of first degree in  $\epsilon$ , we may, from equation (12), take

$$\phi(q) = \epsilon [P - \frac{1}{4}fDP + \frac{1}{6\frac{1}{4}}f^2D^2P]. \quad (57)$$

the remaining terms disappearing because  $P$  contains no terms of degree higher than four in  $\xi, \eta, \zeta$ . The whole potential of the solid of unit density, as far as terms in  $\epsilon$ , is from formula (14)

$$V_i(1) + \epsilon \Delta V_i(1) = -\pi abc \int_0^\infty [f + \phi(1)] \frac{d\lambda}{\Delta},$$

so that

$$\Delta V_i(1) = -\pi abc \int_0^\infty [P - \frac{1}{4}fDP + \frac{1}{6\frac{1}{4}}f^2D^2P] \frac{d\lambda}{\Delta}, \quad (58)$$

in which  $q$  is put equal to 1.

Equation (51) now becomes

$$\begin{aligned} & \int_0^\infty [P - \frac{1}{4}fDP + \frac{1}{6\frac{1}{4}}f^2D^2P] \frac{d\lambda}{\Delta} - \theta P_0 \\ & = \frac{1}{2} (\sum J_{AA}x^4 + 2\sum J_{BC}y^2z^2 - J) - \frac{1}{2} (\gamma - 2) \theta \left( \sum \frac{x^2}{a^2} \right)^2 + \Delta n (x^2 + y^2). \quad (59) \end{aligned}$$

Clearly the left-hand member of this equation will be a linear function of  $L, M, N, \dots$  while the right-hand member does not involve these coefficients. Thus the values of  $L, M, N, \dots$  will each be the sum of a number of contributions corresponding to the different terms on the right of the equation. Let us suppose that

$$P_0 = P'_0 + P''_0 (\gamma - 2), \quad (60)$$

and that

$$L = L' + L'' (\gamma - 2), \text{ \&c.}, \quad (61)$$

thus separating the contribution from the term in  $(\gamma - 2)$  from the remainder.

14. It will be remembered that  $\epsilon \Delta V_i(1)$  is the increase of internal potential resulting from deforming the surface of an ellipsoid of unit density so that its surface is changed from

$$x^2/a^2 + y^2/b^2 + z^2/c^2 - 1 = 0, \quad (62)$$

into

$$x^2/a^2 + y^2/b^2 + z^2/c^2 - 1 + \epsilon P_0 = 0. \quad (63)$$

Consider the special deformation in which  $P_0$  is of the form

$$P_0 = \psi \left( \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} \right), \quad (64)$$

where  $\psi$  is any function whatever. Equation (63) can be solved in the form

$$x^2/a^2 + y^2/b^2 + z^2/c^2 - 1 - \eta = 0, \dots \dots \dots (65)$$

and on comparison with equation (62) the deformation is seen to consist of the addition of a thin homeoidal shell of uniform density. By a well-known theorem, the potential of such a shell is constant at all internal points, so that for the particular deformation represented by equation (64), we have  $\Delta V_i(1) = \text{a constant}$ . Incidentally, we may note that  $\delta V_1(1)$  is also constant, and so on to all orders.

15. Returning to equation (59), it appears that  $P''_0$  must satisfy

$$\int_0^x [P'' - \frac{1}{4}f DP'' + \frac{1}{64}f^2 D^2 P''] \frac{d\lambda}{\Delta} - \theta P''_0 = -\frac{1}{2}\theta \left(\sum \frac{x'^2}{a^2}\right)^2$$

and from the considerations brought forward in the last section, it is clear that the solution is

$$P''_0 = \frac{1}{2} \left(\sum \frac{x'^2}{a^2}\right)^2, \dots \dots \dots (66)$$

so that

$$L'' = \frac{1}{2}a^4, \text{ \&c. ; } p'' = q'' = r'' = 0.$$

We are left with the problem of determining  $P'$ , which must satisfy

$$\begin{aligned} \int_0^x [P' - \frac{1}{4}f DP' + \frac{1}{64}f^2 D^2 P'] \frac{d\lambda}{\Delta} - \theta P'_0 \\ = \frac{1}{2} (\sum J_{AA} x^4 + 2\sum J_{BC} y^2 z^2 - J) + \Delta n(x^2 + y^2). \dots \dots \dots (67) \end{aligned}$$

Unfortunately there is no simple means of dealing with this equation, and the general solution obtained by direct algebraic treatment is so complicated as to convey no meaning at all to the mind. Our method will be to consider first an approximate solution of a simple form, this having reference only to the fourth degree terms in  $P'$ ; we shall then attempt to estimate the amount of error involved, giving detailed calculations and precise solutions for two configurations of special importance.

16. The approximate solution we shall consider is

$$L' = -\frac{1}{2} \frac{a^8}{\theta} J_{AA}, l' = -\frac{1}{2} \frac{b^4 c^4}{\theta} J_{BC}, \text{ \&c. } \dots \dots \dots (68)$$

This satisfies equation (67) as regards terms of fourth degree except for the integral on the left-hand, so that the error of the solution is roughly measured by the value of this integral.

Now from the definition of the integrals  $J_{AA}$ , &c., it is clear that the greater part of the value of these integrals arises from contributions from comparatively small values of  $\lambda$ , so that to a moderate approximation we shall have

$$\frac{J_{AA}}{1/a^4} = \frac{J_{BB}}{1/b^4} = \frac{J_{CC}}{1/c^4} = \frac{J_{BC}}{1/b^2 c^2} = \dots = k, \text{ say. } \dots \dots \dots (69)$$



If these relations were strictly true, the value of  $P'_0$  would be

$$P'_0 = -\frac{1}{2} \frac{k}{\theta} \left( \sum \frac{x^2}{a^2} \right)^2, \quad \dots \dots \dots (70)$$

so that, from the consideration of § 14, we should have

$$\int_0^x [P' - \frac{1}{4} f' DP' + \frac{1}{64} f'^2 D^2 P'] \frac{d\lambda}{\Delta} = 0. \quad \dots \dots \dots (71)$$

Thus the error is of the order of the error of the approximation (69) multiplied by the coefficients of the integral (71), which coefficients are found to be small. It may be noticed that equations (69) are strictly true in the spherical configuration in which  $a = b = c$ , and the error increases as  $a, b, c$  become more unequal.

Thus the error in solution (68) is *nil* in the spherical configuration; we shall now evaluate it exactly in two other configurations: (i.) the point of bifurcation of the spheroidal and ellipsoidal series, and (ii.) the point of bifurcation of the ellipsoidal and pear-shaped series.

17. *Ellipsoidal Point of Bifurcation.*—At the point of bifurcation of the series of spheroids with the series of ellipsoids, the semi-axes  $a, b, c$ , and the values of  $n$  and  $\theta$  are given by

$$\begin{aligned} a = b = 1.1972, & \quad c = 0.69766, \\ n = \frac{\omega^2}{2\pi\rho_0} = 0.18712, & \quad \theta = 0.47126, \end{aligned}$$

the scale of length, which is entirely at our disposal, being chosen so as to make  $abc = 1$ .

Since the configuration under discussion is now spheroidal, we have

$$L = M = n, \quad l = m, \quad p = q,$$

so that there are only three coefficients, say,  $L, m$  and  $N$ , to the terms of fourth degree, and two coefficients  $p, r$  to terms of second degree.

For any configuration, formula (48) expresses the internal potential of a solid of uniform unit density, so that

$$\nabla^2 [V_i(1) + \epsilon \Delta V_i(1) + \epsilon^2 \delta V_i(1) + \dots] = -4\pi. \quad \dots \dots \dots (72)$$

It follows that  $\Delta V_i(1), \delta V_i(1),$  &c., are all spherical harmonics.

In the present problem in which  $a = b$ , these harmonics are also symmetrical about the axis of  $z$ , and so are functions of  $x^2 + y^2$  and of  $z$  only, so that we may assume

$$\begin{aligned} & \int_0^\infty [P - \frac{1}{4} f' DP + \frac{1}{64} f'^2 D^2 P] \frac{d\lambda}{\Delta}, \\ & = -\frac{\Delta V_i(1)}{\pi abc}, \\ & = 4c_{11} [(x^2 + y^2)^2 - 8(x^2 + y^2)z^2 + \frac{8}{3}z^4] + 4d_1(x^2 + y^2 - 2z^2), \quad \dots \dots (73) \end{aligned}$$

in which the quantities in square brackets are the most general zonal harmonics of appropriate type, and the coefficients  $c_{11}$ ,  $d_1$ , are chosen so as to be identical with those used in my previous paper. Either by direct calculation or by comparison with the results obtained in this previous paper, we find

$$4c_{11} = L \left( J_{A^4} - \frac{4}{\alpha^2} I_{A^4} + \frac{1}{\alpha^4} H_{A^4} \right) + m \left( -\frac{1}{c^2} I_{A^3C} + \frac{1}{2\alpha^2 c^2} H_{A^3C} \right) + \frac{3}{8c^4} N H_{A^2C^2} \dots \dots \dots (74)$$

$$4d_1 = 2p \left( J_{AA} - \frac{1}{\alpha^2} I_{AA} \right) - \frac{r}{c^2} I_{AC} + \frac{6L}{\alpha^2} I_{A^3} - \frac{2L}{\alpha^4} I_{A^2} + \frac{m}{c^2} \left( 2I_{A^2C} - \frac{1}{\alpha^2} I_{AC} \right) - \frac{3}{4c^2} N \left( \frac{1}{c^2} I_{AC} - I_{AC^2} \right), \dots \dots (75)$$

in which the notation is that already defined in formula (37), supplemented by the further abbreviations :

$$I_{AB\dots} = \int_0^\infty \frac{\lambda d\lambda}{\Delta(\alpha^2 + \lambda)(b^2 + \lambda)\dots}; \quad H_{AB\dots} = \int \frac{\lambda^2 d\lambda}{\Delta(\alpha^2 + \lambda)(b^2 + \lambda)\dots}, \dots \dots (76)$$

and the further abbreviations  $G_{AB\dots}$ ,  $F_{AB\dots}$ , will be used when required, to denote similar integrals having terms  $\lambda^3$ ,  $\lambda^4$  in the numerator.

18. For computation, it is necessary to construct tables of these integrals. The table on the next page contains values which are required both here and later in the paper. The method of computation has been fully described elsewhere.\*

Using these values, I find in place of equation (74)

$$4c_{11} = 0.010947L - 0.064325m + 0.094707N. \dots \dots \dots (77)$$

On equating coefficients of  $x^4$ ,  $x^2z^2$  and  $z^4$  in equation (59) we obtain

$$\left. \begin{aligned} 4c_{11} - \theta \frac{L}{\alpha^8} &= \frac{1}{2} J_{AA} - \frac{1}{2} (\gamma - 2) \frac{\theta}{\alpha^4} \\ -16c_{11} - \theta \frac{m}{\alpha^4 c^4} &= \frac{1}{2} J_{AC} - \frac{1}{2} (\gamma - 2) \frac{\theta}{\alpha^2 c^2} \\ \frac{3}{2} c_{11} - \theta \frac{N}{c^8} &= \frac{1}{2} J_{CC} - \frac{1}{2} (\gamma - 2) \frac{\theta}{c^4} \end{aligned} \right\} \dots \dots \dots (78)$$

\* 'Phil. Trans.,' A, vol. 215, p. 60.

TABLE of Integrals.

( $a = 1.19723$ ,  $c = 0.69766$ .)

	J.	I.	H.	G.	F.
A	0.51589				
C	0.96821				
AA	0.22938	0.18712			
AC	0.47781	0.28334			
CC	1.05115	0.45659			
AAA	0.11850	0.05953	0.10177		
AAC	0.26244	0.10164	0.13766		
ACC	0.60567	0.18302	0.19425		
CCC	1.44620	0.34725	0.28757		
A <sup>4</sup>	0.06589	0.02406	0.02506	0.06585	
A <sup>3</sup> C	0.15204	0.04451	0.03786	0.08335	
A <sup>2</sup> C <sup>2</sup>	0.36257	0.08599	0.05983	0.10849	
AC <sup>3</sup>	0.88791	0.17349	0.09857	0.14629	
C <sup>4</sup>	2.22418	0.36363	0.17026	0.20470	
A <sup>5</sup>	0.03828	0.01102	0.00826	0.01322	0.0469
A <sup>4</sup> C	0.09100	0.02162	0.01352	0.01848	0.0569
A <sup>3</sup> C <sup>2</sup>	0.22240	0.04381	0.02321	0.02656	0.0704
A <sup>2</sup> C <sup>3</sup>	0.55496	0.09243	0.04102	0.03978	0.0893
AC <sup>4</sup>	1.41157	0.20087	0.07573	0.06171	0.1162
A <sup>6</sup>	0.02290	0.00545	0.00321	0.00366	0.0080
A <sup>5</sup> C	0.05570	0.01120	0.00555	0.00557	0.0105
A <sup>4</sup> C <sup>2</sup>	0.13876	0.02345	0.01025	0.00852	0.0143
A <sup>3</sup> C <sup>3</sup>	0.35131	0.05136	0.01881	0.01407	0.0198
A <sup>2</sup> C <sup>4</sup>	0.90490	0.11455	0.03668	0.02315	0.0285
A <sup>7</sup>	—	0.00284	0.00138	0.00123	0.0019
A <sup>6</sup> C	—	0.00608	0.00247	0.00201	0.0027
A <sup>5</sup> C <sup>2</sup>	—	0.01294	0.00496	0.00314	0.0040
A <sup>4</sup> C <sup>3</sup>	—	0.02948	0.00904	0.00586	0.0057
A <sup>2</sup> C <sup>4</sup>	—	0.06675	0.01887	0.00964	0.0093

Introducing the value (77) for  $4c_{11}$ , these become three linear equations in  $L$ ,  $m$  and  $N$ , of which I find the solution to be

$$\left. \begin{aligned} L = M = n &= 1.0273(\gamma - 2) - 1.0466 \\ l = m &= 0.3488(\gamma - 2) - 0.2378 \\ N &= 0.11845(\gamma - 2) - 0.06328 \end{aligned} \right\} \text{(exact solution).} \quad (79)$$

This may be compared with the approximate solution obtained in § 16, which

may be referred to as "Approximation A." Inserting numerical values, this stands as follows:—

$$\left. \begin{aligned} L = M = n &= 1.0273(\gamma - 2) - 1.0273 \\ l = m &= 0.3488(\gamma - 2) - 0.2467 \\ N &= 0.11845(\gamma - 2) - 0.0626 \end{aligned} \right\} \text{(Approximation A).} \quad (80)$$

It will be observed that the error in Approximation A is greatest when  $\gamma = 2$ , when it is of the order of 2 per cent. of the whole value.

19. *Pear-Shaped Point of Bifurcation.*—We proceed now to evaluate the exact solution for the configuration at which the Jacobian ellipsoid gives place to the pear-shaped figure. At this point we have

$$\begin{aligned} a &= 1.88583, & b &= 0.814975, & c &= 0.650659, \\ n &= \frac{\omega^2}{2\pi\rho_0} = 0.141999, & \theta &= 0.413607, \end{aligned}$$

the lengths again being chosen so that  $abc = 1$ . The values of the integrals necessary for the evaluation of the potentials have been given in previous papers.\* The values of  $L', M', N', l', m', n'$  are now distinct, and are determined by six equations of the type (*cf.* equations (78))

$$\left. \begin{aligned} 4c_{11} - \theta \left( \frac{L'}{a^8} \right) &= \frac{1}{2} J_{AA}, \text{ \&c.} \\ 4c_{23} - \theta \left( \frac{2l'}{b^4c^4} \right) &= J_{BC}, \text{ \&c.} \end{aligned} \right\}, \dots \dots \dots (81)$$

in which the coefficients  $c_{11}, c_{22}, c_{33}, c_{12}, c_{23}$  and  $c_{31}$  are now distinct, the condition that the potential shall be harmonic being expressed by three linear relations connecting them. The values of these six potential coefficients have been calculated in my previous paper; inserting these and solving the six equations (81) I find the set of values given in the second column of the following table, the values given by "Approximation A" being given in the adjacent column for comparison:—

Coefficient.	Exact solution.	Approximation A.	Difference per cent.
$L'$	- 15.4353	- 10.1768	- 34
$M'$	- 0.15560	- 0.15329	- 1
$N'$	- 0.04733	- 0.04677	- 1
$l'$	- 0.08468	- 0.08424	0
$m'$	- 0.49850	- 0.62860	+ 26
$n'$	- 0.95103	- 1.18103	+ 24

\* 'Phil. Trans.,' A, vol. 215, p. 61, and vol. 217, p. 21.

Clearly the error is quite large, but is concentrated in the coefficients  $L', m', n'$  which multiply terms in  $x$ . It is remarkable that the cross section of the figure by the plane  $x = 0$  is given accurately to within 1 per cent. by this approximation.

20. It appears that Approximation A will give a solution accurate to within 2 per cent. for spheroidal figures, but of error varying from 2 to about 20 per cent. for ellipsoidal figures. A tolerable approximation to any required ellipsoidal figure could perhaps be got by regarding Approximation A as a first approximation, and obtaining the error in this by interpolation between the two errors which have been accurately estimated.

21. A second approximate solution, which has an interest other than that of accuracy, may be referred to here. We may use the approximate equations (69) to simplify the approximate solution (68), and so obtain a still less accurate approximation, which we shall call Approximation B. The approximation is

$$L' = -\frac{k}{2\theta} \alpha^4, \quad l' = -\frac{k}{2\theta} b^2 c^2, \text{ \&c., . . . . . } (82)$$

and the complete value of  $P_0$  becomes

$$P_0 = \frac{1}{2} \left[ (\gamma - 2) - \frac{k}{\theta} \left( \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} \right)^2 \right] \text{ . . . . . } (83)$$

In this approximation the quantity  $k$  is at our choice; we must select it so as to give as good an average value as possible for the approximately equal quantities which occur in equations (69).

Choosing a suitable value of  $k$ , I find for the coefficients at the ellipsoidal point of bifurcation

$$\left. \begin{aligned} L = M = n &= 1.0273(\gamma - 2) - 0.7705 \\ l = m &= 0.3488(\gamma - 2) - 0.2616 \\ N &= 0.11845(\gamma - 2) - 0.0888 \end{aligned} \right\} \text{(Approximation B). . . . } (84)$$

Comparing this with the exact solution given in equations (79), it appears that the error is as great as 20 per cent. when  $\gamma = 2$ .

The corresponding approximation at the pear-shaped point of bifurcation is almost worthless, the error being one of fully 50 per cent.

The significance of these approximations will appear later.

22. We turn now to the evaluation of the terms of second degree in  $x, y, z$ . It has already been seen (p. 172) that  $p'' = q'' = r'' = 0$ , so that  $p, q, r$  are identical with  $p', q', r'$ . Or, in other words,  $p, q, r$  do not involve  $(\gamma - 2)$ .

Let us suppose that in the general ellipsoidal solution (*cf.* equation (73))

$$\int_0^\infty \left[ P - \frac{1}{4} f DP + \frac{1}{8} f^2 D^2 P \right] \frac{d\lambda}{\Delta} = \text{fourth degree terms} + 4(d_1 x^2 + d_2 y^2 + d_3 z^2). \text{ . . } (85)$$

Then on equating coefficients of  $x^2$ ,  $y^2$  and  $z^2$  in equation (59) we obtain

$$4d_1 - \frac{2p\theta}{a^4} = \Delta n, \dots \dots \dots (86)$$

$$4d_2 - \frac{2q\theta}{b^4} = \Delta n, \dots \dots \dots (87)$$

$$4d_3 - \frac{2r\theta}{c^4} = 0. \dots \dots \dots (88)$$

The value of  $4d_1$  is readily found to be\*

$$4d_1 = 2pJ_{AA} - \frac{p}{a^2}I_{AA} - \frac{q}{b^2}I_{AB} - \frac{r}{c^2}I_{AC} + 4e_1, \dots \dots \dots (89)$$

where

$$4e_1 = -\frac{3}{4}\left(\frac{L}{a^4}H_{A^3} + \frac{M}{b^4}H_{AB^2} + \frac{N}{c^4}H_{AC^2}\right) - \frac{1}{2}\left(\frac{l}{b^2c^2}H_{ABC} + \frac{m}{c^2a^2}H_{AAC} + \frac{n}{a^2b^2}H_{AAB}\right) + \frac{3L}{a^2}I_{A^3} + \frac{n}{b^2}I_{A^2B} + \frac{m}{c^2}I_{A^2C}. \dots \dots \dots (90)$$

The values of  $4d_2$  and  $4d_3$  can of course be written down from symmetry.

It is immaterial whether we insert the values of  $L, M, N, \dots$ , or of  $L', M', N', \dots$ , in these equations in evaluating  $4e_1$ , &c., since the contributions from  $L'', M'', N'', \dots$ , which are proportional to  $a^4, b^4, c^4, \dots$ , must vanish by § 14.

23. If we are content to use Approximation B, the solution of our problem assumes a very simple form. For  $L', M', N', \dots$  are now proportional to  $a^4, b^4, c^4, \dots$ , and therefore

$$e_1 = e_2 = e_3 = 0 \text{ (Approximation B)}. \dots \dots \dots (91)$$

Thus equations (86), &c., reduce to

$$2pJ_{AA} - \frac{p}{a^2}I_{AA} - \frac{q}{b^2}I_{AB} - \frac{r}{c^2}I_{AC} - \frac{2p\theta}{a^4} = \Delta n, \dots \dots \dots (92)$$

and two similar equations.

The quantity  $\Delta n$ , which has been introduced for convenience only, is entirely at our disposal. Let us take  $\Delta n = 0$ , then the solution of the equations is

$$p = q = r = 0 \text{ (Approximation B)}. \dots \dots \dots (93)$$

Thus, corresponding to Approximation B, the solution corresponding to rotation  $\omega$  given by  $\omega^2/2\pi\rho_0 = n$  has for density

$$\rho = \rho_0 - (\rho_0 - \sigma)\left(\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2}\right) - \frac{(\rho_0 - \sigma)^2}{2\rho}\left(\frac{k}{\theta} - (\gamma - 2)\right)\left(\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2}\right)^2, \dots (94)$$

\* Cf. 'Phil. Trans.,' A, vol. 215, p. 60.

while the boundary is

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 - \frac{\rho_0 - \sigma}{2\rho_0} \left( \frac{k}{\theta} - (\gamma - 2) \right), \dots \dots \dots (95)$$

and so is still ellipsoidal. So far as this approximation goes, it appears that the shape of the ellipsoid, as given by the ratio of the semi-axes, depends only on  $\omega^2/2\pi\rho_0$ ; it is the same as for a homogeneous mass of uniform density  $\rho_0$ , equal to the density at the centre of the compressible mass, rotating with the same angular velocity.

24. When this somewhat unsatisfactory approximation is abandoned there is no means of procedure except to calculate  $e_1$ ,  $e_2$  and  $e_3$  directly from equations (89), &c.

Suppose that instead of being given by equation (33) the tidal potential had been given by

$$V_T + \epsilon \Delta V_T = (\tau_1 + \epsilon \Delta \tau_1) x^2 + (\tau_2 + \epsilon \Delta \tau_2) y^2 + (\tau_3 + \epsilon \Delta \tau_3) z^2. \dots \dots (96)$$

Then on equating terms independent of  $\epsilon$  in the principal equation we should obtain the same equation as before, but in place of equations (86) to (88), there would be three equations such as

$$4d_1 - \frac{2p\theta}{a^4} = \Delta n + \frac{\Delta \tau_1}{\pi\rho_0 abc},$$

or, inserting the value of  $4d_1$  from equation (89),

$$2pJ_{AA} - \frac{p}{a^2} I_{AA} - \frac{q}{b^2} I_{AB} - \frac{r}{c^2} I_{AC} + 4e_1 - \frac{2p\theta}{a^4} = \Delta n + \frac{\Delta \tau_1}{\pi\rho_0 abc}. \dots \dots (97)$$

These equations become identical with equations (92) if we take

$$\Delta \tau_1 = 4\pi\rho_0 abc e_1, \text{ \&c., } \dots \dots \dots (98)$$

and the equations then have the simple solution

$$p = q = r = 0, \quad \Delta n = 0.$$

Thus the exact solution can be found by superposing the fourth degree terms already calculated on to an ellipsoid which is a figure of equilibrium under an additional tidal potential

$$\epsilon \Delta V_T = 4\pi\rho_0 abc \epsilon (e_1 x^2 + e_2 y^2 + e_3 z^2), \dots \dots \dots (99)$$

this necessarily being harmonic, since  $e_1 + e_2 + e_3 = 0$ .

25. Let  $a'$ ,  $b'$ ,  $c'$  be the semi-axes of a figure of equilibrium under this additional tidal force, these differing from the old quantities  $a$ ,  $b$ ,  $c$  by small quantities of the order of  $\epsilon$ . The equations determining  $a'$ ,  $b'$ ,  $c'$  are (*cf.* equations (38) to (41))

$$J'_A - \frac{\tau_1}{\pi\rho_0 a' b' c'} + 4\epsilon e_1 - \frac{\omega'^2}{2\pi\rho_0 a' b' c'} = \frac{\theta'}{a'^2} \dots \dots \dots (100)$$

and two similar equations, accented letters all referring to the new figure of equilibrium, and the value of  $\theta'$  being now given by (*cf.* equation (41))

$$\theta' = \frac{\kappa\gamma\epsilon\rho_0^{\gamma-2}}{\pi a' b' c'}, \dots \dots \dots (101)$$

so that, by comparison with equation (41),

$$\theta' a' b' c' = \theta abc. \dots \dots \dots (102)$$

There will, of course, be a solution for the compressible mass corresponding to each solution of these equations, which are virtually equations giving a solution of an incompressible mass under tidal forces.

When the main tidal force disappears ( $\tau_1 = \tau_2 = \tau_3 = 0$ ) the solutions will correspond, except for small tidal terms, to Maclaurin spheroids and Jacobian ellipsoids. The compressible solution which corresponds to the Maclaurin-Jacobian point of bifurcation will represent a point of bifurcation for the compressible mass. Let us proceed to determine this point of bifurcation exactly.

At the point of bifurcation the configuration is spheroidal, so that  $e_1 = e_2$ . By subtraction of corresponding sides of equation (100) and the similar equation in  $b$ , we obtain

$$J'_A - J'_B = \theta' \left( \frac{1}{a'^2} - \frac{1}{b'^2} \right),$$

or

$$(a'^2 - b'^2) (J'_{AB} - \theta' / a'^2 b'^2) = 0. \dots \dots \dots (103)$$

The spheroidal series is determined by the vanishing of the first factor, and the ellipsoidal series by the vanishing of the second factor. At the point of bifurcation both factors vanish, so that  $a' = b'$ , and

$$a'^4 J'_{AA} = \theta',$$

or again, using relation (102),

$$a'^6 c' J'_{AA} = \theta a^2 c. \dots \dots \dots (104)$$

This equation, together with (100) and its companion, will determine the values of  $a'$ ,  $c'$  and  $\omega'$  at the point of bifurcation.

26. The values of these quantities differ by terms of the order of  $\epsilon$  from the corresponding quantities  $a$ ,  $b$ ,  $c$  at the Maclaurin-Jacobian point of bifurcation, so that we may suppose that

$$\frac{1}{a'^2} = \frac{1}{a^2} + \epsilon \Delta \left( \frac{1}{a^2} \right), \text{ \&c.,} \quad \omega'^2 = \omega^2 + \epsilon \Delta \omega^2. \dots \dots \dots (105)$$

The equation of the figure of equilibrium is now

$$\frac{x^2 + y^2}{a^2} + \frac{y^2}{b^2} + \epsilon \left[ (x^2 + y^2) \Delta \left( \frac{1}{a^2} \right) + z^2 \Delta \left( \frac{1}{c^2} \right) + \frac{Lx^4}{a^8} + \dots \right],$$



and this agrees exactly with the figure previously considered if we take

$$\Delta\left(\frac{1}{a^2}\right) = \frac{2p}{a^4}; \quad \Delta\left(\frac{1}{c^2}\right) = \frac{2r}{c^4}. \quad \dots \quad (106)$$

Using relations (105) and (106), equation (100) transforms to

$$abc \left[ J_A - \frac{\tau_1}{\pi\rho_0 abc} - \frac{\omega^2}{2\pi\rho_0 abc} - \frac{\theta}{a^2} \right] + \epsilon abc \left[ 4e_1 + p \left( 2J_{AA} - \frac{2}{a^2} I_{AA} \right) - \frac{r}{c^2} I_{AC} - \frac{\Delta\omega^2}{2\pi\rho_0 abc} - \frac{2p\theta}{a^4} \right] = 0. \quad \dots \quad (107)$$

The first line vanishes in virtue of equation (38) and the equation reduces to

$$4e_1 + p \left( 2J_{AA} - \frac{2}{a^2} I_{AA} \right) - \frac{r}{c^2} I_{AC} - \frac{2p\theta}{a^4} = \Delta n, \quad \dots \quad (108)$$

which agrees with equation (86), as of course it ought to do, and there is a similar equation agreeing with equation (88).

27. Equation (104) may be written in the slightly symbolical form

$$a^6 c J_{AA} + \epsilon \Delta (a^6 c J_{AA}) = \theta a^2 c, \quad \dots \quad (109)$$

and the condition which determines the ordinary Maclaurin-Jacobian point of bifurcation is

$$a^4 J_{AA} = \theta.$$

Thus equation (109), which expresses the condition to be satisfied at the point of bifurcation on the compressible series, reduces to

$$\Delta (a^6 c J_{AA}) = 0. \quad \dots \quad (110)$$

Now from the definition of  $J_{AA}$  we have

$$a^6 c J_{AA} = \int_0^x \frac{d\lambda}{(1 + \lambda/a^2)^3 (1 + \lambda/c^2)^{\frac{1}{2}}},$$

whence we readily find that equation (110) is equivalent to

$$6I_{A^3} \left( \frac{p}{a^2} \right) + I_{A^2C} \left( \frac{r}{c^2} \right) = 0. \quad \dots \quad (111)$$

Equation (111), together with equation (108) and its companion, determine the values of  $p$ ,  $r$  and  $\Delta n$  at the point of bifurcation on the series of compressible configurations.

28. The material for numerical computations has already been given in § 18. Using the exact solution there given, I find, by direct computation from equation (90),

$$4e_1 = 4e_2 = -0.03404; \quad 4e_3 = 0.06808. \quad \dots \quad (112)$$

From equation (111), and the companion to (108), I now find

$$\frac{p}{a^2} = -0.016037; \quad \frac{r}{c^2} = 0.056337, \quad \dots \quad (113)$$

and equation (108) now gives

$$\Delta n = \frac{\Delta \omega^2}{2\pi\rho_0 abc} = -0.04400. \quad \dots \quad (114)$$

These quantities are all comparatively small; they would all have vanished under Approximation B.

*Second Order Solution.*

29. We now pass to the solution of higher order still. On equating terms in  $\epsilon^2$  in equation (50), we obtain

$$\begin{aligned} & \frac{1}{\pi abc} (\delta V_i(1) - \Delta E_i) + \delta n (x^2 + y^2) \\ & = -\theta \left[ Q_0 - (\gamma - 2) P_0 \left( \sum \frac{x^2}{a^2} \right) + \frac{1}{6} (\gamma - 2) (\gamma - 3) \left( \sum \frac{x^2}{a^2} \right)^3 \right]. \quad (115) \end{aligned}$$

30. From equation (28), taking terms as far as first powers of  $\epsilon$  only,

$$E_i + \Delta E_i = \pi abc \int_0^\infty \left[ \int_q^1 q^2 \left( 1 - \frac{\partial \phi(q)}{\partial q^2} \right) dq^2 \right] \frac{d\lambda}{\Delta}, \quad \dots \quad (116)$$

in which the lower limit  $q$  is given by

$$\frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} + \frac{z^2}{c^2 + \lambda} + \phi(q) = q^2 \quad \dots \quad (117)$$

As far as  $\epsilon$ , equation (12) gives

$$\phi(q) = \epsilon \left[ P - \frac{1}{4} f DP + \frac{1}{64} f^2 D^2 P \right], \quad \dots \quad (118)$$

while from § 8,

$$q^2 f = \frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} + \frac{z^2}{c^2 + \lambda} - q^2 \quad \dots \quad (119)$$

$$\frac{D}{q^2} = \left( \frac{1}{a^2} - \frac{1}{a^2 + \lambda} \right) \frac{\partial^2}{\partial \xi^2} + \left( \frac{1}{b^2} - \frac{1}{b^2 + \lambda} \right) \frac{\partial^2}{\partial \eta^2} + \left( \frac{1}{c^2} - \frac{1}{c^2 + \lambda} \right) \frac{\partial^2}{\partial \zeta^2}, \quad \dots \quad (120)$$

The value of  $D/q^2$  is independent of  $q$ , and  $\phi(q)$  may be rearranged in the form

$$\phi(q) = \epsilon \left[ P - \frac{1}{4} (q^2 f) \frac{D}{q^2} P + \frac{1}{64} (q^2 f)^2 \left( \frac{D}{q^2} \right)^2 P \right],$$

whence, on differentiation

$$\frac{\partial \phi(q)}{\partial q^2} = \epsilon \left[ \frac{1}{4} \frac{D}{q^2} P - \frac{1}{32} (q^2 f) \left( \frac{D}{q^2} \right)^2 P \right],$$

so that

$$q^2 \left( 1 - \frac{\partial \phi(q)}{\partial q^2} \right) = q^2 \left[ 1 - \frac{\epsilon}{4} \frac{D}{q^2} P + \frac{\epsilon}{32} \left( \sum \frac{x^2}{a^2 + \lambda} \right) \left( \frac{D}{q^2} \right)^2 P \right] - \frac{\epsilon}{32} q^4 \left( \frac{D}{q^2} \right)^2 P.$$

This gives on integration, since  $D/q^2$  is independent of  $q$ ,

$$\int_q^1 q^2 \left( 1 - \frac{\partial \phi(q)}{\partial q^2} \right) dq^2 = \frac{1}{2} (1 - q^4) \left[ 1 - \frac{\epsilon}{4} \frac{D}{q^2} P + \frac{\epsilon}{32} \left( \sum \frac{x^2}{a^2 + \lambda} \right) \left( \frac{D}{q^2} \right)^2 P \right] - \frac{\epsilon}{96} (1 - q^6) \left( \frac{D}{q^2} \right)^2 P. \quad \dots \dots \dots (121)$$

The value of  $q^2$  on the right of this equation is the root of equation (117),  $\phi(q)$  being given by equation (118) in which  $f$  is in turn given by equation (119). Thus  $q^2$  will be obtained by the elimination of  $\phi(q)$  and  $f$  from equations (117) to (119), omitting terms in  $\epsilon^2$ . From these three equations we obtain

$$q^2 f = -\phi(q) = -\epsilon \left[ P - \frac{1}{4} f D P + \frac{1}{64} f^2 D^2 P \right],$$

so that  $f$  is a small quantity of the order of  $\epsilon$ , and, omitting terms in  $\epsilon^2$ ,

$$\phi(q) = \epsilon P,$$

which is independent of  $q$ . Equation (117) now gives, as the value of  $q^2$ ,

$$q^2 = \sum \frac{x^2}{a^2 + \lambda} + \epsilon P. \quad \dots \dots \dots (122)$$

The coefficient of  $\epsilon$  on the right hand of equation (121) now reduces to

$$-P \sum \frac{x^2}{a^2 + \lambda} - \left[ 1 - \left( \sum \frac{x^2}{a^2 + \lambda} \right)^2 \right] \left[ \frac{1}{8} \frac{D}{q^2} P - \frac{1}{64} \left( \sum \frac{x^2}{a^2 + \lambda} \right) \left( \frac{D}{q^2} \right)^2 P \right] - \frac{1}{96} \left[ 1 - \left( \sum \frac{x^2}{a^2 + \lambda} \right)^3 \right] \left( \frac{D}{q^2} \right)^2 P.$$

The value of  $P$  is given by equation (56), and that of  $D/q^2$  by equation (120). From these we obtain

$$\frac{D}{q^2} P = \sum \left( \frac{1}{a^2} - \frac{1}{a^2 + \lambda} \right) (12L\xi^2 - 4n\eta^2 + 4m\xi^2 + 4p),$$

$$\left( \frac{D}{q^2} \right)^2 P = \sum \left[ 24L \left( \frac{1}{a^2} - \frac{1}{a^2 + \lambda} \right)^2 + 16l \left( \frac{1}{b^2} - \frac{1}{b^2 + \lambda} \right) \left( \frac{1}{c^2} - \frac{1}{c^2 + \lambda} \right) \right],$$

whence we readily obtain, writing A for  $\alpha^2 + \lambda$  and so on,

$$\begin{aligned} \Delta E_i = -\pi abc \int_0^\infty & \left\{ \left( \sum \frac{x^2}{A} \right) \left( \sum L \frac{x^4}{A^4} + 2 \sum l \frac{y^2 z^2}{B^2 C^2} + 2 \sum p \frac{x^2}{A^2} \right) \right. \\ & + \frac{1}{8} \left[ 1 - \left( \sum \frac{x^2}{A} \right)^2 \right] \left[ \sum \frac{\lambda}{a^2 A} \left( 12L \frac{x^2}{A^2} + 4n \frac{y^2}{B^2} + 4m \frac{z^2}{C^2} + 4p \right) \right] \\ & \left. + \left[ \frac{1}{96} - \frac{1}{64} \left( \sum \frac{x^2}{A} \right) + \frac{1}{192} \left( \sum \frac{x^2}{A} \right)^3 \right] \left[ 24 \sum \frac{L \lambda^2}{a^4 A^2} + 16 \sum \frac{l \lambda^2}{b^2 c^2 B C} \right] \right\} \frac{d\lambda}{\Delta}. \end{aligned} \quad (123)$$

31. From § 8, the value of  $V_i(1)$  is given by

$$V_i(1) + \epsilon \Delta V_i(1) + \epsilon^2 \partial V_i(1) = -\pi abc \int_0^\infty [f + \phi(1)] \frac{d\lambda}{\Delta}, \quad (124)$$

in which the value of  $\phi(1)$  is now (*cf.* equations (12) and (47))

$$\begin{aligned} \phi(1) = \epsilon & \left[ P - \frac{1}{4} f D P + \frac{1}{64} f^2 D^2 P \right] \\ & - \frac{1}{8} \epsilon^2 \left[ D P^2 - \frac{1}{8} f D^2 P^2 + \frac{1}{192} f^2 D^3 P - \frac{1}{9216} f^3 D^4 P^2 \right] \\ & + \epsilon^2 \left[ Q - \frac{1}{4} f D Q + \frac{1}{64} f^2 D^2 Q - \frac{1}{2304} f^3 D^3 Q + \dots \right] \\ & + \text{terms in } \epsilon^3, \text{ \&c.} \end{aligned} \quad (125)$$

Thus the value of  $\partial V_i(1)$ , being the coefficient of  $\epsilon^2$  on the right hand of equation (124), is given by

$$\begin{aligned} \partial V_i(1) = -\pi abc \int_0^\infty & \left[ Q - \frac{1}{4} f D Q + \frac{1}{64} f^2 D^2 Q - \frac{1}{2304} f^3 D^3 Q + \dots \right] \frac{d\lambda}{\Delta} \\ & + \frac{1}{8} \pi abc \int_0^\infty \left[ D P^2 - \frac{1}{8} f D^2 P^2 + \frac{1}{192} f^2 D^3 P^2 - \frac{1}{9216} f^3 D^4 P^2 \right] \frac{d\lambda}{\Delta}. \end{aligned}$$

32. Collecting and rearranging terms equation (115) now becomes

$$\begin{aligned} & \int_0^\infty \left[ Q - \frac{1}{4} f D Q + \frac{1}{64} f^2 D^2 Q - \frac{1}{2304} f^3 D^3 Q + \dots \right] \frac{d\lambda}{\Delta} - \theta Q_0 \\ & = \theta (\gamma - 2) \left[ \frac{1}{6} (\gamma - 3) \left( \sum \frac{x^2}{a^2} \right)^3 - [P'_0 + (\gamma - 2) P''_0] \left( \sum \frac{x^2}{a^2} \right) \right] \\ & \quad + \frac{1}{8} \int_0^\infty \left[ D P^2 - \frac{1}{8} f D^2 P^2 + \frac{1}{192} f^2 D^3 P^2 - \frac{1}{9216} f^3 D^4 P^2 \right] \frac{d\lambda}{\Delta} \\ & \quad - \frac{\Delta E_i}{\pi abc} + \delta n (x^2 + y^2). \end{aligned} \quad (126)$$

This is an equation for the determination of Q, all the terms involving Q being on the left hand, and all the terms independent of Q on the right. The terms on the right are all of degrees 6, 4, and 2 in  $x, y, z$ , so that the value of Q will clearly consist of terms of degrees 6, 4, and 2 in  $x, y, z$ . Further, from the linearity of the

equation, it is clear that the value of  $Q$  will be the sum of a number of contributions arising from the separate terms on the right.

Consider now what is the contribution from the first term on the right. Or, in other words, consider what would be the solution if the whole equation were reduced to

$$\int_0^\infty [Q - \frac{1}{4}fDQ + \frac{1}{64}f^2D^2Q - \frac{1}{2304}f^3D^3Q + \dots] \frac{d\lambda}{\Delta} - \theta Q_0 = \frac{1}{6}\theta(\gamma-2)(\gamma-3)\left(\sum \frac{x^2}{a^2}\right)^3.$$

The solution would be

$$Q_0 = -\frac{1}{6}(\gamma-2)(\gamma-3)\left(\sum \frac{x^2}{a^2}\right)^3, \dots \dots \dots (127)$$

for, in accordance with the principles arrived at in § 14, this value makes the integral on the left vanish, and the equation is then satisfied.

Similarly the contribution from the term in  $P''_0$  on the right is

$$Q_0 = (\gamma-2)^2 P''_0 \left(\sum \frac{x^2}{a^2}\right), \dots \dots \dots (128)$$

for  $P''_0$  is equal to  $\frac{1}{2}(\sum x^2/a^2)^2$ , and so the integral on the left again vanishes.

The contribution from the term in  $P'_0$  in equation (126) cannot be so simply evaluated. If, however, we are content to use Approximation B for  $P'_0$ , then  $P'_0$  becomes proportional to  $P''_0$ , and an approximate solution is

$$Q_0 = (\gamma-2) P'_0 \left(\sum \frac{x^2}{a^2}\right). \dots \dots \dots (129)$$

On referring back to § 16, it becomes clear that the accuracy of the approximate solution is of the same order as that which we previously called Approximation A.

Again, if we use Approximation B for  $P_0$ , the contribution from the whole second line in equation (126) will be

$$Q_0 = 0,$$

for the whole second line in question now represents merely the second order terms in the potential of a thick homeoidal shell, and so vanishes.

We proceed next to the contribution from the term in  $\Delta E_i$ . From equation (123) it appears that if we use Approximation B for the values of  $L, M, N, \dots$ , and also use equations of the type of (69), the first line in  $\Delta E_i$ , as given by equation (123), becomes a function of  $(\sum x^2/a^2)$ , while the remaining lines vanish.

It follows that an approximate solution is

$$Q_0 = \frac{\Delta E_i}{\pi abc\theta}.$$

There remains the contribution from the term  $\delta n(x^2+y^2)$  on the right of equation (126). This contribution will consist of second degree terms in  $Q_0$ , which represent merely a step along the fundamental series of ellipsoids to allow for the altered rotation, and the requisite terms can be easily calculated.

Collecting all the approximate partial solutions which have been obtained, we find the complete approximate solution

$$Q_0 = -(\gamma-2) \left[ \frac{1}{6}(\gamma-3) \left( \sum \frac{x^2}{a^2} \right)^3 - [P'_0 + (\gamma-2)P''_0] \left( \sum \frac{x^2}{a^2} \right) \right] + \frac{\Delta E_i}{\pi abc\theta} + \text{terms in } \delta n. \dots \dots \dots (130)$$

Clearly this approximation is of a degree of accuracy comparable with that of our previous Approximation A for  $P_0$ , with which it may be compared. This former approximation can be put in the form

$$P_0 = \frac{1}{2}(\gamma-2) \left( \sum \frac{x^2}{a^2} \right)^2 + \frac{E_i}{\pi abc\theta} + \text{terms in } \Delta n. \dots \dots \dots (131)$$

33. A less good approximation, comparable with the former Approximation B, can be obtained by further simplifying equation (130) by the help of approximate equations such as (69). The value of  $Q_0$  simplified in this way is found to reduce to a function of  $(\sum x^2/a^2)$ , so that the whole solution becomes ellipsoidal.

34. The accurate solution for  $Q_0$  may be supposed to be

$$Q_0 = Q'_0 + Q''_0(\gamma-2),$$

where  $Q''_0(\gamma-2)$  is the part of  $Q_0$  which is accurately given by formulæ (127) and (128); thus

$$Q''_0 = \left[ \frac{1}{3}(\gamma-2) + \frac{1}{6} \right] \left( \sum \frac{x^2}{a^2} \right)^3.$$

I have calculated the value of  $Q'_0$  accurately for one configuration only, namely, the ellipsoidal point of bifurcation. At this point  $a = b$  and  $x, y$  enter only through  $x^2+y^2$ . Let us write

$$x^2+y^2 = w^2; \quad \xi^2+\zeta^2 = \varpi^2.$$

The general value of  $Q_0$  will be of the form

$$Q_0 = \frac{R}{a^{12}} w^6 + \frac{3S}{a^8 c^4} w^4 z^2 + \frac{3T}{a^4 c^8} w^2 z^4 + \frac{U}{c^{12}} z^6 + \frac{r}{a^8} w^4 + \frac{2s}{a^4 c^4} w^2 z^2 + \frac{t}{c^8} z^4 + \frac{2u}{a^4} w^2 + \frac{2v}{c^4} z^2.$$

We may further put

$$R = R' + R''(\gamma-2), \text{ \&c.},$$

then the values of  $R''$ , &c., are

$$R'' = \left[ \frac{1}{3}(\gamma-2) + \frac{1}{6} \right] a^6, \text{ \&c.},$$

and the value of  $Q'_0$  is

$$Q'_0 = \frac{R'}{a^{12}} w^6 + \frac{3S'}{a^8 c^4} w^4 z^2 + \dots,$$

so that

$$Q' = R' \varpi^6 + 3S' \varpi^4 \zeta^2 + 3T' \varpi^2 \zeta^4 + U' \zeta^6 + r' \varpi^1 + 2s' \varpi^2 \zeta^2 + t' \zeta^4 + 2u' \varpi^2 + 2v' \zeta^2. \quad (132)$$

Let us now assume that

$$\int_0^\infty (Q' - \frac{1}{4} f DQ' + \frac{1}{64} f^2 D^2 Q' - \frac{1}{2304} f^3 D^3 Q') \frac{d\lambda}{\Delta} \\ = h_1 (5w^6 - 90w^4 z^2 + 120w^2 z^2 - 16z^4) + h_2 (3w^4 - 24w^2 z^2 + 8z^4) + h_3 (w^2 - 2z^2), \quad (133)$$

this being the most general form possible, since the integral in question is necessarily a zonal harmonic. In calculating the value of  $DQ'$ , we may use the transformation

$$D = \frac{\lambda}{a^2 A} \frac{1}{\varpi} \frac{\partial}{\partial \varpi} \left( \varpi \frac{\partial}{\partial \varpi} \right) + \frac{\lambda}{c^2 C} \frac{\partial^2}{\partial \zeta^2},$$

and on equating coefficients in equation (133), we obtain

$$5h_1 = \int_0^\infty \left[ \frac{R'}{A^6} - \frac{1}{4A^5} \left( \frac{\lambda}{a^2 A} 36R' + \frac{\lambda}{c^2 C} 6S' \right) + \frac{1}{64A^4} \left( \frac{\lambda^2}{a^4 A^2} 576R' + \frac{\lambda^2}{a^2 c^2 AC} 192S' + \frac{\lambda^2}{c^4 C^2} 72T' \right) \right. \\ \left. - \frac{1}{2304A^3} \left( \frac{\lambda^3}{a^6 A^3} 2304R' + \frac{3\lambda^3}{a^4 c^2 A^2 C} 384S' + \frac{3\lambda^3}{a^2 c^4 AC^2} 288T' + \frac{\lambda^3}{c^6 C^3} 720U' \right) \right] \frac{d\lambda}{\Delta}, \quad (134)$$

$$3h_2 = \int_0^\infty \left[ \frac{r'}{A^4} - \frac{1}{4A^3} \left( \frac{\lambda}{a^2 A} 16r' + \frac{\lambda}{c^2 C} 4s' \right) + \frac{1}{4A^4} \left( \frac{\lambda}{a^2 A} 36R' + \frac{\lambda}{c^2 C} 6S' \right) \right. \\ \left. + \frac{1}{64A^2} \left( \frac{\lambda^2}{a^4 A^2} 64r' + \frac{2\lambda^2}{a^2 c^2 AC} 16s' + \frac{\lambda^2}{c^4 C^2} 24t' \right) \right. \\ \left. - \frac{1}{32A^3} \left( \frac{\lambda^2}{a^4 A^2} 576R' + \frac{2\lambda^2}{a^2 c^2 AC} 96S' + \frac{\lambda^2}{c^4 C^2} 72T' \right) \right. \\ \left. + \frac{3}{2304A^2} \left( \frac{\lambda^3}{a^6 A^3} 2304R' + \frac{3\lambda^3}{a^4 c^2 A^2 C} 384S' + \frac{3\lambda^3}{a^2 c^4 AC^2} 288T' + \frac{\lambda^3}{c^6 C^3} 720U' \right) \right] \frac{d\lambda}{\Delta}, \quad (135)$$

$$h_3 = \int_0^\infty \left[ \frac{2u'}{A^2} - \frac{1}{4A} \left( \frac{\lambda}{a^2 A} 8u' + \frac{\lambda}{c^2 C} 4v' \right) + \frac{1}{4A^2} \left( \frac{\lambda}{a^2 A} 16r' + \frac{\lambda}{c^2 C} 4s' \right) \right. \\ \left. - \frac{1}{32A} \left( \frac{\lambda^2}{a^4 A^2} 64r' + \frac{2\lambda^2}{a^2 c^2 AC} 16s' + \frac{\lambda^2}{c^4 C^2} 24t' \right) \right. \\ \left. + \frac{1}{64A^2} \left( \frac{\lambda^2}{a^4 A^2} 576R' + \frac{2\lambda^2}{a^2 c^2 AC} 96S' + \frac{\lambda^2}{c^4 C^2} 72T' \right) \right. \\ \left. - \frac{3}{2304A} \left( \frac{\lambda^3}{a^6 A^3} 2304R' + \frac{3\lambda^3}{a^4 c^2 A^2 C} 384S' + \frac{3\lambda^3}{a^2 c^4 AC^2} 288T' + \frac{\lambda^3}{c^6 C^3} 720U' \right) \right] \frac{d\lambda}{\Delta}, \quad (136)$$

35. The value of P is

$$P = L\omega^4 + 2m\omega^2\zeta^2 + N\zeta^4 + 2p\omega^2 + 2r\zeta^2,$$

whence we find

$$DP^2 = \mathbf{K}\omega^6 + 3\mathbf{S}\omega^4\zeta^2 + 3\mathbf{T}\omega^2\zeta^4 + \mathbf{U}\zeta^6 + r\omega^4 + 2\mathbf{s}\omega^2\zeta^2 + t\zeta^4 + 2u\omega^2 + 2\mathbf{v}\zeta^2,$$

in which

$$\begin{aligned} \mathbf{K} &= \frac{\lambda}{a^2A} \times 64L^2 & + \frac{\lambda}{c^2C} \times 8Lm \\ \mathbf{S} &= \left| \begin{array}{l} 48Lm \\ \frac{1}{3}(4m^2 + 2LN) \end{array} \right| & 4(4m^2 + 2LN) \\ \mathbf{T} &= \left| \begin{array}{l} \frac{1}{3}(4m^2 + 2LN) \\ 40mN \end{array} \right| & 40mN \\ \mathbf{U} &= \left| \begin{array}{l} 16mN \\ 56N^2 \end{array} \right| & 56N^2 \\ r &= \left| \begin{array}{l} 144pL \\ 2(8pm + 4rL) \end{array} \right| & 2(8pm + 4rL) \\ \mathbf{s} &= \left| \begin{array}{l} 8(8pm + 4rL) \\ 6(4pN + 8rm) \end{array} \right| & 6(4pN + 8rm) \\ t &= \left| \begin{array}{l} 4(4pN + 8rm) \\ 120Nr \end{array} \right| & 120Nr \\ u &= \left| \begin{array}{l} 32p^2 \\ 8pr \end{array} \right| & 8pr \\ \mathbf{v} &= \left| \begin{array}{l} 16pr \\ 24r^2 \end{array} \right| & 24r^2 \end{aligned}$$

We may now assume (*cf.* equation (133))

$$\int_0^\infty (DP - \frac{1}{8}fD^2P^2 + \frac{1}{192}f^2D^3P^2 - \frac{1}{9216}f^3D^4P^2) \frac{d\lambda}{\Delta} = j_1(5w^6 - 90w^4z^2 + 120w^2z^4 - 16z^6) + j_2(3w^4 - 24w^2z^2 + 8z^4) + j_3(w^2 - 2z^2), \quad (137)$$

in which, on comparing coefficients, we obtain

$$\begin{aligned} 5j_1 &= \int_0^\infty \left[ \frac{\mathbf{K}}{A^6} - \frac{1}{8A^5} \left( \frac{\lambda}{a^2A} 36\mathbf{K} + \frac{\lambda}{c^2C} 6\mathbf{S} \right) + \frac{1}{192A^4} \left( \frac{\lambda^2}{a^4A^2} 576\mathbf{K} + \frac{\lambda^2}{a^2c^2AC} 192\mathbf{S} + \frac{\lambda^2}{c^4C^2} 72\mathbf{T} \right) \right. \\ &\quad \left. - \frac{1}{9216A^3} \left( \frac{\lambda^3}{a^6A^3} 2304\mathbf{K} + \frac{3\lambda^3}{a^4c^2A^2C} 384\mathbf{S} + \frac{3\lambda^3}{a^2c^4AC^2} 288\mathbf{T} + \frac{\lambda^3}{c^3C^3} 720\mathbf{U} \right) \right] \frac{d\lambda}{\Delta}. \end{aligned} \quad (138)$$

There are corresponding equations for  $3j_2$  and  $j_3$ , but these are not written down as they can readily be obtained from equations (135) and (136). To change  $3h_2$  into  $3j_2$ , change all accented coefficients into black letter type, and change  $\lambda, \lambda^2, \lambda^3$  wherever they occur explicitly, into  $\frac{1}{2}\lambda, \frac{1}{3}\lambda^2, \frac{1}{4}\lambda^3$  respectively. The same procedure changes  $h_3$  into  $j_3$ .

The values of these coefficients at the ellipsoidal point of bifurcation can be calculated from the material already provided in § 18 and the values of  $p$  and  $r$  given in formulæ (113). Using the exact solution throughout, I find

$$\begin{aligned} 5j_1 &= 0.01931(\gamma - 2) - 0.01473, \\ 3j_2 &= 0.01080(\gamma - 2) + 0.00576, \\ j_3 &= 0.5715(\gamma - 2) + 0.4094, \end{aligned}$$

all terms in  $(\gamma - 2)^2$  vanishing in accordance with the result of § 14.



36. We turn now to the evaluation of  $\Delta E_i$ . The potential of the whole mass at an internal point,  $V_i$ , is given, as in equation (20), by

$$V_i = \rho_0 (V_i(1) + \epsilon \Delta V_i(1) + \dots) - (\rho_0 - \sigma) (E_i + \epsilon \Delta E_i + \dots).$$

We have also

$$\nabla^2 V_i = -4\pi\rho = -4\pi\rho_0 + 4\pi(\rho_0 - \sigma) \left( \Sigma \frac{x^2}{a^2} + \epsilon P_0 + \epsilon^2 Q_0 + \dots \right),$$

whence, by comparison

$$\nabla^2 (\Delta E_i) = -4\pi P_0 = -4\pi \left( \frac{L}{a^8} w^4 + \frac{2m}{a^4 c^4} w^2 z^2 + \frac{N}{c^8} z^4 + \frac{2p}{a^4} w^2 + \frac{2r}{c^4} z^2 \right). \quad (139)$$

We may assume

$$\Delta E_i = -4\pi [k_1 w^6 + 3k_2 w^4 z^2 + 3k_3 w^2 z^4 + k_4 z^6 + k_5 w^4 + 2k_6 w^2 z^2 + k_7 z^4 + 2k_8 w^2 + 2k_9 z^2],$$

in which equation (139) necessitates the following relations between the coefficients

$$\begin{cases} 36k_1 + 6k_2 = \frac{L}{a^8}, \\ 48k_2 + 36k_3 = \frac{2m}{a^4 c^4}, \\ 12k_3 + 30k_4 = \frac{N}{c^8}, \end{cases} \quad \begin{cases} 16k_5 + 4k_6 = \frac{2p}{a^4}, \\ 8k_6 + 12k_7 = \frac{2r}{c^4}, \\ 2k_8 + k_9 = 0. \end{cases}$$

By comparison with equation (123)

$$k_1 = \frac{1}{4}abc \left[ LJ_{A^3} - \frac{2L}{a^2} I_{A^3} - \frac{m}{2c^2} I_{A^2C} + \frac{1}{192} \left( 64 \frac{L}{a^4} H_{A^3} + 32 \frac{m}{a^2 c^2} H_{A^2C} + 24 \frac{N}{c^4} H_{A^3C^2} \right) \right],$$

$$k_5 = \frac{1}{4}abc \left[ 2pJ_{A^3} - \frac{p}{a^2} I_{A^3} - \frac{1}{2} \frac{r}{c^2} I_{A^2C} \right],$$

$$2k_8 = \frac{1}{4}abc \left[ \frac{2L}{a^2} I_{A^3} + \frac{1}{2} \frac{m}{c^2} I_{A^2C} - \frac{1}{64} \left( 64 \frac{L}{a^4} H_{A^3} + 32 \frac{m}{a^2 c^2} H_{A^2C} + 24 \frac{N}{c^4} H_{A^3C^2} \right) \right].$$

By direct computation from these values I find

$$\frac{4k_1}{abc} = 0.019734 (\gamma - 2) - 0.021633,$$

$$\frac{4k_5}{abc} = -0.007359,$$

$$\frac{8k_8}{abc} = -0.017022.$$

37. We now return to equation (126). The solution has been assumed to be

$$Q_0 = Q'_0 + (\gamma - 2) Q''_0,$$

in which  $(\gamma - 2) Q''_0$  is the contribution from the terms on the right

$$\theta(\gamma - 2) \left[ \frac{1}{6} (\gamma - 3) \left( \sum \frac{x^2}{a^2} \right)^3 - (\gamma - 2) P''_0 \left( \sum \frac{x^2}{a^2} \right) \right].$$

It follows that  $Q'_0$  must satisfy the equation

$$\begin{aligned} & \int_0^\infty [Q' - \frac{1}{4} f DQ' + \frac{1}{64} f^2 D^2Q' - \frac{1}{2304} f^3 D^3Q' + \dots] \frac{d\lambda}{\Delta} - \theta Q'_0 \\ & = -\theta(\gamma - 2) P'_0 \left( \sum \frac{x^2}{a^2} \right) + \frac{1}{8} \int_0^\infty [DP^2 - \frac{1}{8} f D^2P^2 + \dots] \frac{d\lambda}{\Delta} \\ & \quad - \frac{\Delta E_i}{\pi abc} + \delta n (x^2 + y^2). \end{aligned}$$

Substituting the values which have been assumed for the various terms in this equation, it becomes

$$\begin{aligned} & h_1 (5w^6 - 90w^4z^2 + 120w^2z^4 - 16z^6) + h_2 (3w^4 - 24w^2z^2 + 8z^4) + h_3 (w^2 - 2z^2) \\ & - \theta \left[ \frac{R'}{a^{12}} w^6 + \frac{3S'}{a^8 c^4} w^4 z^2 + \frac{3T'}{a^4 c^8} w^2 z^4 + \frac{U'}{c^{12}} z^6 + \frac{r'}{a^8} w^4 + \frac{2s'}{a^4 c^4} w^2 z^2 + \frac{t'}{c^8} z^4 + \frac{2u'}{a^4} w^2 + \frac{2v'}{c^4} z^2 \right] \\ & = -\theta(\gamma - 2) \left( \frac{w^2}{a^2} + \frac{z^2}{c^2} \right) \left( \frac{L'}{a^8} w^4 + \frac{2m'}{a^4 c^4} w^2 z^2 + \frac{N'}{c^8} z^4 + \frac{2p}{a^4} w^2 + \frac{2r'}{c^4} z^2 \right) \\ & + \frac{1}{8} [j_1 (5w^6 - 90w^4z^2 + 120w^2z^4 - 16z^6) + j_2 (3w^4 - 24w^2z^2 + 8z^4) + j_3 (w^2 - 2z^2)] \\ & + \frac{4}{abc} [k_1 w^6 + 3k_2 w^4 z^2 + 3k_3 w^2 z^4 + k_4 z^6 + k_5 w^4 + 2k_6 w^2 z^2 + k_7 z^4 + 2k_8 w^2 + 2k_9 z^2] \\ & + \delta n (x^2 + y^2). \dots \dots \dots (140) \end{aligned}$$

Equating coefficients of  $w^6$ ,  $w^4z^2$ ,  $w^2z^4$  and  $z^6$ , we find

$$5h_1 - \theta \left[ \frac{R' - (\gamma - 2) L' a^2}{a^{12}} \right] = \frac{5}{8} j_1 + \frac{4k_1}{abc}, \dots \dots \dots (141)$$

$$-90h_1 - \theta \left[ \frac{3S' - (\gamma - 2)(2m' a^2 + L' c^2)}{a^8 c^4} \right] = -\frac{90}{8} j_1 + \frac{12k_2}{abc}, \dots \dots \dots (142)$$

$$120h_1 - \theta \left[ \frac{3T' - (\gamma - 2)(N' a^2 + 2m' c^2)}{a^4 c^8} \right] = 120 j_1 + \frac{12k_3}{abc}, \dots \dots \dots (143)$$

$$-16h_1 - \theta \left[ \frac{U' - (\gamma - 2) N' c^2}{a^{12}} \right] = -\frac{16}{8} j_1 + \frac{4k_4}{abc} \dots \dots \dots (144)$$

On multiplying equations (141) and (142) by 18, 1, and adding, we obtain, with the help of the relations of § 36,

$$18 \left[ \frac{R' - (\gamma - 2) L' a^2}{a^{12}} \right] + \left[ \frac{3S' - (\gamma - 2) (2m' a^2 + L' c^2)}{a^8 c^4} \right] = -\frac{2}{\theta} \frac{L}{a^8}. \quad (145)$$

Equations (142) to (144), treated in a similar manner, give

$$4 \left[ \frac{3S' - (\gamma - 2) (2m' a^2 + L' c^2)}{a^8 c^4} \right] + 3 \left[ \frac{3T' - (\gamma - 2) (N' a^2 + 2m' c^2)}{a^4 c^8} \right] = -\frac{2}{\theta} \frac{m}{a^4 c^4}, \quad (146)$$

$$2 \left[ \frac{3T' - (\gamma - 2) (N' a^2 + 2m' c^2)}{a^4 c^8} \right] + 15 \left[ \frac{U' - (\gamma - 2) N' c^2}{c^{12}} \right] = -\frac{2}{\theta} \frac{N}{c^8}. \quad (147)$$

These equations, taken with one other, suffice to determine R', S', T', U'. For additional equation we shall use equation (141).

The values of  $j_1$  and  $k_1$  have already been given. For  $5h_1$  I find, by direct computation from formula (134),

$$5h_1 = 0.00152R' - 0.01345S' + 0.03926T' - 0.03813U',$$

so that equation (141) reduces to

$$\begin{aligned} -\theta \left[ \frac{R' - (\gamma - 2) L' a^2}{a^{12}} \right] + 0.00152R' - 0.01345S' + 0.03926T' - 0.03183U' \\ = 0.02214(\gamma - 2) - 0.02347. \end{aligned} \quad (148)$$

Solving the system of four equations (145) to (148), I find

$$\frac{R' - (\gamma - 2) L' a^2}{a^{12}} = 0.04794 - 0.04309(\gamma - 2),$$

$$\frac{3S' - (\gamma - 2) (2m' a^2 + L' c^2)}{a^8 c^4} = 0.1894 - 0.2573(\gamma - 2),$$

$$\frac{3T' - (\gamma - 2) (N' a^2 + 2m' c^2)}{a^4 c^8} = 0.4388 - 0.6707(\gamma - 2),$$

$$\frac{U' - (\gamma - 2) N' c^2}{c^{12}} = 0.2605 - 0.5077(\gamma - 2),$$

leading to the values

$$\left. \begin{aligned} R' &= 0.4155 - 1.7799(\gamma - 2), \\ 3S' &= 0.1894 - 1.4585(\gamma - 2), \\ 3T' &= 0.0506 - 0.4124(\gamma - 2), \\ U' &= 0.00346 - 0.0375(\gamma - 2). \end{aligned} \right\} \text{(exact solution).} \quad (149)$$

This may be compared with the approximation expressed by equation (130), which gives

$$\left. \begin{aligned} R' &= (\gamma-2) L'a^2 - \frac{4}{abc} k_1 \frac{a^{12}}{\theta} &= 0.3981 - 1.7691(\gamma-2), \\ 3S' &= (\gamma-2) (2m'a^2 + L'c^2) - \frac{4}{abc} 3k_2 \frac{a^8 c^4}{\theta} &= 0.2013 - 1.4659(\gamma-2), \\ 3T' &= (\gamma-2) (N'a^2 + 2m'c^2) - \frac{4}{abc} 3k_3 \frac{a^4 c^8}{\theta} &= 0.0452 - 0.4090(\gamma-2), \\ U' &= (\gamma-2) N'c^2 - \frac{4}{abc} k_4 \frac{c^{12}}{\theta} &= 0.00355 - 0.0381(\gamma-2). \end{aligned} \right\} \text{(Approximation A) . (150)}$$

The error of Approximation A is now something like 5 per cent. in the terms independent of  $(\gamma-2)$ , and there is also an additional small error of less than 1 per cent. in the terms containing  $(\gamma-2)$ .

38. We pass now to the discussion of terms of degree 4. Equating coefficients of  $w^4$ ,  $w^2 z^2$ , and  $z^4$  in equation (140) gives

$$\left. \begin{aligned} 3h_2 - \theta \left[ \frac{r' - 2(\gamma-2)pa^2}{a^8} \right] &= \frac{3j_2}{8} + \frac{4k_5}{abc}, \\ -24h_2 - \theta \left[ \frac{2s' - 2(\gamma-2)(ra^2 + pc^2)}{a^4 c^4} \right] &= -\frac{24j_2}{8} + \frac{8k_5}{abc}, \\ 8h_2 - \theta \left[ \frac{t' - 2(\gamma-2)rc^2}{c^8} \right] &= \frac{8j_2}{8} + \frac{4k_7}{abc}. \end{aligned} \right\} \dots (151)$$

Following the method of the last section, the last two equations may be replaced by

$$8 \left[ \frac{r' - 2(\gamma-2)pa^2}{a^8} \right] + \left[ \frac{2s' - 2(\gamma-2)(ra^2 + pc^2)}{a^4 c^4} \right] = -\frac{2}{\theta} \frac{2p}{a^4}, \dots (152)$$

$$\left[ \frac{2s' - 2(\gamma-2)(ra^2 + pc^2)}{a^4 c^4} \right] + 3 \left[ \frac{t' - (\gamma-2)rc^2}{c^8} \right] = -\frac{2}{\theta} \frac{r}{c^4}, \dots (153)$$

The three equations (151) to (153) determine  $r'$ ,  $s'$  and  $t'$ . The values of  $4k_5/abc$  and of  $3j_2$  have already been given. For  $3h_2$  I obtain by direct computation from formula (135)

$$\begin{aligned} 3h_2 &= 0.010972r' - 0.064324s' + 0.094925t' \\ &\quad + 0.01031R' - 0.007283S' - 0.04422T' + 0.32343U', \end{aligned}$$

which, on inserting the exact solution (149) for  $R'$ ,  $S'$ ,  $T'$ ,  $U'$ , becomes

$$3h_2 = 0.010972r' - 0.064324s' + 0.094925t' + 0.00179 - 0.00166(\gamma-2).$$

The smallness of the last two terms of course measures the closeness of the approximation (130).

Equation (151) now reduces to

$$-\theta \left[ \frac{r' - 2(\gamma - 2)pa^2}{a^8} \right] + 0.010972r' - 0.064324s' + 0.094925t' = -0.00843 + 0.00310(\gamma - 2). \quad (154)$$

On solving equations (152) to (154) directly, I find

$$\begin{aligned} \frac{r' - 2(\gamma - 2)pa^2}{a^8} &= 0.02074 - 0.01055(\gamma - 2), \\ \frac{2s' - 2(\gamma - 2)(ra^2 + pc^2)}{a^4c^4} &= -0.07096 + 0.08440(\gamma - 2), \\ \frac{t' - 2(\gamma - 2)rc^2}{c^8} &= -0.14008 - 0.02813(\gamma - 2), \end{aligned}$$

whence the values of  $r'$ ,  $s'$ ,  $t'$  are

$$\left. \begin{aligned} r' &= 0.08755 - 0.10962(\gamma - 2), \\ s' &= -0.01727 + 0.04871(\gamma - 2), \\ t' &= -0.007862 + 0.02511(\gamma - 2). \end{aligned} \right\} \text{(exact solution).} \quad (155)$$

This may be compared with Approximation A, namely,

$$r' = 2(\gamma - 2)pa^2 - \frac{4k_5}{abc} \frac{a^8}{\theta}, \text{ \&c.,}$$

which leads to the approximate values

$$\left. \begin{aligned} r' &= 0.06590 - 0.06509(\gamma - 2), \\ s' &= -0.00728 + 0.02815(\gamma - 2), \\ t' &= -0.007929 + 0.02669(\gamma - 2). \end{aligned} \right\} \text{(Approximation A).}$$

The percentage error is large, although the absolute error in the coefficients is fairly small. This will be readily understood on noticing that under Approximation B,  $r'$ ,  $s'$  and  $t'$  would vanish altogether.

39. Finally equating coefficients of  $w^2$  and  $z^2$  in equation (140) and making use of the relation  $k_9 = -2k_8$ , we obtain

$$h_3 - \frac{2u'}{a^4} \theta = \frac{1}{8}j_3 + \frac{8k_8}{abc} + \delta n, \quad (156)$$

$$-2h_3 - \frac{2v'}{c^4} \theta = -\frac{1}{4}j_3 - \frac{16k_8}{abc}. \quad (157)$$

Multiplying by 2, 1 and adding,

$$\delta n = -2\theta \left( \frac{2u'}{a^4} + \frac{v'}{c^4} \right), \dots \dots \dots (158)$$

an equation which may be used to replace (156).

By direct computation from equation (136), I find

$$\begin{aligned} h_3 &= 0.19769u' - 0.58215v' \\ &\quad + 0.06706r' + 0.01164s' - 0.61497t' \\ &\quad + 0.04270R' + 0.03778S' - 0.07530T' - 1.1894U' \\ &= 0.19769u' - 0.58215v' + 0.02348 - 0.11113(\gamma - 2), \end{aligned}$$

so that equation (157) reduces to

$$0.39538u' + 2.8142v' = 0.0212 + 0.0794(\gamma - 2). \dots \dots \dots (159)$$

Equations (158) and (159) are adequate to give  $u'$  and  $v'$  in terms of any assigned value of  $\delta n$ . We require especially the solution at the actual point of bifurcation of the compressible series, and to obtain this the two equations must be combined with a third equation expressing the condition for a point of bifurcation.

The third equation is

$$\delta(a^6 c J_{AA}) = 0,$$

or, transforming by the method of § 27,

$$\frac{6u'}{a^2} I_{AAA} + \frac{v'}{c^2} I_{AAC} = \frac{24p^2}{a^4} H_{A^4} + \frac{6pr}{a^2 c^2} H_{A^3C} + \frac{3r^2}{2c^4} H_{A^2C^2}.$$

Inserting numerical values, this becomes

$$0.24919u' + 0.20878v' = 0.00024. \dots \dots \dots (160)$$

From this and equation (159), I found by direct solution

$$\left. \begin{aligned} u' &= -0.00550 - 0.02651(\gamma - 2) \\ v' &= 0.00778 + 0.03195(\gamma - 2) \end{aligned} \right\}, \dots \dots \dots (161)$$

and equation (158) now gives

$$\delta n = -0.01292 - 0.05495(\gamma - 2). \dots \dots \dots (162)$$

The solution which has just been completed, combined with the two exact solutions (127) and (128) previously known, will give the exact solution for a compressible mass at the point of bifurcation at which the pseudo-spheroidal series gives up its stability to the pseudo-ellipsoidal series.

40. The rotation at this point of bifurcation is given by

$$\begin{aligned} \frac{\omega^2}{2\pi\rho_0} &= n + \epsilon \Delta n + \epsilon^2 \delta n \\ &= 0.18712 - 0.04400 \left( \frac{\rho_0 - \sigma}{\rho_0} \right) - [0.01292 + 0.05495 (\gamma - 2)] \left( \frac{\rho_0 - \sigma}{\rho_0} \right)^2. \end{aligned} \quad (163)$$

The first point of interest about this equation is that the term in  $(\rho_0 - \sigma)$  is independent of  $\gamma$ . This must necessarily be the case, for we have seen that for an incompressible mass, regarded as a special case of the compressible mass that has been under discussion,  $\gamma - 2$  is infinite while  $\rho_0 - \sigma$  vanishes, and the product of the two remains finite. Thus for an incompressible mass (163) reduces to

$$\omega^2/2\pi\rho_0 = 0.18712,$$

which is the true value, but if there has been a term in  $(\gamma - 2)$  multiplying  $(\rho_0 - \sigma)$ , equation (163) would have led to a wrong value.

When  $\gamma = 2$ , equation (163) reduces to

$$\omega^2/2\pi\rho_0 = 0.18712 - 0.04400\epsilon - 0.01292\epsilon^2 - \dots$$

Although we cannot be perfectly sure, the series is almost certainly convergent right up to the limiting case of  $\sigma = 0$  or  $\epsilon = 1$ . In this case, it appears to converge to a limit of about  $\omega^2/2\pi\rho_0 = 0.120$ , but unfortunately it is impossible to evaluate the limit for other values of  $\gamma$ .

A more important question is the relation between  $\omega^2$  and  $\bar{\rho}$  at the point of bifurcation.

We have evaluated  $\rho$  as far as  $\epsilon^3$ , but for comparison with the value of  $\omega^2$  given by equation (163), it will be enough to evaluate  $\bar{\rho}$  as far as  $\epsilon^2$ . Furthermore, to avoid a very complicated integration, we shall use Approximation B for the terms in  $\epsilon^2$ , and so take

$$\rho = \rho_0 - (\rho_0 - \sigma) \left[ \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} + \epsilon\eta \left( \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} \right)^2 \right],$$

where  $\eta = \frac{1}{2}(\gamma - 2.75)$ , this being the approximation given by equation (84). By a simple projective transformation, it follows that the mean density is the same as that in a sphere in which the law of density is

$$\rho = \rho_0 - (\rho_0 - \sigma) \left( \frac{r^2}{a^2} + \epsilon\eta \frac{r^4}{a^4} \right).$$

As far as terms in  $\epsilon$ , the radius of this sphere is given by  $r_0 = (1 - \frac{1}{2}\epsilon\eta)a$ , and the mass taken as far as  $\epsilon^2$  is

$$4\pi \int_0^{r_0} \rho r^2 dr = 4\pi \left[ \frac{r_0^3}{3} \rho_0 - (\rho_0 - \sigma) \left( \frac{r_0^5}{5a^2} + \epsilon\eta \frac{r_0^7}{7a^4} \right) \right],$$

whence the mean density, as far as  $\epsilon^2$ , is found to be

$$\bar{\rho} = \rho_0 \left(1 - \frac{3}{5}\epsilon + \frac{6}{35}\epsilon^2\eta\right) = \rho_0 \left[1 - \frac{3}{5}\epsilon - \frac{9}{140}\epsilon^2 - \dots + \frac{3}{35}(\gamma - 2)\epsilon^2 + \dots\right]. \quad (164)$$

From these equations we obtain

$$\frac{\omega^2}{2\pi\bar{\rho}} = 0.18712 + 0.06827\epsilon + (0.01602 + 0.07098(\gamma - 2))\epsilon^2 + \dots \quad (165)$$

*Ratio of Centrifugal Force to Gravity.*

41. [§ 41 revised August 31, 1918].—The ratio of centrifugal force to gravity is interesting only when it becomes equal to unity. When this occurs a stream of matter is ejected at the points at which centrifugal force equals gravity. Centrifugal force will first become equal to gravity at points which are furthest from the axis of rotation, and these will be points on the equator of the rotating mass. Considering a point on the axis of  $x$ , the condition for centrifugal force to be equal to gravity is

$$\partial V/\partial x + \omega^2 x = 0,$$

or

$$\partial \Omega/\partial x = 0.$$

Since, by equation (30),  $\Omega = \frac{\kappa\gamma}{\gamma-1} \rho^{\gamma-1} + a$  constant, this may equally well be expressed in the form

$$\partial \rho/\partial x = 0.$$

The general value of  $\rho$  is given by equation (45). On the  $x$ -axis this reduces to

$$\rho = \rho_0 (1 - \epsilon F),$$

where

$$F = \frac{x^2}{a^2} + \epsilon \left[ \frac{Lx^4}{a^8} + \frac{2px^2}{a^4} \right] + \epsilon^2 \left[ \frac{Rx^6}{a^{12}} + \frac{rx^4}{a^8} + \frac{2ux^2}{a^2} \right] + \dots \quad (166)$$

The intercepts on the axis of  $x$  are determined by the condition  $\rho = \sigma$ , and so are given by  $F = 1$ . The solution of this equation is found to be

$$\frac{x^2}{a^2} = 1 - \epsilon \left( \frac{L}{a^4} + \frac{2p}{a^2} \right) - \epsilon^2 \left[ \frac{R}{a^6} + \frac{r}{a^4} + \frac{2u}{a^2} - \left( \frac{L}{a^4} + \frac{2p}{a^2} \right) \left( \frac{2L}{a^4} + \frac{2p}{a^2} \right) \right] + \dots \quad (167)$$

The points on the  $x$ -axis at which  $\partial \rho/\partial x = 0$  are given by  $\partial F/\partial x = 0$ , so that it appears that  $\partial \rho/\partial x$  will just vanish at the extremities of the  $x$ -axis if  $\partial F/\partial x$  vanishes for the value of  $x$  given in equation (167).

The equation  $\partial F/\partial x = 0$  becomes, on division by  $2x/a^2$

$$1 + \epsilon \left[ \frac{2L}{a^4} \left( \frac{x^2}{a^2} \right) + \frac{2p}{a^2} \right] + \epsilon^2 \left[ \frac{3R}{a^6} \left( \frac{x^4}{a^4} \right) + \frac{2r}{a^4} \left( \frac{x^2}{a^2} \right) + \frac{2u}{a^2} \right] + \dots = 0,$$



and, on inserting the value of  $x^2/\alpha^2$  given by equation (167), this becomes

$$1 + \epsilon \left[ \frac{2L}{\alpha^4} + \frac{2p}{\alpha^2} \right] + \epsilon^2 \left[ \frac{3R}{\alpha^6} + \frac{2r}{\alpha^4} + \frac{2u}{\alpha^2} - \frac{2L}{\alpha^4} \left( \frac{L}{\alpha^4} + \frac{2p}{\alpha^2} \right) \right] + \dots = 0.$$

42. Let us examine in particular the special form assumed by this equation for the special configuration at which the pseudo-spheroidal form becomes unstable, giving place to a pseudo-ellipsoidal form. Inserting the numerical values for  $L$ ,  $p$ ,  $R$ , &c., obtained in §§ 18–39, the equation becomes

$$1 + \epsilon [(\gamma - 2) - 1.0509] + \epsilon^2 \left[ \frac{1}{2} (\gamma - 2)^2 - 0.4063 (\gamma - 2) - 0.0510 \right] + \dots = 0. \quad (168)$$

For a given value of  $\gamma$  this equation determines the value of  $\epsilon$  for which centrifugal force just outbalances gravity as the pseudo-spheroidal form gives place to the pseudo-ellipsoidal.

For instance, for the value  $\gamma = 2$ , the equation becomes

$$1 - 1.0509\epsilon - 0.0510\epsilon^2 - \dots$$

The values of  $\epsilon$  obtained by using terms as far as  $\epsilon$  and  $\epsilon^2$  respectively are 0.9516 and 0.9112. The true root is perhaps somewhere near  $\epsilon = \frac{9}{10}$ . Thus a mass of rotating matter obeying LAPLACE'S law ( $\gamma = 2$ ) will throw off matter from its equator before reaching the ellipsoidal point of bifurcation if  $\epsilon > \frac{9}{10}$ , or if  $\sigma$  is less than  $\frac{1}{10}\rho$ .

The root  $\epsilon = \frac{9}{10}$  agrees well with the corresponding quantity in the two-dimensional problem. For cylindrical masses obeying LAPLACE'S law ( $\gamma = 2$ ) the problem can be solved exactly and the root is found to be  $\epsilon = 1$ , giving  $\sigma = 0$ .\*

Equation (168) may more usefully be regarded as giving  $\gamma$  when the value of  $\epsilon$  is assigned. The only value of  $\epsilon$  which is of any astronomical interest is the value  $\epsilon = 1$ , the value for a mass whose density reduces to zero at the boundary. Putting  $\epsilon = 1$ , we obtain an equation giving a critical value of  $\gamma$ .

From terms as far as  $\epsilon$  only, the value of  $\gamma$  is clearly enough

$$\gamma = 2.0509.$$

On including terms as far as  $\gamma^2$ , this value becomes

$$\gamma = 2.1521.$$

These values of  $\gamma$  appear to be converging to a limit; we cannot state it with great accuracy, but we shall perhaps not be far wrong if we assume it to be  $\gamma = 2.2$ .

Here again we may compare the problem with the simpler two-dimensional one in which, as follows from what has already been said, the root of  $F = 0$ , when  $\epsilon = 1$ , is  $\gamma = 2$  exactly.

\* 'Phil. Trans.,' A, vol. 213, p. 471.

*The Influence of other Physical Factors.*

43. The discussion from § 10 onwards has been limited to material in which the relation between pressure and density is of the form

$$p = \kappa\rho^\gamma - \text{const.}, \dots \dots \dots (169)$$

an equation which implies that the mass is composed of matter of similar properties throughout. In an actual mass there must be at least some tendency for the substances of greater atomic or molecular weight to sink towards the centre, although it is far from clear to what extent this tendency will actually prevail under astronomical conditions.

In equation (169),  $\gamma$  is usually regarded as expressing the measure of a property of the material, being the ratio of the specific heats when the matter is gaseous. We have, however, only used this equation in its differential form

$$dp = \kappa\gamma\rho^{\gamma-1} d\rho. \dots \dots \dots (170)$$

Now with any structure whatever of the mass of matter under consideration the surfaces of constant pressure and density must coincide. Our use of equation (170) has in no sense referred to a change of state of a single element of matter, it has referred to a passage from one surface of constant density to the next. Thus, in strictness,  $\gamma$  refers to the arrangement of the matter and not to a physical property of the matter. In the case so far considered in which the matter has been supposed to have the same physical properties throughout, the two meanings become identical, but when the mass under discussion is an aggregate of imperfectly mixed types of matter, it becomes important to distinguish clearly between the two meanings.

When  $p$  and  $\rho$  both vanish at the surface of the mass, equation (170) is equivalent to

$$d \log \rho = \frac{1}{\gamma} d \log p, \dots \dots \dots (171)$$

where the differentials are supposed to refer to passage from one surface of constant density to the next. In passing from one surface to the next,  $\rho$  will increase partly on account of the increase of pressure, but partly also on account of the higher atomic weight of which the materials of the layer of higher density may be supposed composed. Thus we may suppose equation (171) replaced by

$$d \log \rho = \left( \frac{1}{\gamma_M} + \frac{1}{\gamma_A} \right) d \log p, \dots \dots \dots (172)$$

where  $\gamma_M$  is the value of  $\gamma$  defined by equation (169) as a property of the material, while  $\gamma_A$  is such that the additional term on the right of equation (172) represents the increase in  $d \log \rho$  owing to increase of atomic weight of the materials as we pass to layers of greater density.

In any arrangement of matter whatever,  $\gamma_A$  will have some value for each layer of constant density, being virtually defined by equation (172). There is no reason to expect that  $\gamma_A$  will be constant, or even approximately constant throughout the mass. But in the present complex problem we must be content to discover tendencies rather than exact results, and so may think of  $\gamma_A$  as a constant. An increase of atomic weight on passing to layers of greater density will give a positive value to  $\gamma_A$ , while similarly a diminution of atomic weight would give a negative value of  $\gamma_A$ .

The whole of the foregoing analysis will now apply to the present case if we put

$$\frac{1}{\gamma} = \frac{1}{\gamma_M} + \frac{1}{\gamma_A} \dots \dots \dots (173)$$

It has been seen that for values of  $\gamma$  less than a critical value, which may be taken (although only as a rough approximation) to be 2.2, it will be impossible for the rotating mass to assume the ellipsoidal form, and so impossible for it to separate into two detached masses. The condition for assuming the ellipsoidal form now becomes

$$\frac{1}{\gamma_M} + \frac{1}{\gamma_A} < \frac{1}{2.2} \dots \dots \dots (174)$$

Thus, if  $\gamma_A$  is positive (atomic weight increasing towards centre), the critical value of  $\gamma_M$  will be greater than 2.2; with  $\gamma_A$  negative, the critical value of  $\gamma_M$  will be less than 2.2. It is possible for a heterogeneous but perfectly incompressible mass ( $\gamma_M = \infty$ ) to fail to attain the ellipsoidal shape if  $\gamma_A$  is small enough—*i.e.*, if the layers increase sufficiently rapidly in density from increase of atomic weight alone.

44. In the foregoing discussion we have considered only the effects of continuous changes of atomic weight. Entirely confirmatory results may be obtained from a consideration of excessively abrupt changes.

Let us consider only the simplest case in which the mass is formed of completely separated layers of two substances only, one very light and the other very heavy—to make the picture definite, let us think of an inner mass of iron vapour surrounded by an atmosphere of hydrogen, and let us suppose the density of the hydrogen may be neglected in comparison with that of the iron, so that the gravitational field will be the same as if the iron alone were present.

For any given value of  $\omega$  we can draw the equipotentials  $\Omega = \text{cons.}$ , and the boundary of the mass of iron must be one of these, say  $\Omega = C_1$ . Proceeding outwards and drawing the exterior equipotentials we must in time come to one having a double point, say  $\Omega = C_x$ , and at the double point on this equipotential centrifugal force will be exactly equal to gravity ( $\partial\Omega/\partial n = 0$ ). The space between the equipotentials  $\Omega = C_1$  and  $\Omega = C_x$  can be filled with hydrogen without matter being thrown off by rotation, but clearly no greater volume of hydrogen than this can be retained.

As the rotation  $\omega$  increases from zero upwards, the equipotential  $\Omega = C_x$  starts from infinity and moves inwards, so that the maximum volume of hydrogen which

can be retained continually decreases. With an allotted amount of hydrogen, the ellipsoidal point of bifurcation may or may not be reached before matter has begun to be ejected from the equator of the figure.

The simplest case for accurate discussion occurs when the core is treated as incompressible. In fig. 3 the thick curve represents the cross-section through the axis of rotation of an incompressible mass at the Maclaurin-Jacobian point of bifurcation, while the thin curve represents the equipotential  $\Omega = C_x$ , which has a series of double points round its equator. If the volume of light material surrounding the core is just equal to the volume between these surfaces, matter will begin to be thrown off at the equator precisely at the moment at which the ellipsoidal point of bifurcation is reached. If the volume of light matter is at first

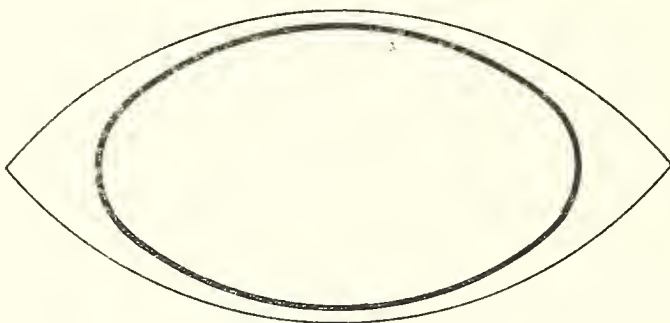


Fig. 3.

greater than this critical volume, matter will be thrown off equatorially before the ellipsoidal point of bifurcation is reached, the amount ejected being such that the volume is just reduced to the critical volume when this point is reached. Conversely, of course, if the volume of light matter is initially less than this, the point of bifurcation will be reached before any matter is thrown off equatorially.

A rough estimate shows that the critical volume, when the matter is incompressible, is about one-third of the volume of the core. For a compressible core for which  $\gamma > 2.2$ , it is of course less, becoming equal to zero when  $\gamma = 2.2$  (approximately).

This completes our collection of theoretical results. They may now be recapitulated and discussed with reference to actual astronomical conditions.

#### *Summary and Discussion of Results.*

45. Our discussion began with a general survey of the types of configurations which can be assumed by compressible astronomical masses in rotation. The result announced in a previous paper\* that the incompressible mass provides a good model from which to study the behaviour of compressible masses has on the whole been fully confirmed. A mass of incompressible matter, shrinking while rotating, will assume first the shape of a spheroid, then that of an ellipsoid, afterwards becoming unstable

\* 'Phil. Trans.,' A, vol. 213, p. 457.

and probably dividing into two detached masses after passing through a series of pear-shaped configurations. In the present investigation it has been found that, except for an alternative possibility to be discussed later, a shrinking compressible mass will experience a very similar sequence of changes. It will pass through a sequence of figures which from their similarity to the spheroids and ellipsoids of incompressible masses, may be described as pseudo-spheroids and pseudo-ellipsoids. The pseudo-spheroids become unstable when a certain degree of flatness is reached and give place to a series of pseudo-ellipsoids, these in turn become unstable when a certain degree of elongation is reached and give place to a series of pear-shaped figures which probably end by fission into detached masses.

46. It may simplify the presentation of the detailed results obtained, if we confine our attention at first to the innermost strata, this being supposed to mean strata so near the centre (which is taken as origin) that terms in  $x^4$ ,  $x^2y^2$ , &c., may be neglected in comparison with terms in  $x^2$ ,  $y^2$ ,  $z^2$ . It has been found that these strata will be first truly spheroidal, then truly ellipsoidal, then pear-shaped, each change of figure corresponding, as in the incompressible mass, to a passage through a point of bifurcation of the system as a whole.

The problem has been studied in detail for a pressure-density law of the form

$$p = \kappa\rho^\gamma - \text{const.}, \quad \dots \quad (175)$$

and special attention has been paid to the exact position of the configuration at which pseudo-spheroidal configurations give place to pseudo-ellipsoidal ones. This configuration we may refer to as the ellipsoidal point of bifurcation; its special importance will appear later. The corresponding configuration for an incompressible mass is the Maclaurin-Jacobian point of bifurcation; at this point the semi-axes  $a_0$ ,  $c_0$  and the angular velocity  $\omega_0$  are given by

$$a_0 = 1.1972, \quad c_0 = 0.69766, \quad \omega_0^2/2\pi = 0.18712\rho,$$

so that the equation of the boundary is

$$\frac{x^2 + y^2}{a_0^2} + \frac{z^2}{c^2} = 1.$$

For a compressible mass, the equations of the innermost strata of constant density at the ellipsoidal point of bifurcation have been found to be

$$\begin{aligned} & \frac{x^2 + y^2}{a_0^2} [1 - 0.016307\epsilon - (0.00384 + 0.01850(\gamma - 2))\epsilon^2 - \dots] \\ & + \frac{z^2}{c_0^2} [1 + 0.05634\epsilon + (0.01598 + 0.06565(\gamma - 2))\epsilon^2 + \dots] = \frac{\rho_0 - \rho}{\rho_0 - \sigma}, \quad \dots \quad (176) \end{aligned}$$

where  $\rho_0$  is the density at the centre,  $\sigma$  that at the surface, and  $\epsilon$  stands for  $(\rho_0 - \sigma)/\rho_0$ . For the important case of a gaseous mass,  $\epsilon$  is of course equal to unity.

Thus at the ellipsoidal point of bifurcation, the innermost strata of equal density are of flatter shape than those for an incompressible mass, showing that compressibility tends to postpone instability for the spheroidal mass.

The value of  $\omega$ , the angular velocity at this point of bifurcation has been found to be given by

$$\omega^2/2\pi\rho_0 = 0.18712 - 0.04400\epsilon - (0.01292 + 0.05495(\gamma-2))\epsilon^2 - \dots, \quad (177)$$

or, if we evaluate  $\omega^2$  in terms of  $\bar{\rho}$ , the mean density of the whole mass,

$$\omega^2/2\pi\bar{\rho} = 0.18712 + 0.06827\epsilon + (0.01602 + 0.07098(\gamma-2))\epsilon^2 - \dots, \quad (178)$$

the coefficient of  $\epsilon^2$  now being only approximate. We notice that  $\omega^2/2\pi\bar{\rho}$  is greater for a compressible mass than for an incompressible mass, so that again compressibility may be said to postpone the instability of the spheroidal form.\*

Equation (176) applies only to the innermost strata for which  $x^4$ , &c., may be neglected. The equation of the outer strata, both at the point of bifurcation and elsewhere, are found to contain terms of degrees four and higher, there being terms of degrees four and two multiplied by  $\epsilon$ , terms of degrees six, four and two multiplied by  $\epsilon^2$ , and so on. The terms of degrees six and four have been calculated for the ellipsoidal point of bifurcation and the terms of degree four for the pear-shaped point of bifurcation.

The presence of these terms destroys the spheroidal or ellipsoidal shape of the outer strata. In general it is found that the outer strata are more lens-shaped than the inner strata when these latter are spheroidal, and more spindle-shaped than the inner strata when these latter are ellipsoidal. The lens-shaped form of the outer strata may go so far that the outer boundary develops a sharp edge. When this occurs, centrifugal force is exactly equal to gravity at points on the periphery of the lens, and any further increase in the rotation of the mass results in matter being thrown off from round this periphery. Similarly the spindle-shaped figure may develop sharp ends, in which case matter will be thrown off here also.

47. Consider now a gradually shrinking mass of gas or other compressible matter, the rotation increasing as the shrinkage proceeds. For a very slow rotation the strata and the boundary will all be spheroidal. As the rotation increases, the boundary departs more and more from the spheroidal form, taking a series of forms

\* All terms in  $\omega^2/2\pi\bar{\rho}$  are positive because  $\gamma - 2$  is necessarily positive; for, as we shall see, if  $\gamma < 2$ , the compressibility so far postpones the occurrence of the ellipsoidal point of bifurcation that it does not occur at all. Incidentally equation (178) has an important bearing on the origin of the solar system. It shows that for every mass which has broken up by fission  $\omega^2/2\pi\bar{\rho}$  must at some time have exceeded the value 0.18712. This provides the keystone, which has so far been wanting, in an argument I have given elsewhere ('M. N. Royal Ast. Soc.,' 77, p 191) to show that the solar system is very unlikely to have broken up by rotation alone.

which we have called pseudo-spheroidal, these being more lens-shaped than true spheroids. There are two alternatives. It may be that the point of bifurcation will be reached before a sharp edge forms at the equator of the pseudo-spheroids, and if this happens the innermost strata will become ellipsoidal, and the outer strata and the boundary will be pseudo-ellipsoidal; the mass will proceed towards the pear-shaped form and ultimate fission. But, instead of this happening, it may be that a sharp edge will be formed before the point of bifurcation is reached, and the mass will disintegrate through equatorial loss of matter. It is of the utmost importance to determine which of these events will happen first for a particular mass.

48. Some information may be obtained from a general survey of the problem. The spherical solutions for a mass of matter at rest obeying the law  $p = \kappa\rho^\gamma$  have been investigated by RITTER, DARWIN, EMDEN\* and others. Excepting the special case of  $\gamma = 2$ , in which the equation reduces to a linear equation, the solution can be expressed in finite terms in one case only, namely  $\gamma = 1\frac{1}{5}$ . In this case the solution, first given by SCHUSTER,† is

$$\rho = A(1+r^2/a^2)^{-\frac{5}{2}}. \quad \dots \quad (179)$$

This happens also to give the lowest value of  $\gamma$  for which the mass is finite. For values of  $\gamma$  less than  $1\frac{1}{5}$ , the matter extends to infinity and the total mass is infinite; when  $\gamma = 1\frac{1}{5}$ , the matter extends to infinity but the total mass is finite; when  $\gamma > 1\frac{1}{5}$ , the matter is of finite extent and of finite total mass. As  $\gamma$  increases the variations in density becomes less rapid and finally the value  $\gamma = \infty$  corresponds to an incompressible mass in which the density is uniform throughout.

Now clearly a mass for which  $\gamma = 1\frac{1}{5}$  will lose matter equatorially with even the slightest amount of rotation. For all except an infinitesimal fraction of the whole mass is concentrated in regions near the centre, and the potential near the edge may accordingly be taken to be  $M/r$ . The value of  $\Omega$  is therefore

$$\Omega = \frac{M}{r} + \frac{1}{2}\omega^2(x^2 + y^2).$$

The problem is now seen to be identical with one which has been studied by ROCHE.‡ There is a critical equipotential on which double points occur all round the equator, and this is the equipotential

$$\Omega = \frac{3}{2}(M\omega)^{\frac{2}{3}}.$$

\* R. EMDEN, 'Gaskugeln' (Leipzig, 1907), where references to the work of previous investigators will be found.

† 'British Assoc. Report,' 1883, p. 428.

‡ "Essai sur la constitution et l'origine du Système Solaire," 'Acad. de Montpellier. Section des Sciences,' VIII., p. 235. A more accessible account is to be found in POINCARÉ'S 'Leçons sur les Hypothèses Cosmogoniques,' 2nd edition, p. 15.

The equatorial radius is  $M^{\frac{1}{3}}\omega^{-\frac{2}{3}}$ . By a simple integration the volume of this critical equipotential is found to be

$$32\pi M\omega^{-2} \int_0^{\frac{1}{2}\pi} \frac{4 \cos^2 \theta - 3}{4 \cos^2 \theta - 1} \cos^2 \theta \sin \theta d\theta = 32\pi M\omega^{-2} \times 0.0225466.$$

This volume is of course equal to  $M/\bar{\rho}$  where  $\bar{\rho}$  is the mean density, from which we find

$$\omega^2/2\pi\bar{\rho} = 0.360746. \dots \dots \dots (180)$$

Since  $\bar{\rho} = 0$ , the critical value of  $\omega$  is also zero, and the innermost strata differ only imperceptibly from spheres. Thus, when  $\gamma = 1\frac{1}{5}$ , equatorial break-up occurs as soon as the mass is set into rotation at all, and therefore long before there can be any question of the pseudo-ellipsoidal form being attained.

At the other end of the scale ( $\gamma = \infty$ ) comes the incompressible mass, for which the ellipsoidal form is attained long before there is any question of equatorial breaking up.

Thus for some value of  $\gamma$ , intermediate between  $\gamma = 1\frac{1}{5}$  and  $\gamma = \infty$ , there must be a crossing over from equatorial break-up to fission through pseudo-ellipsoidal and pear-shaped figures. For a mass for which  $\gamma$  has this critical value, the point of bifurcation is reached and the pseudo-ellipsoidal form assumed at the very instant at which equatorial break-up is about to begin.

49. A comparison with the corresponding two-dimensional problem is of interest at this stage. Here again a solution in finite terms is only possible for one value of  $\gamma$  other than  $\gamma = 2$ , and here again this value happens to be that one for which the total mass is first finite, while the matter extends to infinity. The value in question is  $\gamma = 1$  and the solution is

$$\rho = A(1+r^2/a^2)^{-2}, \dots \dots \dots (181)$$

which may be compared with the three-dimensional solution (179). Again it is clear that, somewhere between  $\gamma = 1$  and  $\gamma = \infty$ , there must be a critical value of  $\gamma$  at which a transition occurs from equatorial break-up to fission into two detached masses. The two-dimensional problem can, however, be fully solved, and the critical value is found to be  $\gamma = 2$  exactly.\*

Seeing that the two problems run fairly close together in all their essential features, we might suspect that the critical value in the three-dimensional problem would not be very far from 2. An alternative guess might be  $\gamma = 2\frac{2}{5}$ , this corresponding more closely to the two-dimensional value  $\gamma = 2$ , since  $\gamma = 1\frac{1}{5}$  in the three-dimensional problem has been found to correspond to  $\gamma = 1$  in the two-dimensional problem.

50. In the present paper the critical value of  $\gamma$  has been shown to be determined in the three-dimensional problem by the equation

$$1 + \epsilon[(\gamma - 2) - 1.0509] + \epsilon^2[\frac{1}{2}(\gamma - 2)^2 - 0.4063(\gamma - 2) - 0.0510] + \dots = 0, \dots (182)$$

\* 'Phil. Trans.,' A, vol. 213, p. 471.



in which  $\epsilon$  must of course be put equal to unity for a gas in which  $\sigma = 0$  at the boundary. The series on the right is probably rapidly convergent, but sufficient terms have not been calculated for the value of  $\gamma$  to be determined with accuracy. Neglecting all terms beyond those written down, the root of equation (182), when  $\epsilon = 1$ , is found to be  $\gamma = 2.1521$ , but the remaining terms appear likely to increase this value somewhat, and we may perhaps take  $\gamma = 2.2$  as an approximate value. This, we may notice, is just half-way between the two guess-values considered in § 50.

When the density at the boundary is not zero, the critical value of  $\gamma$  is less than this; for instance, a critical value  $\gamma = 1$  corresponds to a value of  $\epsilon$  equal to about three-quarters.

An approximately accurate drawing of the critical figure, when  $\epsilon = 1$ , is shown in fig. 4, the inner curves being strata of constant density.

51. We have considered the effect of heterogeneity in the structure of the matter, and have found that a sinking of the heavier elements to the centre of the mass will result in an increase in the critical value of  $\gamma$ . There is no limit to the amount of

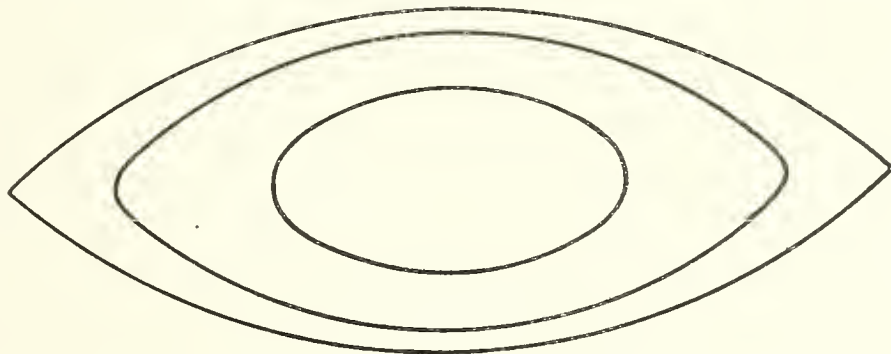


Fig. 4.

increase that can be produced in this way, although naturally the amount of increase depends on the extent to which the light and heavy elements are separated and on the ratio of their amounts. As an illustration, we considered the extreme case of a core of heavy incompressible material which we called iron, surrounded by an atmosphere of much lighter material which we called hydrogen, the two elements being supposed to be completely separated. If the volume of hydrogen was initially greater than about one-third of that of iron, the composite mass set into rotation will first disintegrate through equatorial loss of matter.

A drawing of the critical figure has already been shown on fig. 3 (p. 200); this may be compared with fig. 4.

52. There is, however, a very essential difference between the failure of a uniform mass to attain the ellipsoidal form and the corresponding failure of a heterogeneous mass. Briefly speaking the former is permanent, while the latter is transitory.

Consider for simplicity a mass of perfectly uniform gas—say helium for which  $\gamma = 1\frac{2}{3}$ —set into rotation and continually shrinking by cooling. The value of  $\gamma$  is

certainly below the critical value (about 2·2), so that as the rotation increases matter will be thrown off from the equator before the ellipsoidal shape can be reached. No matter how much material is ejected in this way, the central mass remains a mass of helium with  $\gamma = 1\frac{2}{3}$ , and so can never attain the ellipsoidal form. The mass will disintegrate completely by loss of matter from its equator, and there can be no fission into separate masses—unless, of course, the helium ultimately so changes its character that the average value of  $\gamma$  becomes greater than about 2·2.

Contrast this with the behaviour of the mass of iron and hydrogen already considered. The mass will lose matter by equatorial ejection, but the matter lost will consist entirely of hydrogen, and so this process will continually diminish the ratio of hydrogen to iron, and as the process continues the mass will continually approximate to a mass of incompressible iron. As soon as the ratio of hydrogen to iron is reduced to about one-third, the pseudo-spheroidal form becomes unstable, and the mass will assume a pseudo-ellipsoidal form.

53. We are now in a position to follow the changes in a mass of gas whose rotation continually increases through shrinkage. At first we may assume the gas to obey the ideal laws, so that  $\gamma$  will be less than  $1\frac{2}{3}$ , and, as the rotation increases, a stage will be reached at which matter is ejected from the equator. Some of this matter will perhaps fall back on to the rotating mass, but some must also pass to infinity, this latter representing a real loss of mass and of angular momentum to the rotating body. The loss must be at such a rate that the figure of the rotating body always remains a pseudo-spheroid with a sharp edge, and the velocity of rotation remains always exactly equal to the critical velocity corresponding to this critical figure.

When  $\gamma$  is equal to  $1\frac{1}{5}$ , the critical angular velocity is given by equation (180), so that  $\omega^2 = 0\cdot36 \times 2\pi\bar{\rho}$ . For the greatest value of  $\gamma$  for which the pseudo-spheroidal figure is possible (about  $\gamma = 2\cdot2$ ), the value of the critical angular velocity is given by equation (178), and this seems to be converging to a value not far from  $\omega^2 = 0\cdot36 \times 2\pi\bar{\rho}$ . We may perhaps conjecture that for all masses of gas which are throwing off matter equatorially the value of  $\omega^2$  is nearly equal to  $0\cdot36 \times 2\pi\bar{\rho}$ .

As the mass shrinks  $\bar{\rho}$  becomes greater, so that rotation becomes more and more rapid. A stage is reached in time in which the ideal gas laws no longer hold, owing to the distance apart of the molecules having become comparable with their diameters. The value of  $\gamma$  now increases beyond its value for an ideal gas, and values of  $\gamma$  greater than  $1\frac{2}{3}$  become possible. When a value of  $\gamma$  is reached which is about equal to 2·2 if the mass of gas is perfectly mixed, but may be greater if the mixing is imperfect, the pseudo-spheroidal form becomes unstable, the mass assumes the pseudo-ellipsoidal form and the process probably ends by fission into two detached masses.

54. The value  $\gamma = 2\cdot21$  has been found by KOCH for air at a pressure of 100 atmospheres and a temperature of  $-79\cdot3$  C., the corresponding density being 0·23. Partly from this observational material, and partly from general theoretical principles, we may anticipate that the value  $\gamma = 2\cdot2$  will be attained at a density

of about one-quarter of that of the substance in its solid state, and for the permanent gases this may be taken to be about a quarter of the density of water.

Thus a mass of gas will lose matter equatorially until it has shrunk to a density of about a quarter of that of water, after which it will elongate and divide up. Assuming the relation  $\omega^2 = 0.36 \times 2\pi\bar{\rho}$ , the mean density  $\bar{\rho}$  and the period of rotation in days (P), will be connected, so long as the mass is losing matter equatorially, by the relation

$$\bar{\rho} = 0.035 \div P^2,$$

the density  $\bar{\rho} = \frac{1}{4}$  corresponding to a period of about 9 hours and  $\bar{\rho} = \frac{1}{2}$  to a period of  $6\frac{1}{2}$  hours. When this stage is reached the process of elongation followed by fission begins. Assuming that when fission is complete we have two stars of approximately equal mass and mean densities  $\bar{\rho} = \frac{1}{2}$  revolving round one another almost in contact, the period of this system would be about a day.

55. The critical density which we have conjectured to be about one quarter is perhaps not far from that of the average B-type star.\* Thus, subject to the assumptions on which we have been working, fission ought to begin at about B-type. This is in very close agreement with the results obtained by CAMPBELL in his "Second Catalogue of Spectroscopic Binary Stars."†

It is not, however, in agreement with the results obtained by SHAPLEY‡ in his "Study of the Orbits of Eclipsing Binaries." Adopting RUSSELL'S view of stellar evolution, our result would show that giant stars (except, possibly, of A-type) should be pseudo-spheroids; only B and dwarf stars could form binaries. SHAPLEY discusses 93 systems; 88 are of B or dwarf type, but only 21 have densities greater than 0.316, and only 57 have densities greater than 0.1. For one star, W Crucis, of which the orbit has been determined by RUSSELL,§ the density of the brighter component appears to be of the order of 0.000002. We are led to inquire under what physical conditions, different from those we have assumed, it can be possible for fission to occur while the density is still far below the value to which our analysis has led.

56. Consider the simplest problem of a spherical mass at rest, the equations of equilibrium being

$$\frac{\partial p}{\partial r} = \rho \frac{\partial V}{\partial r} = \frac{4\pi G \rho}{r^2} \int_0^r \rho r^2 dr,$$

where G is the gravitation constant. If  $p_0$  is the pressure at the centre and R the radius, we obtain, on integrating from the boundary to the centre,

$$p_0 = 4\pi G \int_0^R \frac{\rho}{r^2} \int_0^r \rho r^2 dr dr.$$

\* RUSSELL estimates the density of a giant A-type star at 0.1 ('Nature,' 113, p. 282).

† 'Lick Observatory Bulletin,' 1910.

‡ 'Princeton Observatory Contributions, No. 3' (1915).

§ 'Astrophysical Journal,' 36, p. 146.

If for any reason the ratio of increase of pressure to density is about that corresponding to the critical value  $\gamma = 2.2$ , the variation of density, except near the surface, will not be very great. An approximation which will be accurate as regards order of magnitude at least will be

$$p_0 = 4\pi G \bar{\rho}^2 \int_0^R \frac{1}{r^2} \int_0^r r'^2 dr' dr = \frac{2\pi}{3} G \bar{\rho}^2 R^2,$$

or, since  $\frac{4}{3}\pi \bar{\rho} R^3 = M$  (the mass of the body),

$$p_0 = \frac{1}{2} G \left(\frac{4\pi}{3}\right)^{\frac{2}{3}} M^{\frac{2}{3}} \bar{\rho}^{\frac{2}{3}} = 5 \times 10^{-8} M^{\frac{2}{3}} \bar{\rho}^{\frac{2}{3}} \dots \dots \dots (183)$$

Assuming the gas law

$$p = \frac{R}{m} T \rho B, \dots \dots \dots (184)$$

where  $R$  is the gas constant, and  $B$  a multiplying factor introduced by deviations from BOYLE'S law, we find for the temperature at the centre

$$T_0 = \frac{m}{RB} \frac{p_0}{\rho_0} = 5 \times 10^{-8} \frac{m}{RB} M^{\frac{2}{3}} \bar{\rho}^{\frac{2}{3}} (\bar{\rho}/\rho_0),$$

in which  $\rho/\rho_0$  may, in the case of equilibrium with  $\gamma$  equal to about 2.2, be put equal to about 0.6, giving

$$T_0 = 3 \times 10^{-8} \frac{m}{RB} M^{\frac{2}{3}} \bar{\rho}^{\frac{2}{3}} \dots \dots \dots (185)$$

The energy of radiation at the centre is  $\sigma T_0^4$  per unit volume, where  $\sigma$  is STEFAN'S constant of which KURLBAUM'S value is  $7.06 \times 10^{-15}$ , and the pressure of radiation, being one-third of this, is  $\frac{1}{3}\sigma T_0^4$  in all directions.

Denote the pressure of radiation by  $p_R$  and the gas pressure by  $p_G$ . If  $p_0$ , the pressure at the centre may be regarded as arising mainly from gas pressure, we have

$$\frac{p_R}{p_G} = \frac{\frac{1}{3}\sigma T_0^4}{p_0} = 4 \times 10^{-38} \left(\frac{m}{RB}\right)^4 M^2, \dots \dots \dots (186)$$

which is independent of  $\bar{\rho}$ .

For a gas of molecular or atomic weight 32 the value of  $m/R$  is about  $4 \times 10^{-7}$ , while the value of  $B$  will not differ greatly from unity until very high densities are reached. Thus equation (186) becomes approximately

$$\frac{p_R}{p_G} = 10^{-63} M^2 \dots \dots \dots (187)$$

It will only be when this ratio is small that the radiation pressure will be negligible in comparison with gas pressure at the centre of the star, and this fixes a limit to  $M$  of the order of  $10^{31}$ , independently of the density of the star.

Most stars whose mass is known\* have a mass comparable with that of our sun ( $M = 2 \times 10^{33}$ ), and for these the ratio (187) is far from negligible. Thus it appears that for stars of mass comparable with our sun, and of molecular or atomic weight about 32, the pressure of radiation will not be negligible in comparison with gas pressure;† the equations of equilibrium must be replaced by

$$\frac{\partial}{\partial r} (p_G + \frac{1}{3}\sigma T^4) = \rho \frac{\partial V}{\partial r},$$

and our calculation fails from equation (184) onwards.

57. If we had taken a molecular weight 2, instead of 32, the value of  $p_R/p_G$  would have been reduced by a factor  $(16)^{-4}$ , and we should have had approximately

$$\frac{p_R}{p_G} = 10^{-68} M^2,$$

a ratio which may be considered small when  $M$  is of the order of  $10^{33}$ . Now whether we consider that radiation pressure is comparable with gas pressure or not, the temperature at the centre of stars such as we have considered is of the order of  $10^7$  degrees Centigrade, and at such temperatures it seems probable that matter would to a large extent be broken up into its constituent electrons and nuclei. For purposes of calculation of gas pressure each electron behaves like the molecule of a gas, and the effect of electronic disintegration is to reduce the effective molecular weight. It is readily seen that when electronic disintegration is complete, a limiting effective molecular weight of 2 is reached for all substances except hydrogen.‡

Further, radiation pressure when it is appreciable may be treated as arising from molecules of molecular weight zero, and so the effective molecular weight may be still further decreased.

\* The stars whose masses are known are bright binaries—binaries because there is no means of determining mass except by the mutual action of two bodies on one another, and bright because the fainter binaries escape observation. The conclusion of this paper is that bright binaries are binaries of large mass, the mass being of order of magnitude greater than  $10^{31}$  gm. This is borne out by the observed masses of those binaries which are bright enough to have attracted attention, but there is nothing to show that there are not a great number of less bright binaries of smaller mass. It rather appears as if the few well-determined masses of binaries are not likely to give a good sample of the masses of all stars. It is perhaps significant that RUSSELL'S well-known diagram of absolute magnitudes ('Nature,' vol. 113, p. 252) shows a range of something like five magnitudes (ratio 100 to 1) for dwarf stars of similar spectral type, suggesting a range of masses enormously greater than that calculated from observations on binary stars.

† This agrees with the result stated by EDDINGTON ('M.N., Royal Ast. Soc.,' vol. 77, p. 16), but as the question is of some importance for our present investigation, I have thought it worth giving a separate discussion freed from the special assumptions of EDDINGTON'S paper. EDDINGTON'S statement that radiation pressure is practically negligible for dwarf stars does not appear to be altogether confirmed by my equation (187).

‡ Cf. EDDINGTON, 'M.N., Royal Ast. Soc.,' vol. 77, p. 596.

Thus the effective molecular weight, regarded as being determined by equation (184), may fall to very small values as we pass to the interior of a star. In § 43 we considered the tendency for greater molecular weights to occur in the interior of the star, and found that it would delay the stage at which the pseudo-spheroidal form would become unstable. It now appears that, in order to represent actual conditions, we should have examined the reverse tendency. Effectively lighter molecular weights may be expected to occur in the interior of a star, and this will cause the process of fission to begin at lower densities. In a general way we may expect that stars of greatest mass will begin the processes of fission in the earliest stages of their careers. If so, such a star as W Crucis, assuming that its two components have been formed out of the fission of a single body, must be a star of very great mass indeed.

58. To sum up, we have found that a star of small mass (say  $\frac{1}{10}$ th that of our sun), in which there is no great amount of atomic disintegration, and in which pressure of radiation does not play a prominent part dynamically, will not begin to break up into a binary star until it reaches a density of from one-quarter to one-half that of water. In more massive stars there will be considerable atomic disintegration, and pressure of radiation will be dynamically important. Such stars will break up at lower densities than smaller stars.

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[PLATE 1.]

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ON THE PROPAGATION OF SOUND  
IN THE FREE ATMOSPHERE  
AND THE ACOUSTIC EFFICIENCY OF FOG-SIGNAL MACHINERY:  
AN ACCOUNT OF EXPERIMENTS CARRIED OUT  
AT FATHER POINT, QUEBEC, SEPTEMBER, 1913.

BY

LOUIS VESSOT KING, M.A. (CANTAB.), D.Sc. (McGILL),  
ASSOCIATE PROFESSOR OF PHYSICS, MCGILL UNIVERSITY, MONTREAL.

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By LOUIS VESSOT KING, *M.A. (Cantab.), D.Sc. (McGill), Associate Professor of Physics, McGill University, Montreal.*

*Communicated by Prof. HOWARD T. BARNES, F.R.S.*

[PLATE 1.]

Received May 11,—Read June 14, 1917.

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PART I.—ON THE MATHEMATICAL THEORY OF THE PROPAGATION  
OF SOUND IN A HOMOGENEOUS ATMOSPHERE WITH SPECIAL  
REFERENCE TO WAVES OF LARGE AMPLITUDE.

§ 1. INTRODUCTION.

THE theory of the propagation of sound-waves of small amplitude such as are produced by ordinary acoustic instruments has received repeated experimental verification on almost every point. Over such distances as are available for indoor experiments, the atmosphere may be regarded as a homogeneous medium of constant temperature. The variations of pressure in such sound-waves are so small that the

medium may be considered as a perfectly elastic fluid for which the relation between pressure and volume (per unit mass) is expressed by the adiabatic law

$$pv^\gamma = \text{const.} \quad \text{or} \quad p/p_0 = (\rho/\rho_0)^\gamma \dots \dots \dots (1)$$

where  $p_0$  and  $\rho_0$  refer to the pressure and density at standard temperature and pressure. It has long ago been verified by experiment that in the extremely rapid compressions and rarefactions which constitute sound-waves, equalization of the resulting inequalities of temperature by thermal conduction cannot take place with sufficient rapidity to bring about uniformity of temperature: the compressions and rarefactions may therefore be considered to take place under conditions of no heat-transfer, that is, under *adiabatic* conditions.  $\gamma$  is a constant which for air has the value  $\gamma = 1.414$ . It was first pointed out by LAPLACE that under these conditions the Newtonian formula for the velocity of sound,  $\sqrt{(p_0/\rho_0)}$ , should be modified to

$$a = \sqrt{(\gamma p_0/\rho_0)} \dots \dots \dots (2)$$

Applying the above formula to the propagation of sound in air at standard pressure and temperature, and inserting  $p_0 = 1.013 \times 10^6$  dynes/cm.<sup>2</sup>,  $\rho_0 = 1.293 \times 10^{-3}$  gr./cm.<sup>3</sup>, we obtain for the calculated velocity of sound the value  $a = 332$  metres/sec. = 1089 feet/sec., in good agreement with observation.

§ 2. PLANE WAVES OF SMALL AMPLITUDE.

For convenience of reference we write down several formulæ relating to the quantities employed to specify the state of motion in a plane sound-wave. Following RAYLEIGH'S\* notation, we denote the velocity-potential at a time  $t$  and distance  $x$  in the direction of propagation of a harmonic train of waves by

$$\phi = A \cos 2\pi (x-at)/\lambda \dots \dots \dots (3)$$

where  $A$  is a constant depending on the amplitude and  $\lambda$  is the wave-length. If  $n$  be the frequency, we have the fundamental relation of wave-motion

$$a = n\lambda \dots \dots \dots (4)$$

If  $[dW/dt]$  represent the average rate of propagation of energy across unit area of the wave-front it is shown that

$$[dW/dt] = 2\pi^2 A^2 \rho_0 n^2 / a, \dots \dots \dots (5)$$

while the maximum pressure variation or pressure amplitude  $|\delta p|$  is given by

$$|\delta p| = 2\pi \rho_0 A n \dots \dots \dots (6)$$

\* RAYLEIGH, 'Theory of Sound,' vol. II., p. 15 (1896).

Hence expressing the rate of propagation of energy in terms of the pressure amplitude we have

$$|\delta p|^2 = 2\alpha\rho_0 [dW/dt]. \quad (7)$$

It is convenient to specify the state of affairs in the medium at any instant by the *condensation*  $s$  defined by the equations

$$s = \delta\rho/\rho_0 = (1/\gamma) \delta p/p_0. \quad (8)$$

The displacement amplitude in the medium  $|\xi|$  is given by the formulæ

$$|\xi| = A/\alpha = |\delta p|/(2\pi n\alpha\rho_0) = \alpha|s|/(2\pi n), \quad (9)$$

and the velocity displacement by

$$|\dot{\xi}| = 2\pi A/\lambda = |\delta p|/(\alpha\rho_0) = \alpha|s|. \quad (10)$$

One of the most important results arising from the fact that waves of small amplitude are propagated with a constant velocity independent of their intensity is the application of the principle of superposition of vibrations. By the use of FOURIER'S Theorem it is proved that a periodic disturbance of any wave form may be analysed into a number of simple harmonic waves whose sum gives rise to the complex disturbance considered. It is thus sufficient in the case of sound-waves of ordinary intensity to consider the propagation of a simple wave, as discussed in equations (3) to (10). The relative harmonic constituents of the complex wave preserve their relative amplitudes unaltered during propagation; in other words, the *quality* of the sound is propagated to a distance without change. This fact is well illustrated by the everyday experience that the various notes from a number of musical instruments played simultaneously can be individually recognized over long distances. These points are emphasized because, as will be seen later, they no longer remain true in the case of waves of very great amplitude such as those emitted by a powerful fog siren.

It may be mentioned in passing that sound-waves of ordinary intensity are propagated with extremely little dissipation of energy due to viscosity or heat-conduction, the calculations having been carried out by STOKES\* as long ago as 1845; here again the circumstances are different in the case of very intense waves, the experiments to be discussed in the sequel indicating that sound-waves of sufficient power to be audible at great distances can only be generated at the expense of heavy atmospheric losses, especially in the immediate neighbourhood of the generator.

### § 3. SPHERICAL WAVES OF SMALL AMPLITUDE.

An important practical case of propagation of sound is that of waves emanating from a concentrated source. As in the case of plane waves we assume for simplicity

\* STOKES, 'Cambridge Transactions,' vol. VIII., p. 287, 1845. See RAYLEIGH'S 'Sound,' vol. II. p. 315 (1898).

a simple harmonic type, small amplitude and negligible atmospheric losses. If we suppose the waves to be confined in a conical surface of solid angle  $\omega$ , the velocity potential which determines the motion at a distance  $r$  from the source is

$$\phi = (A/\omega r) \cos \kappa (at-r) \dots \dots \dots (11)$$

If  $\lambda$  is the wave-length and  $n$  the frequency we have

$$\kappa = 2\pi/\lambda \text{ and } n = \kappa a/(2\pi) \dots \dots \dots (12)$$

The rate of introduction of air at the source is  $A \cos \kappa at$ , and it is easily proved\* that the pressure amplitude is given by

$$|\delta p| = \rho_0 |\partial \phi / \partial t| = \rho_0 \kappa a A / (\omega r) \dots \dots \dots (13)$$

If the source be situated close to a rigid plane, we have  $\omega = 2\pi$ , and obtain

$$|\delta p| = \rho_0 n A / r \text{ and } a |s| = n A / (a r) \dots \dots \dots (14)$$

The total rate of emission of energy as sound is given by the relation

$$[dW/dt] = \rho_0 \kappa^2 a A^2 / (4\pi) = \pi n^2 \rho_0 A^2 / a \dots \dots \dots (15)$$

We have here assumed that the propagation takes place in a *homogeneous* medium so that the *intensity* of the sound as measured by  $|\delta p|^2$  falls off inversely as the square of the distance, and the wave-surfaces are spheres expanding outwards with the velocity of sound. In practice this condition is very far from being realized; the atmosphere, even on an apparently calm day, is the seat of innumerable discontinuities of density due to the presence of eddies and convection currents arising from unequal heating. The amplitude of sound from a fog-signal falls off with distance in a manner which varies very greatly from day to day, the manner of propagation depending on the state of wind and weather to a remarkable degree, as an inspection of the charts of the acoustic survey described in Appendix II. clearly indicates. Under these conditions one must imagine the wave-surface to be undergoing severe distortions as it is being propagated outwards, with the formation at times of so-called "silent zones" and zones of abnormal intensity. Several illustrations of these are to be seen in the charts just referred to.

§ 4. ON THE EFFICIENCY OF SOUND-PRODUCING INSTRUMENTS.

The changes of pressure and density which occur in a sound-wave near the limits of audibility are of extremely small magnitude. The question appears to have

\* RAYLEIGH, 'Phil. Mag.,' vol. 6, pp. 289-305, 1903; 'Scientific Papers,' vol. v., p. 126.





Inserting for  $|s|$  BOLTZMANN'S estimate,  $6.5 \times 10^{-8}$ , we obtain for the total flux of energy across a hemisphere of radius  $r = 18.4$  km.,

$$2\pi r^2 [dW/dt] = \frac{1}{2} \times (3.32 \times 10^4)^3 \times (6.5 \times 10^{-8})^2 \times 0.0129 \times 2\pi (1.84 \times 10^6)^2$$

$$= 222 \times 10^7 \text{ ergs/sec.} = 0.3 \text{ H.P.}$$

It will be noticed that the energy propagated as sound at this distance is a very small fraction of the power required to produce it; also that this estimate makes no assumption as to the mode of propagation. We are not justified, however, in taking this estimate of energy flux to hold for all distances as would be required by the inverse square law of propagation, and in particular for the proportion of power converted into sound at the generator itself: actual tests with the Webster phonometer over long distances show that the inverse square law is not even approximately true in consequence of atmospheric refractions, while measurements of acoustic output by a special thermodynamical method indicate that relatively large amounts of power (about 2.4 H.P.) may be converted into sound at the vertex of the siren trumpet. The attenuation of energy-flux to quantities of the order of 0.3 H.P. at 18.4 km. is attributed by the writer to "atmospheric" losses, the greater part of which probably occur in the trumpet itself and in its immediate vicinity. The cause of these losses yet remains to be investigated, and will probably be found to be intimately associated with the question of the abnormal mode of propagation of waves of great intensity, a subject which we shall discuss briefly in the following sections.

§ 5. SOUND-WAVES OF FINITE AMPLITUDE.

(i.) *Note on the Results of Previous Investigations.*

The equation for the propagation of sound-waves of small amplitude may be written in the familiar form

$$\partial^2 y / \partial t^2 = \alpha^2 \partial^2 y / \partial x^2, \quad \dots \dots \dots (17)$$

where  $y$  represents the displacement of a layer of air from the equilibrium position. The derivation of this equation assumes that it is legitimate to neglect higher powers of the condensation  $s$  than the first. The exact equations governing the mode of propagation of waves of finite amplitude were first derived by POISSON\* as long ago as 1808, and were discussed in further detail by STOKES† in 1848. In the case of adiabatic propagation, the exact equation was first derived by EARNSHAW‡ (1860) in the form

$$(\partial y / \partial x)^{\gamma+1} (\partial^2 y / \partial t^2) = \alpha^2 \partial^2 y / \partial x^2. \quad \dots \dots \dots (18)$$

\* POISSON, "Mémoire sur la Théorie du Son," 'Journ. de l'Ecole Polytechnique,' vol. VII., p. 319, *et seq.*, 1808.

† STOKES, "On a Difficulty in the Theory of Sound," 'Phil. Mag.,' Nov., 1848 'Mathematical and Physical Papers,' vol. II., p. 51.

‡ EARNSHAW, 'Roy. Soc. Proc.,' Jan. 6, 1859; 'Phil. Trans. Roy. Soc.,' 1860, p. 133.

The discussion of the mode of propagation of waves according to the above equation has been dealt with by RIEMANN\* (1860), RANKINE† (1870), HUGONIO‡ (1887, 1889). In an important memoir, RAYLEIGH§ (1910) gives a critical and historical account of the subject under discussion, and discusses in further detail special solutions of the problem of finite waves and the influence of viscosity and thermal conductivity on their mode of propagation. It is there shown that in the case of adiabatic propagation the velocity  $u$  in the medium due to the wave-motion expressed by equation (18) is rigorously given by

$$u = f[x - (\alpha + \epsilon u)t], \dots \dots \dots (19)$$

where  $\epsilon = \frac{1}{2}(\gamma + 1)$  and  $f[\dots]$  is an arbitrary function depending on the circumstances of the motion at the instant  $t = 0$ .

The above solution reduces to the case of isothermal propagation ( $\gamma = 1$ ) previously considered by POISSON,

$$u = f[x - (\alpha + u)t]. \dots \dots \dots (20)$$

The discussion of the propagation of a wave according to equation (19) in the particular harmonic form

$$u = U \sin 2\pi [x/\lambda - (1 + \epsilon u/\alpha)nt] \dots \dots \dots (21)$$

has been discussed by STOKES||; it was pointed out that a wave thus represented undergoes a gradual change of form, the condensation overtaking the rarefaction until the motion becomes physically impossible for the least value of  $t$  for which  $\partial x/\partial u = 0$ . At this stage other phenomena due to physical causes not included in the above statement of the problem come into play.¶ Applying this condition to (21) we obtain for the interval  $t$  the relation

$$2\pi\epsilon |nt| = \alpha (1/U) (1 - u^2/U^2)^{-\frac{1}{2}} = (1/U) \sec 2\pi [x/\lambda - (1 + \epsilon u/\alpha)nt],$$

from which it follows that discontinuity must occur after an interval not less than that given by

$$t_1 = \alpha/(2\pi U\epsilon n). \dots \dots \dots (22)$$

The distance  $x_1$  travelled in this interval lies between two limits assigned by the inequality

$$\alpha^2/(2\pi U\epsilon n) < x_1 < \alpha^2 (1 + \epsilon U/\alpha)/(2\pi U\epsilon n), \dots \dots \dots (23)$$

\* RIEMANN, 'Gött. Abh.,' t. VIII., p. 43 (1858-9); 'Werke,' 2nd Ed., Leipzig, 1892, p. 157.

† RANKINE, 'Phil. Trans.,' vol. 160, p. 277, 1870; 'Misc. Sc. Papers,' p. 530.

‡ HUGONIO‡, 'Journ. de l'Ecole Polytechnique,' 1887, 1889.

§ RAYLEIGH, "Aerial Plane Waves of Finite Amplitude," 'Roy. Soc. Proc.,' A, vol. 84, pp. 247-284, 1910; 'Scientific Papers,' vol. v., pp. 573-619.

|| STOKES, *loc. cit.*

¶ For a discussion of the problem under these conditions see a paper by TAYLOR, G. I., "The Conditions Necessary for Discontinuous Motion in Gases," 'Roy. Soc. Proc.,' 84, A, 1910, pp. 371-377.

or, in terms of the maximum condensation,  $|s| = U/u$

$$\alpha/(2\pi\epsilon n|s|) < x_1 < \alpha(1 + \epsilon|s|)/(2\pi\epsilon n|s|). \dots \dots \dots (24)$$

By writing  $\gamma = 1$  in the above equations we obtain the values for the corresponding case of isothermal propagation given by RAYLEIGH.\*

(ii.) *On a Contribution to the Theory of the Propagation of Aerial Plane Waves of Finite Amplitude.*

With a view to the future discussion of the theory of ideal sound-generators, we proceed to examine in greater detail the question of the propagation of aerial plane-waves of large amplitude. Following the main lines of RAYLEIGH'S exposition,† we denote by  $y$  and  $y + \partial y/\partial x \cdot dx$  the actual positions at time  $t$  of neighbouring layers of air whose initial positions are defined by  $x$  and  $x + dx$ . The equation of continuity of mass gives us the relation  $\rho_0 = \rho \partial y/\partial x$ . If the expansions and condensations are supposed to take place according to the adiabatic law,  $p/p_0 = (\rho/\rho_0)^\gamma$ , we have  $p/p_0 = (\partial y/\partial x)^{-\gamma}$ . The mass of unit area of the slice is  $\rho_0 dx$ , and the force acting on it is  $-(\partial p/\partial x) dx$ , so that the equation of motion,  $\rho_0 (\partial^2 y/\partial t^2) + (\partial p/\partial x) = 0$ , gives on eliminating  $p$  and writing  $\alpha^2 = (p_0\gamma/\rho_0)$ ,

$$(\partial y/\partial x)^{\gamma+1} (\partial^2 y/\partial t^2) = \alpha^2 \partial^2 y/\partial x^2,$$

which is EARNSHAW'S equation already quoted. EARNSHAW'S solution of the exact equation proceeds on the assumption that there is at every point a definite relation between the particle velocity ( $u = \partial y/\partial t$ ) and the density,  $\rho/\rho_0 = (\partial y/\partial x)^{-1}$  in the sound-wave, symbolized by the relation

$$u = \partial y/\partial t = F(\partial y/\partial x).$$

If we differentiate this equation with respect to  $t$  we obtain

$$\partial^2 y/\partial t^2 = [F'(\partial y/\partial x)]^2 (\partial^2 y/\partial x^2).$$

This equation may be identified with EARNSHAW'S equation by choosing the arbitrary function  $F$  to satisfy the equation

$$[F'(\partial y/\partial x)]^2 = \alpha^2 (\partial y/\partial x)^{-(\gamma+1)},$$

or, writing for brevity  $\alpha = (\partial y/\partial x) = \rho_0/\rho$ ,  $F$  is determined from

$$F'(\alpha) = \pm \alpha \alpha^{-\frac{1}{2}(\gamma+1)}.$$

\* RAYLEIGH, 'Scientific Papers,' vol. v., p. 575.

† RAYLEIGH, 'Sound,' 2nd edition, 1896, vol. II., pp. 31, *et seq.*

Taking the lower sign, corresponding to a wave propagated along the positive direction of the  $x$ -axis, we have

$$u = F(\alpha) = C + [2a/(\gamma - 1)] \alpha^{-\frac{1}{2}(\gamma - 1)}, \dots \dots \dots (25)$$

$C$  being a constant of integration which takes into account a possible progressive motion of the medium as a whole. If the velocity of the medium as a whole is  $U$  when undisturbed by sound-waves, we have  $u = U$  when  $\alpha = 1$ , which gives  $C = U - 2a/(\gamma - 1)$ , so that the relation between the particle velocity and the density in the medium is given by

$$u = U - \frac{2a}{\gamma - 1} \left[ 1 - \left( \frac{\rho}{\rho_0} \right)^{\frac{1}{2}(\gamma - 1)} \right] \dots \dots \dots (26)$$

It is not difficult to verify that if  $f$  is any arbitrary function corresponding to  $u = f(t)$  when  $x = 0$ ,

$$u = f \left[ t - \alpha^{\frac{1}{2}(\gamma + 1)} \frac{x}{a} \right] = U - \frac{2a}{\gamma - 1} [1 - \alpha^{-\frac{1}{2}(\gamma - 1)}] \dots \dots \dots (27)$$

is a solution of EARNSHAW'S equation which may be written in the form

$$\partial u / \partial t = a^2 \alpha^{-(\gamma + 1)} \partial \alpha / \partial x \dots \dots \dots (28)$$

From equation (25) we derive

$$a (\partial \alpha / \partial x) = -a^{\frac{1}{2}(\gamma + 1)} \partial u / \partial x, \dots \dots \dots (29)$$

so that (28) becomes

$$\partial u / \partial t = -a \alpha^{-\frac{1}{2}(\gamma + 1)} \partial u / \partial x \dots \dots \dots (30)$$

Differentiating (27) we have

$$\frac{\partial u}{\partial t} = \left[ 1 - \frac{1}{2}(\gamma + 1) \alpha^{\frac{1}{2}(\gamma - 1)} \left( \frac{x}{a} \right) \left( \frac{\partial \alpha}{\partial t} \right) \right] f' [\dots] \dots \dots \dots (31)$$

$$a \frac{\partial u}{\partial x} = \left[ -\alpha^{\frac{1}{2}(\gamma + 1)} - \frac{1}{2}(\gamma + 1) x \alpha^{\frac{1}{2}(\gamma - 1)} \frac{\partial \alpha}{\partial x} \right] f' [\dots]$$

$$= \left[ -\alpha^{\frac{1}{2}(\gamma + 1)} + \frac{1}{2}(\gamma + 1) \frac{x}{a} \alpha^\gamma \frac{\partial u}{\partial x} \right] f' [\dots],$$

giving

$$-a \alpha^{-\frac{1}{2}(\gamma + 1)} \frac{\partial u}{\partial x} = \left[ 1 - \frac{1}{2}(\gamma + 1) \alpha^{\frac{1}{2}(\gamma - 1)} \frac{x}{a} \frac{\partial u}{\partial x} \right] f' [\dots] \dots \dots \dots (32)$$

Since  $\partial \alpha / \partial t = \partial^2 y / \partial x \partial t = \partial u / \partial x$ , we notice that (31) and (32) are identical, from which it follows that (30) is satisfied, *i.e.*, that (27) is a complete solution of EARNSHAW'S equation. From equation (26) we may write the solution in the form

$$u = f \left[ t - \frac{x/a}{\left\{ 1 + \frac{1}{2}(\gamma - 1)(u - U)/a \right\}^{\frac{\gamma + 1}{\gamma - 1}}} \right] \dots \dots \dots (33)$$

From equations (33) or (27) we are enabled to trace out the progress of a finite wave corresponding to given velocity conditions at the origin  $x = 0$ . As has already been mentioned, the wave will give rise to a "discontinuity" after having travelled a distance which, in any given circumstances, may be determined from the complete solution which has just been given. Little is known either theoretically or experimentally regarding the state of affairs which exists in the wave in the neighbourhood of the discontinuity. It is not impossible, as suggested by STOKES, that the discontinuity may give rise to a species of reflected wave which will travel backwards towards the seat of the initial disturbance, thus complicating the state of affairs in the medium as represented by the original equations for finite waves. In applying these equations it is therefore necessary to assume that the waves, supposed to be propagated along a cylindrical tube, are completely absorbed by some mechanism before discontinuity sets in. It is interesting to note that HADAMARD\* has pointed out that, under conditions most likely to exist in practice, the discontinuity to which finite plane waves tend might give rise to the formation of vortices. It is easy to see from physical considerations that waves of large amplitude would tend to set up vortices in the neighbourhood of solid obstacles or of pre-existing eddies. Gaseous viscosity and thermal conductivity must play an important part in the sequence of events, but the inclusion of these factors in the equations of propagation complicates the problem beyond hope of solution.

(iii.) *Application of Preceding Theory to the Generation of Finite Waves by the Harmonic Motion of a Piston.*

It will be evident from the remarks already made that the conditions under which waves of large amplitude are generated and propagated have an important bearing on the theory and design of fog-signal sound generators. Owing to the limitations of the existing theory in leaving out of account thermal conduction and viscosity, it is desirable that the subject be studied from an experimental point of view. A simple apparatus capable of practical realization consists of a circular piston made to vibrate harmonically in a cylinder of sufficient length that the effect of the end open to the free atmosphere may be neglected. One of the first questions to be studied is the formation of the discontinuity.

If the motion of the piston at  $x = 0$  is given by

$$u = u_0 \sin 2\pi nt,$$

the velocity in the wave at distance  $x$  from the origin is given by

$$u = u_0 \sin 2\pi n \left[ t - \frac{x/a}{\left\{ 1 + \frac{1}{2} (\gamma - 1) u/a \right\}^{\frac{\gamma+1}{\gamma-1}}} \right] \dots \dots \dots (34)$$

\* HADAMARD, J., 'Leçons sur la Propagation des Ondes,' Paris, 1903. The same idea has also been advanced in another connection by FESSENDEN, R. A., 'Science,' Oct. 17, 1913.

The discontinuity occurs for the least value of  $t$  for which  $\partial x/\partial u = 0$ : writing  $\xi = [1 + \frac{1}{2}(\gamma - 1)u/a]$ , this condition may be written  $\partial x/\partial \xi = 0$ .

In the application of these formulæ to air, we take  $\gamma = 1.40$ , so that (34) may be written

$$x = at\xi^5 - a\xi^6/(2\pi n) \sin^{-1} [5(1 - \xi) a/u_0]. \dots \dots \dots (35)$$

The condition  $\partial x/\partial \xi = 0$  leads to the equation

$$x + \frac{5}{8}a^2\xi^7/(2\pi nu_0) \sec 2\pi n(t - \xi^{-6}x/a) = 0, \dots \dots \dots (36)$$

where  $\xi$  is given in terms of  $x$  and  $t$  by equation (35), from which it is seen that discontinuity will occur for some value of  $t$  for which  $2\pi n(t - \xi^{-6}x/a)$  lies between  $\frac{1}{2}\pi$  and  $\pi$ . In this interval it follows from equation (34) that  $u$  is positive, so that the minimum value of  $\xi$  is unity. Thus we may assert from (36) that the discontinuity will certainly not occur in the distance  $x$  given by

$$x = \frac{5}{8}a^2/(2\pi nu_0), \dots \dots \dots (37)$$

this estimate agreeing with the lesser estimate of the two given in (23) when the numerical value for  $\epsilon = \frac{1}{2}(\gamma + 1) = 1.20$  is inserted therein.

It is not without interest to calculate the rate at which the vibrating piston communicates energy to the atmosphere in the form of sound-waves. The rate at which the piston (of area  $S$ ) does work is given by

$$\dot{W} = Spu = p_0S(\rho/\rho_0)^\gamma u,$$

where  $u$  is the velocity of the piston and  $\rho$  is the density of the air over the section in contact with the piston.

From the theory of finite waves the density is given in terms of the velocity in the wave by equation (26) in which we write  $U = 0$ ,

$$\rho/\rho_0 = [1 + \frac{1}{2}(\gamma - 1)u/a]^{2/(\gamma - 1)}, \dots \dots \dots (38)$$

so that

$$\dot{W} = p_0S [1 + \frac{1}{2}(\gamma - 1)u/a]^{2\gamma/\gamma - 1} u,$$

and the average rate at which work is done is given by the expression

$$[\dot{W}] = p_0S \frac{1}{T} \int_0^T u \{1 + \frac{1}{2}(\gamma - 1)u/a\}^{2\gamma/\gamma - 1} dt. \dots \dots \dots (39)$$

Taking  $\gamma = 1.40$ , the above expression may be evaluated in finite terms for a harmonic motion of the piston,  $u = u_0 \sin(2\pi nt)$ .

Expanding  $\{1 + \frac{1}{2}(\gamma - 1)u/a\}^{2\gamma/\gamma - 1} = (1 + \frac{1}{5}u/a)^7$ , and integrating term by term, we obtain the expression

$$[\dot{W}] = \frac{7}{10}S(p_0u_0^2/a) \left[ 1 + \frac{1}{4} \left(\frac{u_0}{5a}\right)^2 + \frac{1}{8} \left(\frac{u_0}{5a}\right)^4 + \frac{5}{64} \left(\frac{u_0}{5a}\right)^6 \right] \dots \dots \dots (40)$$

Even when  $u_0$  approaches half the velocity of sound, this expression differs by only some four per cent. from the corresponding expression for waves of small amplitude as given by equations (7) and (10), to which (40) reduces when  $u_0/a$  is negligible.

§ 6. ON THE THERMODYNAMIC BASIS FOR THE MEASUREMENT OF THE ACOUSTIC OUTPUT OF A COMPRESSED AIR SIREN.

It is manifest from what has been said in the preceding sections that the theory of finite waves gives us no basis according to which the acoustic output of a siren may be calculated. We may, however, develop experimental means of estimating the rate at which energy is converted into sound. If we denote by  $\dot{M}$  the total rate of air consumption, we suppose that a certain part  $\dot{m}$  is utilized in the production of external work propagated away as sound, and that the work so done is performed adiabatically from pressure, density and absolute temperature  $p_1, \rho_1$  and  $\Theta_1$ , respectively, to atmospheric conditions represented by  $p_0, \rho_0$  and  $\Theta_0$ . The calculation of acoustic output will depend on the particular mechanism by which the utilizable air is allowed to perform external work. That representing conditions in a siren may be represented as follows:—We suppose the ports to be suddenly opened, allowing a volume  $v_1$  of air under conditions  $(p_1, \rho_1, \Theta_1)$  to pass into the resonator. We then suppose the ports to close while the volume of air  $v_1$  expands adiabatically to a volume  $v_0$  under atmospheric conditions  $(p_0, \rho_0, \Theta_0)$ , performing external work in compressing the layers of air in the resonator ahead of it, thus generating a single sound-wave. This cycle of operations is supposed to be repeated  $n$  times a second, so that in terms of the effective mass-flow

$$\dot{m} = n\rho_1v_1 = n\rho_0v_0 \dots \dots \dots (41)$$

The remainder of the air-consumption ( $\dot{M}-\dot{m}$ ) may be taken to include continuous leakage of air between the siren-cylinders, and that part of the intermittent flow through the ports which is in a violent state of eddy-motion. This eddy-motion probably dies out an appreciable fraction of a period after the ports are closed, so that the full expansion resulting from this portion of the flow is developed out of phase with the main wave and contributes nothing on the average to the energy in the wave. This portion will be referred to as “leakage.” The work done per cycle by the volume  $v_1$  of air is

$$\int_{v_1}^{v_0} p \, dv = \frac{p_1v_1}{\gamma-1} \left[ 1 - \left( \frac{v_1}{v_0} \right)^{\gamma-1} \right].$$

Since the work is performed adiabatically, the temperature of this volume of air after expansion is given by  $(v_1/v_0)^{\gamma-1} = \Theta_0/\Theta_1$ , so that the rate at which work is done in the  $n$  cycles per second may be written in either of the forms

$$\dot{w} = \frac{np_1v_1}{\gamma-1} \left[ 1 - \left( \frac{p_0}{p_1} \right)^{\frac{\gamma-1}{\gamma}} \right] = \frac{p_1}{\rho_1} \frac{\dot{m}}{\gamma-1} (\Theta_1 - \Theta_0), \dots \dots \dots (42)$$

making use of (41) and the adiabatic relation  $p_1v_1^\gamma = p_0v_0^\gamma$ .

If  $R$  be the gas-constant, we have  $p_1/\rho_1 = R\Theta_1$ . In terms of the specific heat of air at constant pressure and volume,  $C_p$  and  $C_v$ , we have  $R = J(C_p - C_v)$ , where  $J$  is the mechanical equivalent of heat. Since  $\gamma = C_p/C_v$  we have  $R = JC_v(\gamma - 1)$ , so that (42) may be written

$$\dot{w} = JC_v \dot{m} \Theta_1 [1 - (p_0/p_1)^{\frac{\gamma-1}{\gamma}}] = JC_v \dot{m} (\Theta_1 - \Theta_0). \quad (43)$$

The portion of the air-consumption  $(\dot{M} - \dot{m})$  due to leakage performs no external work (except the negligibly small amount done against intramolecular attraction represented by the Joule-Thomson effect), and thus passes through the siren without change of temperature, but mixes with the effective air to give a temperature  $\Theta$  at some distance from the siren ports, sufficiently far downstream for eddies to have died down and the flow to have become regular except for the motion of the medium due to sound-waves. In these circumstances, as there is no rate of loss of heat,  $\Theta$  is given by

$$C_v \dot{M} \Theta = C_v \dot{m} \Theta_0 + C_v (\dot{M} - \dot{m}) \Theta_1,$$

or

$$\dot{M} (\Theta_1 - \Theta) = \dot{m} (\Theta_1 - \Theta_0).$$

We thus have for the rate at which external work is propagated away as sound from the siren the expression

$$\dot{w} = JC_v \dot{M} (\Theta_1 - \Theta), \quad (44)$$

in which  $\dot{M}$  and  $(\Theta_1 - \Theta)$  are experimentally measurable quantities. As a standard of comparison we shall adopt an ideal siren having no "leakage" and operating according to the cycle described. Replacing  $\dot{m}$  by  $\dot{M}$  in the first of equations (43), the acoustic output of such a siren may be written

$$\dot{W} = JC_v \dot{M} \Theta_1 [1 - (p_0/p_1)^{\frac{\gamma-1}{\gamma}}]. \quad (45)$$

In terms of this standard we may write for the "acoustic efficiency" of the siren the expression

$$\eta = \frac{\dot{w}}{\dot{W}} = \frac{(\Theta_1 - \Theta)}{\Theta_1 [1 - (p_0/p_1)^{\frac{\gamma-1}{\gamma}}]} \quad (46)$$

The results of tests on an actual siren (a "diaphone") based on the above theory are described in Appendix III., together with the precautions to be observed in carrying out the necessary temperature measurements.

The theory of the present section enables us to estimate the acoustic output of types of fog-signal apparatus in which the compressed air is utilized to produce sound in other ways than by escape through siren ports intermittently opened and closed. For instance, by a suitable arrangement of valves as in a compressed-air rivetter, or in the "driving head" of the piston of the diaphone, it might be feasible to cause a piston to vibrate through a large amplitude in a cylinder opening out into a conical resonator, thus realizing the type of apparatus considered theoretically



in Section 5 (ii). Whether such a form of apparatus would be more efficient than the best of existing types of sirens is a question which only a quantitative test can decide.\*

§ 7. ON THE THEORETICAL CALCULATION OF THE CHARACTERISTICS OF FINITE WAVES EMITTED BY A COMPRESSED AIR SIREN.

In the following section an attempt is made to establish the theory of a compressed air siren, combining the results derived for the adiabatic flow of air through an orifice with the formulæ obtained in the preceding sections for the characteristics of aerial plane waves of finite amplitude. While such a theory must, in our present state of knowledge, be very imperfect owing to the neglect of many complex conditions met with in reality, the results thus obtained for what may be called an "ideal siren" may serve a useful purpose in giving in a general way an idea of the state of affairs which may be met with in practice.

The essential features of a siren consist of a reservoir in which air is maintained at constant pressure  $p_1$  and  $\rho_1$ , an orifice or series of orifices periodically opened and closed allowing the air to escape in intermittent puffs into the resonator, which we take for simplicity to be a long cylindrical tube of cross-section  $S$ . The pressure and density in the sound-waves a short distance from the ports of the siren we denote by  $(p, \rho)$ ; these are the pressures and densities in the finite wave generated in the cylindrical resonator, and are therefore connected with the velocity  $u$  in the wave by equation (26). We denote by  $(p_0, \rho_0)$  atmospheric pressure and density.

Applying BERNOULLI'S equation to the steady adiabatic flow of a gas through an orifice, we obtain for the velocity  $q$  at the low-pressure side of the orifice where the pressure is  $p$

$$q^2 = 2 \int_p^{p_1} \frac{dp}{\rho} \dots \dots \dots (47)$$

This result assumes that the flow is stream-line, and that at a sufficient distance from the orifice on the upstream side where the pressure is  $p_1$  the velocity is negligible. Integrating (47) for adiabatic flow when  $p/p_1 = (\rho/\rho_1)^\gamma$  we obtain for the mass-flow the expression

$$\frac{1}{2}q^2\rho^2 = p_1\rho_1 \frac{\gamma}{\gamma-1} \left[ \left(\frac{\rho}{\rho_1}\right)^2 - \left(\frac{\rho}{\rho_1}\right)^{\gamma+1} \right] \dots \dots \dots (48)$$

which is a well-known formula due to SAINT-VENANT and WANTZEL.†

If we denote by  $A(t)$  the total *effective area* of the ports and assume that formula

\* [Added February 14, 1919.—In the opinion of some practical fog-signal engineers the actual velocity of the air in the trumpet of a diaphone has an important effect in determining the loudness of the signal and its atmospheric penetration.]

† LAMB, 'Hydrodynamics,' 3rd edition, 1906, p. 23. The limitation of this formula forms the subject of a recent discussion by RAYLEIGH, 'Phil. Mag.,' vol. 32, Aug., 1916, pp. 177-187.

(48) holds at every instant of time during which  $A(t)$  varies, the rate of mass-flow through the ports of the siren is given by

$$\dot{m} = q\rho A(t). \quad \dots \dots \dots (49)$$

If, now, we assume that the *entire* flow contributes to the velocity  $u$  in the sound-wave in the cylindrical resonator of area  $S$  in the neighbourhood of the siren ports ( $x = 0$ ), the equation of continuity gives

$$\dot{m} = \rho u S, \quad \dots \dots \dots (50)$$

so that from (48) (49) and (50) we obtain for the velocity in the wave the expression

$$u = \frac{A(t)}{S} \left[ \frac{2\gamma}{(\gamma-1)} \frac{p_1}{\rho_1} \left( 1 - \frac{\xi^2}{\kappa} \right) \right]^{\frac{1}{2}}, \quad \dots \dots \dots (51)$$

where we have written  $\kappa = (\rho_1/\rho_0)^{\gamma-1}$  and  $\xi = (\rho/\rho_0)^{\frac{1}{2}(\gamma-1)}$ . Under the assumption just mentioned, writing  $U = 0$  in (26),

$$u = -\{2a/(\gamma-1)\} (1-\xi) = -\{2/(\gamma-1)\} (\gamma p_0/\rho_0)^{\frac{1}{2}} (1-\xi). \quad \dots \dots (52)$$

Identifying (51) and (52) we are enabled to solve for  $\xi$  from the quadratic

$$\xi^2 [1 + \phi(t)] - 2\xi + [1 - \kappa\phi(t)] = 0 \quad \dots \dots \dots (53)$$

where we have written

$$\phi(t) = \frac{1}{2}(\gamma-1) [A(t)/S]^2.$$

The root of (53) which makes  $\xi = 1$  for  $\kappa = 1$  is

$$\xi = (\rho/\rho_0)^{\frac{1}{2}(\gamma-1)} = \frac{1 + [1 - \{1 + \phi(t)\} \{1 - \kappa\phi(t)\}]^{\frac{1}{2}}}{1 + \phi(t)} \dots \dots \dots (54)$$

Inserting this value of  $\xi$  in equation (52) we obtain the initial velocity conditions, so that from the results of § 5 (ii.), we are enabled (theoretically) to trace the progress of the wave generated by any arrangement of siren ports for which the function  $A(t)$  may be expressed as a function of the time.

It will be evident that in the problem under consideration any attempt to estimate the rate at which energy is transmitted along the resonator can have little meaning, as such an expression will include the energy of translation of the air in the resonator as a whole, in addition to what may be called the "acoustic output." The energy transmitted as sound at a distance will depend on the type of wave-motion which results after discontinuity has set in. The present theory, which takes no account of energy dissipation, is entirely inadequate to inform us on this subject and requires to be supplemented by data from suitable experiments which will be referred to in Part II.

## PART II.—ON THE MEASUREMENT OF SOUND INTENSITY AND OF THE ACOUSTIC OUTPUT OF FOG-SIGNAL APPARATUS.

## § 8.—NOTE ON PREVIOUS FOG-SIGNAL EXPERIMENTS.

As the determination of the physical principles underlying the design of sound-generating machinery is of great importance with reference to the construction of these aids to navigation, the testing of fog-signal equipment has in the past been made the subject of several lengthy and detailed reports. The mode of propagation of sound-waves under the conditions which exist at sea has also at various times engaged the attention of a number of scientific men. Among the more important investigations we may mention TYNDALL'S experiments,\* carried out at the South Foreland in 1874 and HENRY'S Report† published in the same year. In these experiments the decrease of intensity with distance and the effect of winds, fog and other atmospheric conditions on the audibility of the signals were investigated. Intensity was estimated in terms of audibility as judged by the unaided ear. The results are now well known and are described in considerable detail in text-books and treatises on sound.‡

An extensive series of tests, carried out at a large number of stations on the North Atlantic coast of the United States, are described in detail in LIVERMORE'S Report§ published in 1894. Here an attempt was made to estimate the intensity of sound in terms of a physical scale. While the ear still remained the instrument of comparison, observations were controlled by means of standards consisting of small musical instruments whose notes imitated in pitch and quality that of the fog-signal as heard from a considerable distance. These were enclosed in small sound-proof boxes, and the intensity of the sound was varied by a sliding cover which could be adjusted to open to different sized apertures. It is stated that estimates of intensity obtained in terms of this arbitrary scale by different observers proved to be in satisfactory agreement.

In 1901 a detailed report was issued by a Committee of the Trinity House|| on experiments carried out at St. Catherine's Point, Isle of Wight, under the scientific direction of Lord RAYLEIGH and Sir THOMAS MATTHEWS. These tests were for the most part confined to an investigation of the relative merits of various forms of sound

\* TYNDALL, "On the Atmosphere as a Vehicle of Sound," 'Phil. Trans.,' vol. 164, pp. 183-244. An account of these experiments is given in TYNDALL'S 'Sound.'

† HENRY, 'Report of the Lighthouse Board of the United States for the year 1874,' Washington.

‡ RAYLEIGH, 'Sound,' 1896, vol. II., p. 129, *et seq.*; LAMB, 'Dynamical Theory of Sound,' 1910, pp. 216-222.

§ LIVERMORE, W. R., "Report upon Fog-Signal Experiments," 'Report of the U.S. Lighthouse Board,' Appendix No. V., 1894, Washington.

|| 'Report of the Trinity House Fog-Signal Committee on Experiments conducted at St. Catherine's Point, Isle of Wight,' 1901. (Published by Darling & Son, London, 1901.)

generators, the estimates of relative intensity being made by ear and indicated by numbers between 1 and 10. For long-range work the superiority of the motor-driven siren operating at about 25 pounds air-pressure was definitely established; in weather conditions associated with a smooth sea, a pitch of 182 complete vibrations per second was found to be most suitable, while a high pitch note of 295 vibrations per second was heard to better advantage during high wind and a rough, noisy sea.

The scientific aspect of the preceding tests is discussed at some length by Lord RAYLEIGH in a later paper,\* it is there pointed out that the increase of power required to operate the sirens so as to generate more powerful sound-waves is entirely out of proportion to the gain in range of audibility. This point is well illustrated by the fact that when the high note of the Scotch siren was sounded, energy was consumed at the rate of about 600 horse-power. The experiments just referred to constitute a final practical test of particular forms of sirens, in that the signals are judged under the same conditions and by the same means as when they are issued as signals to navigators. While there is no difficulty in thus estimating the relative merits of various forms of sound-generating apparatus it is evident that very little information is to be derived in this way as to the proportion of power actually converted into sound or as to the causes of the very large waste of energy which is known to occur in all sound-producing instruments.

An account of recent researches carried out in France is given very briefly by RIBIÈRE,† who mentions several unsuccessful attempts to construct instruments for the purpose of measuring sound-intensity. In the French Lighthouse Service a study of the influence of atmospheric conditions has been made statistically by keeping daily records at various fog-signal stations of the audibility of daily test-signals sent out from neighbouring stations. RIBIÈRE also points out that the sound-waves emitted by a powerful siren are probably different in character from waves of ordinary intensity, and that in the former case the differential equations for waves of small amplitude no longer apply. The question of the acoustic efficiency of fog-sirens is mentioned as one of the unsolved problems of the subject and the importance of its solution is emphasized.

In order to obtain experimental data to form a basis for a discussion of the various problems mentioned above, it was thought desirable by the writer to undertake a systematic investigation of the subject with the experimental means now available for attacking the difficulties mentioned. Owing to the elegant construction of the form of siren adopted in recent years by the Canadian Government (the "diaphone") and the ease with which the air pressure and air consumption could be controlled and varied, successful efficiency tests were carried out by the thermodynamical method

\* RAYLEIGH, "On the Production and Distribution of Sound," 'Phil. Mag.,' vol. 6, pp. 289-305, 1903. 'Scientific Papers,' vol. v., No. 126.

† RIBIÈRE, C., 'Phares et Signaux Maritimes,' Octave Doin et Fils, Paris, 1908. In this work references are given to important technical papers on the subject of fog-signals up to the year 1908.

devised by the writer. The excellent pitch regulation and relatively pure quality of note emitted by the diaphone made the use of the Webster phonometer in the measurement of sound intensity at a distance especially reliable.

### § 9. DESCRIPTION OF THE DIAPHONE.

The essential features of this modification of the siren are shown in fig. 1, where the principal dimensions of the diaphone actually tested at Father Point are also indicated. The apparatus consists essentially of a brass cylinder into which fits accurately a hollow piston. The head of this piston is of somewhat larger size and fits into a corresponding cylinder fitted with valve-ports so arranged that the admission of compressed air into this driving cylinder (referred to as "driving air") causes the piston to oscillate through a small amplitude (0.15 inch) at half the frequency of the note which it is desired to produce. Both the cylinder and piston are cast of brass and carry on the outer surface of the former and the inner surface of the latter, six light longitudinal ribs; in this way the cylinder and piston may be cut transversely by a series of narrow ports ( $\frac{1}{16}$  inch wide) at equal distances apart. As the piston vibrates the main air supply (referred to as the "sounding air") is admitted intermittently from a cast-iron chamber completely surrounding the cylinder and connected through a large relay valve to the compressed-air tanks and compressors.

The variation of pitch with pressure (referred to as "pitch regulation") was measured by means of the phonometer and was found to be relatively small; it is seen from Table III. of Appendix I. that the pitch only increases from 169 to 182 complete vibrations per second for an increase of operating pressure from 12 to 27 lbs./sq. in. above atmospheric. This characteristic, which contributes greatly to the satisfactory performance of the instrument, is probably due to the fact that the frequency is governed largely by the mass of the piston and the elastic reaction of the air in the trumpet (toned to resonance at pitch 180) and in the space behind the piston-head ("cushioning effect").

The operation of the valves so as to give the blasts at the required intervals is automatic. By means of a suitably adjusted cam mechanism connected to the main shaft of the engine driving the compressors, a small valve is first of all opened causing a second valve to admit the "driving air" to the driving cylinder, thus setting the piston into vibration; the same valve also admits air into a large relay valve, allowing the main "sounding air" to pass into the diaphone a fraction of a second later, so that the note begins to sound only when the piston has attained its normal frequency. In fact, the sharp commencement of the note and its sudden termination by a rapid fall in pitch during a small fraction of a second is characteristic of the diaphone signal and is very favourably commented on by navigators as entirely distinct from any siren note which might be sounded from a passing ship and of great value in determining the direction of the sound. During the tests carried out

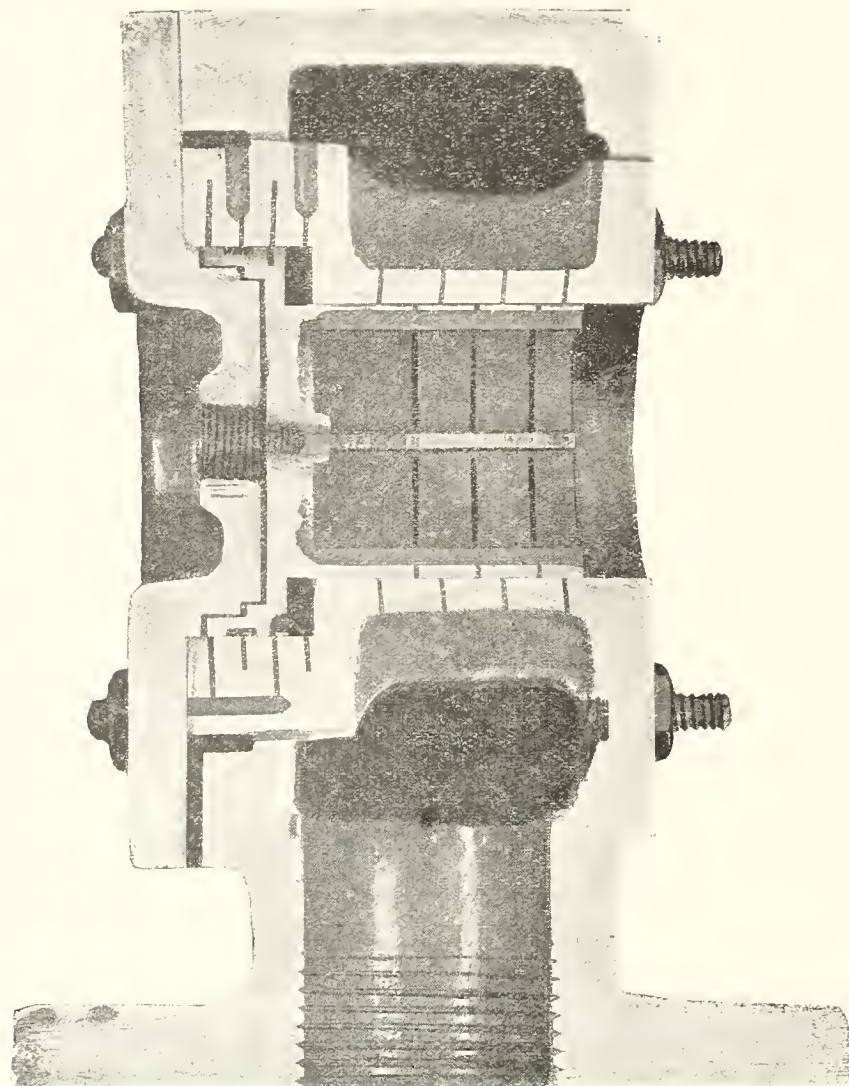


Fig. 1. Small model of the diaphone sectioned to show details of construction.

The principal dimensions of the diaphone tested at Father Point are as follows:—

*Piston.*—Outer diameter  $4\frac{1}{4}$  inches; diameter of driving head 6 inches. Weight  $3\frac{1}{4}$  lbs. The piston contained 10 ports  $\frac{1}{16}$  inch wide at intervals of  $\frac{5}{16}$  inch. Amplitude of piston vibration at 25 lbs. pressure, about 0.15 inch; frequency, 90 complete oscillations per second; ports twice opened during a complete vibration, giving rise to sound-wave of pitch 180.

*Trumpet.*—Conical semi-vertical angle  $6^{\circ}5$ ; diameter of large opening  $16\frac{1}{2}$  inches; diameter at piston  $4\frac{1}{4}$  inches. Slant length to edge of piston 4 feet 10 inches. Over all length  $0.66 \times$  wave-length. Resonance frequency of trumpet 180 complete vibrations per second

*Note.*—In the Father Point diaphone (1903 model) the exhaust from the driving cylinder discharges into the trumpet. In later designs, as that shown in fig. 1, the exhaust (which is out of phase with the main sounding air) is discharged into the atmosphere outside of the trumpet, thereby improving to some extent the acoustic output. The writer is indebted to Mr. J. P. NORTHEY, of Toronto, for the above information and for the loan of the sectioned model from which the photograph reproduced above was made. For further details of the apparatus see NORTHEY, J. P., United States Patents, No. 736,428, August 18, 1903; No. 879,190, February 18, 1908; No. 973,960, October 25, 1910; No. 1,016,187, January 30, 1912.

by the writer this characteristic termination was sometimes heard when the sustained note was completely inaudible.

The air consumption is regulated by a set screw on the main valve; by adjusting this screw so as to allow the valve more or less clearance, the air consumption is regulated until the amount consumed per blast is equal to the pumping capacity of the compressors between blasts. The pressure then attains a stationary state and the signals are issued automatically at the proper intervals without further attention on the part of the station operator.

In fig. 3 is drawn to scale the diaphone tested by the writer at Father Point, showing schematically the arrangement of the differential thermometers employed in the acoustic output determinations. The short conical trumpet (semi-vertical angle  $6^{\circ}5$ , over all length =  $0.66 \times$  wave-length) has been found to be the most efficient as a result of numerous tests carried out by the makers and the Canadian Government engineers.\* This conclusion agrees with the practice of the French Lighthouse Service.† From the evidence discussed in the present paper as to the propagation of fog-signal sound-waves as waves of finite amplitude, it would appear that the function of the trumpet as a resonator is limited by serious propagation losses occurring before spherical divergence reduces the amplitude to such small values that these losses become negligible. It is hoped to study this aspect of the subject experimentally by the method of the oscillating valve mentioned in the next section; data thus obtained may be useful in deciding the most efficient form of trumpet for different purposes.‡

#### § 10. NOTE ON THE PRACTICAL MEASUREMENT OF THE CHARACTERISTICS OF SOUND-WAVES.

Although several laboratory methods have been successfully employed in the measurement of sound intensity, none of these seem to have been suitable for service under the exacting conditions arising in carrying out tests on fog-signal generators. It is sufficient to mention two of these methods, both of which enable the compression in a sound-wave to be measured in absolute units, and at the same time do not depend on the theory of propagation of sound-waves of small amplitude. Both of these methods would seem capable of employment under special conditions in the

\* The original diaphone was invented by Dr. OWEN HOPE-JONES, U.S. Patent, No. 702,557, June 17, 1903. Its utilisation for fog-alarm purposes was first suggested by Lieut.-Col. ANDERSON, Chief Engineer of the Department of Marine and Fisheries of Canada, who, with his chief assistant, Mr. B. H. FRASER, determined from numerous tests the lines along which the diaphone evolved into full-sized fog-signal apparatus in the hands of Mr. J. P. NORTHEY, of Toronto. The present diaphones are the results of several improvements and modifications due to Mr. NORTHEY which have been made the subject of a number of patents dating from 1903. (See under description of fig. 1.)

† 'Trinity House Report,' p. 32 (see footnote, p. 227, above).

‡ [*Added February 14, 1919.*—For conclusions on this point resulting from more recent work, see footnote, p. 247.]

measurement of the wave-form of the sound-waves emitted by fog-signal generators and in studying the effect of the trumpet on the propagation losses.

TÖPLER and BOLTZMANN's\* method, based on the theory of the interferometer, measures the change of optical path of a beam suitably divided by a half-silvered mirror in such a way that one of the beams travels through air subjected to compression and rarefaction, while the other passes through undisturbed air. The two beams are brought together by a second optical mirror under conditions which give rise to interference fringes. The compressions and rarefactions in the sound-wave give rise to synchronous shiftings of the fringes which may either be photographed on a rapidly moving band of sensitive paper† or examined in detail by a stroboscopic method. The change of density in the air at any point in the wave may be easily calculated in absolute units and hence the corresponding compression.

More suitable for practical purposes is a method first employed by RAPS,‡ which may be referred to as the "oscillating or synchronous valve method." In this case a valve connected to a sensitive manometer is operated by mechanical means so as to open and close synchronously with the period of the source of sound; if the time during which the valve remains open is sufficiently small compared to the period of the sound-wave, the pressure registered will give the compression in the sound-wave at some particular phase. By advancing the phase gradually it becomes possible to trace out the complete wave-form. By this means RAPS was able to measure compressions as high as 0.035 atmosphere. It would seem that this method is well adapted to the study of the powerful sound-waves generated by modern fog-signal machinery.

#### § 11. NOTE ON THE WEBSTER PHONOMETER.

As a result of extensive researches carried out by Prof. A. G. WEBSTER, of Clark University, a portable instrument capable of measuring the characteristics of sound-waves over a wide range of pressure amplitudes and under most severe weather conditions is now available for investigating the distribution of sound in the neighbourhood of fog-signal generators. The construction of the particular instrument employed by the writer§ will readily be understood from fig. 2. It consists of a

\* TÖPLER and BOLTZMANN, 'Ann. d. Phys. u. Chem.,' 141, pp. 321-352, 1870. In an account of experimental work carried out in France on the measurement of sound in relation to fog-signals, RIBIÈRE mentions (footnote, p. 228) that interference methods were attempted, but without success, under practical conditions. Preliminary experiments along these lines with the Jamin refractometer led the writer to the same conclusion.

† RAPS, "Ueber Luftschwingungen," 'Ann. d. Phys. u. Chem.,' 50, pp. 193-220, 1893.

‡ RAPS, "Zur objectiven Darstellung der Schallintensität," 'Ann. Phys. u. Chem.,' 36, pp. 273-306, 1888.

§ An early form of this instrument is described by WEBSTER as early as 1904 (see footnote, p. 216). Since the date of construction of the phonometer described above (1913), the instrument has been considerably improved by its inventor.



telescoping cylindrical Helmholtz resonator capable of adjustment to any required pitch by suitably adjusting its volume. Over a circular aperture at the back of this resonator is clamped a mica disc, at the centre of which is firmly fastened a brass pin carefully ground to a fine point. At right angles to this pin, held in a fork carried by the frame of the resonator and capable of fine screw adjustments in two directions at right angles, is mounted a thin steel strip which may be so adjusted that the point of the pin above referred to rests in contact with the strip at any required distance from the neutral axis. A slight displacement of the disc thus causes the strip to rotate through a small angle. This rotation is magnified into an easily

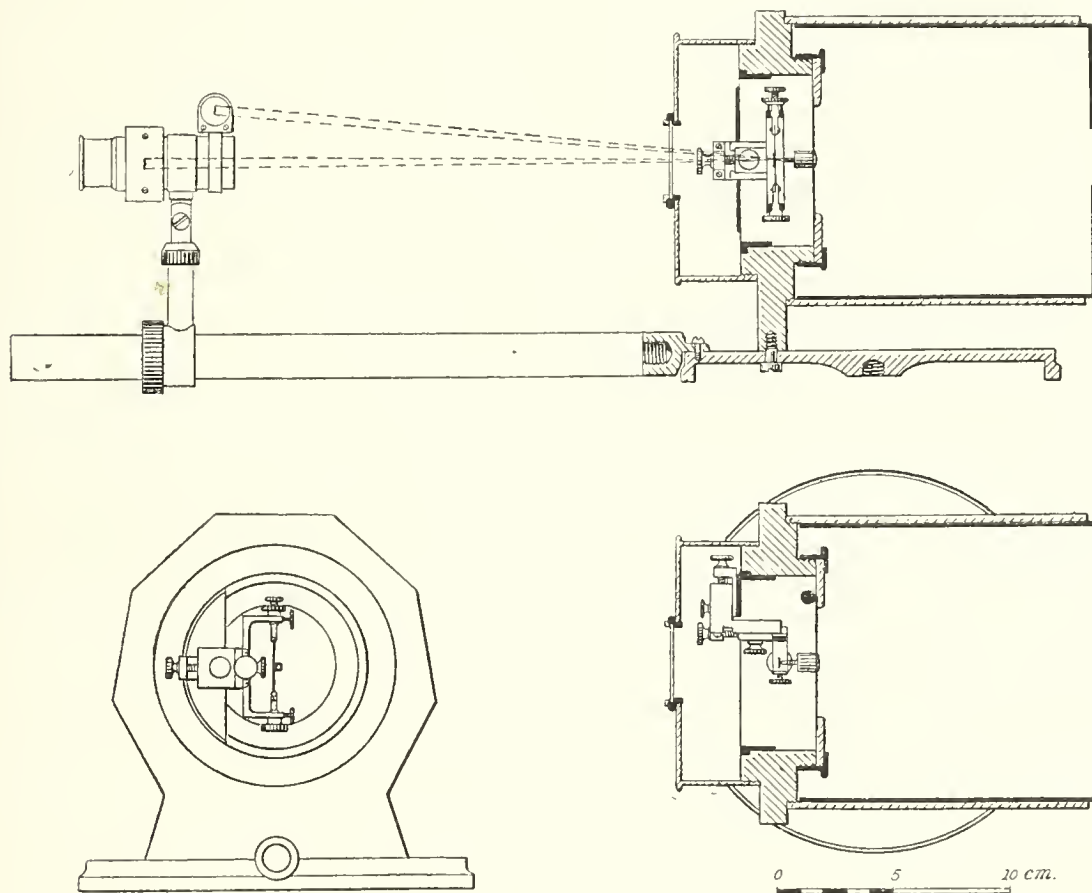


Fig. 2. The Webster phonometer.  
 Designed by Prof. WEBSTER for the Father Point tests.

measurable deflection by viewing the light from the filament of a small tungsten lamp, reflected from a small concave mirror attached to the steel strip, into a micrometer eye-piece fitted with a suitable graduated transparent scale. When the diaphragm is at rest, the image of the filament is seen sharply defined against the micrometer scale; when a sound-wave of the proper pitch passes over the instrument forced oscillations are set up in the air contained in the resonator. The diaphragm (whose free period is much higher than that of the sound-wave to be measured) is thus set into vibration and the image of the filament is drawn out into a luminous band whose breadth may easily be measured to an accuracy of about 1 per cent.

For any given adjustment of the phonometer the breadth of this band is proportional to the amplitude of vibration of the centre of the diaphragm, therefore to the compression of the air in the resonator, and finally to the compression in the sound-wave in the atmosphere outside.

The conversion of the measured width of this luminous band (referred to as the "phonometer reading") into the pressure amplitude of the sound-wave expressed in absolute units requires the determination of the "constant" of the instrument. This is accomplished in several ways by Prof. WEBSTER. The most convenient method of determining the "constant" is by taking simultaneous measurements of the amplitude of the waves from a constant source of sound by means of the instrument to be calibrated and by a "standard phonometer." In the latter instrument the amplitude of vibration of the diaphragm is measured directly by an interference method combined with a stroboscopic arrangement for observing the fringes. From the mathematical theory of the motion of the diaphragm vibrating under the influence of aerial vibrations in the resonator, it is possible to express the compression in the sound-wave outside the instrument in terms of the phonometer reading, making use of separately determined inertia, elastic and damping constants of the vibrating system.

Through the courtesy of Prof. WEBSTER, a phonometer specially designed for the Father Point tests was constructed under his immediate supervision, and was successfully employed under the severe practical conditions met with. An account of experiments carried out with the Webster phonometer in connection with the measurement of sound from the diaphone is given in Appendix I., where further details relating to its manipulation and characteristics are given.

## § 12. ON THE INFLUENCE OF METEOROLOGICAL CONDITIONS ON THE PROPAGATION OF SOUND.

### (i.) *Introduction.*

The capricious behaviour of sound-waves propagated in the open atmosphere has been attributed to the existence of innumerable discontinuities of temperature, density and humidity, and to refraction by gradients of wind-velocity.\*

It has long been known that the retarding effect of the earth's surface on the velocity of the wind is to give rise to a velocity gradient. It was first pointed out by STOKES† in 1851, that as a result, a sound-wave travelling against the wind will have its wave-front continually tilted upwards, so that the sound tends to pass over the

\* An excellent summary, with an extensive bibliography of the work of previous observers, is given by BATEMAN, "The Influence of Meteorological Conditions on the Propagation of Sound," 'Monthly Weather Review,' 42, May, 1914, pp. 258-265.

† STOKES, 'Brit. Assoc. Rep.,' 1857, p. 22; or 'Mathematical and Physical Papers,' vol. IV., p. 110. See also RAYLEIGH's 'Sound,' 1896, vol. II., p. 132.

head of an observer at a distance. On the contrary, when travelling with the wind, the wave-front is continually tilted downwards, thus explaining the familiar fact that sound may be more easily heard, and at a greater distance, when the observer is to leeward of the source. This explanation was given independently by REYNOLDS\* and confirmed by a number of observations. These conclusions have been supported, on the whole, by the results of the various fog-signal tests already referred to. During the last few years, through the development of aviation, a great deal of attention has been directed to the investigation of the structure of the atmosphere. It has been known for a long time that the wind near the earth's surface is the seat of innumerable eddies.† Quite recently the subject of eddy motion in the atmosphere has been definitely formulated in mathematical terms by TAYLOR.‡ Observations by DINES§ and others on the gustiness of the wind are interpreted by TAYLOR as indicating that the eddy-motion has a tolerably regular structure, and that in a wind of given velocity and vertical gradient, a fairly definite diameter may be assigned to the eddies. In atmospheric movements these eddies, which have a certain degree of permanence, play the part of molecules in the kinetic theory of gases. Thus the conception of "eddy-viscosity" and "eddy-conductivity" as regards the transfer of momentum and heat in the atmosphere is employed with success in the interpretation of many meteorological phenomena.

The conception of eddy-motion has recently been employed by TAYLOR|| to account for the attenuation of sound in a windy atmosphere. It is shown that eddies scatter a certain portion of the energy of the sound-waves in all directions at the expense of that in the wave-train advancing in any particular direction. The mechanism of attenuation of sound by eddies is thus somewhat analogous to that of the extinction of light in the atmosphere by the scattering effect of dust or fog particles. In the opinion of the writer many of the results observed in connection with fog-signal tests may be interpreted in terms of the eddy-motion theory. For instance, the remarkably loud and well-sustained echoes often observed after a loud blast has been sounded are probably nothing more than the scattered and re-scattered sound-waves reaching the observer from all directions. It thus appears that in the eddy-structure of the atmosphere we must look for the interpretation of TYNDALL'S state of "acoustic flocculence," while the eddies themselves are the realization of his "acoustic clouds." Further evidence in favour of the "eddy-motion" theory is

\* REYNOLDS, 'Royal Soc. Proc.,' 22, 1874, p. 531; or 'Scientific Papers,' vol. i., p. 89.

† MALLOCK, A., "Note on Wind Velocity and Gusts," 'Technical Report of the Advisory Committee for Aeronautics,' 1912-13, Report No. 93, p. 329.

‡ TAYLOR, G. I., "Eddy Motion in the Atmosphere," 'Phil. Trans.,' 215 A., pp. 1-26.

§ DINES, J. S., 'Technical Report of the Advisory Committee for Aeronautics,' 1911-12, pp. 213-230; 1912-13, pp. 310, *et seq.*

|| The writer is indebted to Mr. TAYLOR for communicating these results by letter and for permission to mention them here prior to the publication of his paper on the subject.

discussed in detail in connection with the Father Point observations described in Appendix II.

(ii.) *Discussion of the Father Point Acoustic Surveys.*

By the use of the Webster phonometer it was found possible to measure from day to day the amplitude of the sound-waves in the neighbourhood of the Father Point fog-signal station, thus obtaining a permanent record of variations in conditions of propagation depending on meteorological conditions as far as the latter could be observed. In many respects this station was extremely well suited to the work in hand. The surrounding country for several miles is very flat and low-lying, thus reducing to a minimum the effect of local topography on the propagation of sound at sea. The existence of a permanent meteorological station at this point, together with good wharfage facilities, proved to be very convenient in carrying out the acoustic surveys.

An inspection of the charts reproduced in Appendix II. indicates at once that wind is by far the most important factor in interfering with the propagation of sound. This is especially marked when the wind velocity exceeds 25 miles an hour. On August 25, 1913, on a course bearing N. from the fog-signal station the sound was lost completely at 8500 feet, the wind blowing from the west with a speed of about 25 miles an hour. On calmer days, with the wind in the same quarter, the signals will easily carry three or four times this distance.

The more important features relating to the influence of wind and eddy-motion on the propagation of sound are pointed out in Appendix II. The curious undulatory character of many of the amplitude gradients (in particular that shown in Chart No. 4, August 30, 1913) may be adduced as evidence of a tolerably regular eddy-structure of the atmosphere. The effect of the wind on the propagation of sound according to the evidence detailed in Appendix II. may be summed up as follows:—

(1) A breeze blowing in the direction of the shore line gave rise to the most unfavourable conditions of sound propagation (Charts 8, 9 and 10); somewhat less unfavourable is an off-shore breeze (Chart 7). These conditions may be so unfavourable as to counteract the propitious effect of a breeze blowing in the direction of sound propagation. During the daytime a shore-line breeze is the seat of noticeable temperature fluctuations which probably assist a very irregular eddy-structure in destroying the sound. An off-shore breeze may owe its destructive character in part to an eddy-formation accentuated by the irregular character of the land (trees, buildings, &c.), and, to a greater extent, in the writer's opinion, to the turbulent character of the atmosphere on the leeward side of the fog-alarm building in the immediate vicinity of the diaphone trumpet.

(2) A breeze blowing shorewards gives rise to comparatively favourable conditions of sound propagation (Charts 5 and 11). This is apparently due to the regular eddy-structure and temperature homogeneity of a wind which has blown over

a large expanse of water.\* When, in addition, the direction of the wind is in the direction of sound propagation, we have the most favourable conditions of audibility. Unfortunately, such conditions are, as a rule, not available to ships at sea. Herein lies the probable explanation of the statements made by inhabitants of the country surrounding a fog-signal station, that the range of audibility is, on the average, considerably greater over the land than it is over the sea, in spite of the directive effect of the diaphone trumpet and of the obstructing effect of the fog-alarm buildings on the landward side.

(iii.) *Note on Atmospheric Losses.*

In order to obtain a rough estimate of energy losses in the atmosphere, phonometer observations were taken over a series of circular courses having the fog-signal station as centre. The results are shown graphically in Charts 6, 9, 12, 13, and 14, and are analysed in detail in Appendix II., Table I. The flux of energy in the sound-waves across portions of spheres of different radii subtending the same solid angle at the diaphone is calculated in C.G.S. units. From a knowledge of the acoustic output as determined in Appendix III., we may estimate the energy flux which should be contained in the same solid angle under ideal conditions of propagation. The results seem to indicate that a large proportion of the atmospheric losses occur at no very great distance from the diaphone trumpet. Once the sound has penetrated beyond a radius of about 3000 feet, it will continue to travel on a fairly calm day (wind not greater than 3 miles per hour) with comparatively little loss. In some cases the observations show that at greater distances the sound may be actually reinforced by contributions arising from reflections or refractions from the upper regions of the atmosphere, and to some extent, possibly, by the sound scattered by atmospheric eddies reaching the observer from all directions.

In future studies of losses occurring in the immediate neighbourhood of a fog-signal station, the influence of the buildings in setting up eddy-motion near the siren trumpet with the wind in certain quarters should be kept in mind. A typical case of the atmospheric disturbance to leeward of a building is described by DINES† in a paper on "cliff eddies."

(iv.) *Note on the Effect of Fog.*

According to the verdict of the 1873 South Foreland tests, it would appear that the passage of sound through the atmosphere is not impeded by fog, or by falling snow, hail, or rain. No fog occurred during the Trinity House experiments conducted at St. Catherine's Point in 1901. It is easily understood that the passage of sound may be favoured by the comparatively calm and homogeneous condition of the

\* The Gulf of St. Lawrence is about 25 miles wide in the neighbourhood of Father Point.

† DINES, J. S., "Fourth Report on Wind Structures," 'Technical Report of the Advisory Committee for Aeronautics,' 1912-13, p. 325.

atmosphere usually met with in foggy weather. When the fog lies over the sea in the form of low-lying, distinctly separated banks, as is often the case in the Gulf of St. Lawrence, conditions are very different. In these circumstances it has been pointed out by CATFORD\* as a result of five years' observations that "when both fog-signal and observer are immersed in the *same* bank of fog, little interference may be expected: if the fog-signal is in fog, and the observer in clear atmosphere, or *vice versa*, great interference may be expected, still more so if the signal is in one fog-bank with the observer in another bank; a bank of fog will often reflect sound very strongly and definitely."

The influence of fog particles on the passage of sound has been studied theoretically by SEWELL,† who found that a fog containing  $10^6$  particles per cubic centimetre having diameters as small as 0.002 mm. would not interfere appreciably with the propagation of waves of small amplitude over the ordinary range of frequencies.

Although preparations were made to navigate during a fog, no opportunity occurred of carrying out an acoustic survey under these conditions during the entire series of Father Point tests. It has been repeatedly asserted to the writer by lighthouse-keepers and others that the sound of a diaphone as heard at a moderate distance (within 1000 feet) seems to be very appreciably stifled. On the only occasion that fog occurred this conclusion was confirmed by the writer as judged by ear. Before the phonometer could be set up to test the point objectively, the fog lifted, and no occasion of carrying out further investigations presented itself subsequently. It is not impossible, in the case of very intense waves in the immediate vicinity of the diaphone trumpet, that a heavy fog may give rise to a marked extinction through its effect on the viscosity, thermal conductivity, and specific heat of the atmosphere. From what has already been said on the subject of the propagation of waves of finite amplitude, it is easily seen how a change in the physical properties of air occasioned by the presence of fog‡ may be the cause of increased energy losses associated with the propagation of waves of large amplitude. The existence of such losses may not be inconsistent with better audibility at a great distance, resulting from propagation under conditions of improved atmospheric homogeneity generally prevailing in foggy weather.

(v.) *Note on the Determination of the Direction of Sound.*

It is important that the navigator be able to ascertain as accurately as possible the bearing of a fog-alarm from the signals which he hears. From what has already

\* CATFORD, E. O. (Engineer-in-charge of the Platte Fougère Fog-signal Station, Guernsey), "Fog Signals," 'Engineer,' 119, Feb. 5, 1915, pp. 129-130.

† SEWELL, C. J. T., "The Extinction of Sound in a Viscous Atmosphere," &c., 'Phil. Trans.,' 210, A, 1910, pp. 239-270.

‡ A study of the physical characteristics of fog has recently been commenced by WELLS, P. V., and THOMAS, A. L., 'Bulletin No. 5 of the International Ice Observation and Ice Patrol Service,' U.S. Treasury Department, Washington, 1916.

been said regarding the existence of echoes from fog-banks and from atmospheric eddies, it will be realized that this is often a matter of some difficulty. The writer has often observed that after a second or two from the moment that a signal is first heard the sound appears to reach the observer from every direction, in many cases before his attention can be fixed to determine its bearing. A peculiar characteristic of the diaphone signal which differentiates it from that of a ship siren is a short and powerful terminal note of diminishing pitch caused by the slowing down of the piston for a few oscillations at the end of a blast. This terminal note (or "grunt," as it is called at sea), being of longer wave-length, not only travels with less attenuation, but is easily distinguished from the reflections or echoes of the first part of the signal. Owing to its short duration it does not overlap its own echoes. Navigators make use of the first part of the signal as a "stand-by," and depend on the terminal "grunt" for fixing direction. If a signal consists of two or more blasts, the bearing of the fog-alarm may be determined in this way with considerable accuracy. The peculiarity of the diaphone note just mentioned was an unexpected development and is emphasized in modern installations.

### § 13. ON THE THERMODYNAMIC MEASUREMENT OF ACOUSTIC OUTPUT.

#### (i.) *Experimental Arrangements.*

In view of the fact that the sound-waves in the immediate neighbourhood of a fog-signal generator are probably propagated as waves of finite amplitude with heavy transmission losses, it was necessary to develop a method of measuring the actual proportion of power converted into sound which would be independent of the theory of the propagation of waves of small amplitude and of propagation according to the law of inverse squares.

The principle of the method which was designed to accomplish this purpose may be briefly stated as follows. Imagine two thermometers inserted, one in the high-pressure side, the other in the side open to the atmosphere, of a siren or other sound-producing instrument operated by compressed air. If the air be allowed to escape without producing sound, there will be no fall of temperature as no external work is done by the escaping air (except for the negligibly small Joule-Thomson effect; the thermometers are supposed to be situated in regions of steady flow, free from eddy-currents). If, now, the siren is allowed to sound, the rate of escape of air being regulated to the same value as before, the low-pressure thermometer will register a fall of temperature, and the difference of the two thermometer readings will give a measure of the external work propagated to a distance as sound according to the theory developed in § 6.

A reference to fig. 3 will indicate the general arrangement of the apparatus. Two resistance thermometers were constructed of fine silk-covered iron wire, wound inside a brass framework and held in position by loops of silk thread; the construction

is illustrated in Plate 1 (iv.) and is described in further detail in Appendix III. The open network formed by the iron wire gave a thermometer of minimum heat-capacity and very small lag. One of these was designed to fit into the large operating-valve of the diaphone, while the other was inserted in the resonator a few inches from the diaphone-piston. The resistance thermometers were connected to form the adjacent arms of a Wheatstone bridge and were thus operated differentially. In measuring a difference of temperature during a blast a rough setting was made on the bridge wire in the neighbourhood of the balance point, and the final reading was obtained in terms of the galvanometer-deflection previously calibrated in bridge-wire units. As the capacity of the air-compressing machinery only allowed of a six-second blast per minute, it was essential that the wire of the thermometer take up its final

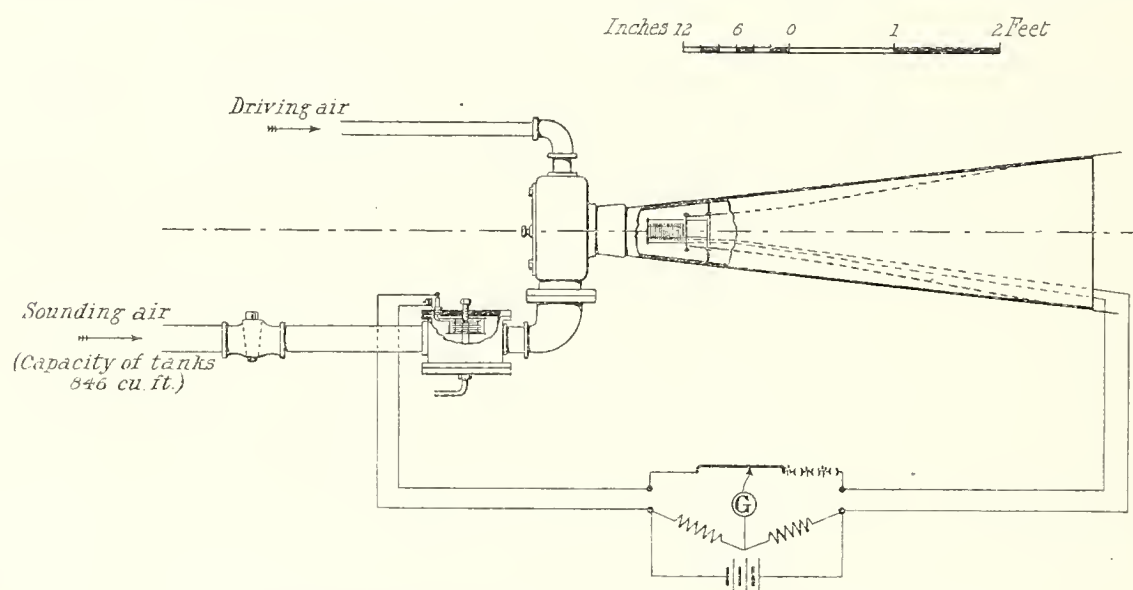


Fig. 3. Determination of acoustic output of Father Point diaphone.

Diagram showing the position of iron-wire resistance thermometers for measuring temperature difference of air on high and low pressure side of diaphone piston.

temperature in this interval; this was verified by noting that the galvanometer deflection attained to a steady value during the last three seconds of blast. The difference of temperature  $\theta$  ( $\theta = (\text{valve-temperature}) - (\text{resonator-temperature})$ ) was measured for a certain pressure and air consumption while the diaphone was emitting a note; the piston of the diaphone was then stopped and so adjusted that for the same pressures the air consumption remained the same as before, while the temperature difference  $\theta'$  was measured under the new conditions. It is a well-known thermodynamical principle, experimentally tested in the celebrated Joule-Thomson porous-plug experiment,\* that when air under pressure is allowed to escape and no external work is done, there is no difference of temperature except for the small Joule-Thomson effect arising from the work done in separating molecules under

\* JOULE AND THOMSON, "On the Thermal Effects of Fluids in Motion"; KELVIN, 'Collected Works,' vol. I., p. 333.



conditions of feeble intramolecular attractions. The experimental conditions for realizing this result is that the two thermometers be placed in regions of flow sufficiently distant from the jet that all eddy-motion has disappeared and the equivalent kinetic energy of mean-motion has been degraded by the action viscosity into mean thermal molecular agitation, *i.e.* into heat returned to the gas.

(ii.) *Sources of Error in the Measurement of Temperatures.*

In the case of the diaphone the energy propagated away as sound must be included as external work done by the air under compression, and there will result a corresponding drop in temperature between the pair of differential thermometers. In the actual experiment it was not possible to place the thermometers in regions free from eddy-motion. Moreover, the velocity with which the air stream impinges on the wires of the thermometer (velocity about 42 metres/sec.) is sufficient to cause a slight rise of temperature, although this source of error is eliminated to a considerable extent by the differential arrangement. The rises of temperature due to this cause are included in the differential temperature measurements  $\theta$  and  $\theta'$ , and are denoted, when the siren is sounding and silent, by  $\delta\theta$  and  $\delta\theta'$  respectively. By adopting the method of taking temperature readings with the siren sounding and silent, the source of uncertainty due to the effect of "kinetic heating" is reduced to a minimum.

Let  $w + \dot{f}$  represent the rate at which the energy of the compressed air is converted into mechanical effect in the diaphone when sounding. We then have, by a slight extension of (44),

$$w + \dot{f} = JC_v \dot{M} (\theta - \Delta\theta). \dots \dots \dots (55)$$

In this equation  $w$  is the rate at which energy is propagated away as sound in ergs/sec. and  $\dot{f}$  includes rate at which energy is converted into vis-viva of eddy-motion in the region where the temperature difference  $\theta$  is observed, plus the rate at which energy is dissipated by thermal conduction into the diaphone piston. The temperature difference due to the Joule-Thomson effect is denoted by  $\Delta\theta$ ;  $C_v$  is the specific heat of air per unit mass at constant volume and  $\dot{M}$  is the total rate of air consumption in grammes/sec. If we denote by accented letters the corresponding quantities referring to a measurement of temperature-differences carried out in the same way with the diaphone silent and adjusted so that the air consumption  $\dot{M}$  remained the same at the same pressures, we have  $w' = 0$ , since there is no external work done as sound. Thus

$$\dot{f}' = JC_v \dot{M} (\theta' - \Delta\theta'). \dots \dots \dots (56)$$

From (55) and (56) we obtain

$$w = JC_v \dot{M} [(\theta - \theta') - (\Delta\theta - \Delta\theta')] - (\dot{f} - \dot{f}'). \dots \dots \dots (57)$$

The extent to which the right-hand side of (57) may be taken to represent the energy propagated away as sound depends on how far we may identify the term  $\dot{f}'$

for steady flow with  $\dot{f}$  in the case of intermittent flow. If it is ascertained that the eddy-motion has entirely disappeared over the regions where the temperatures are measured,  $\dot{f}$  and  $\dot{f}'$  are steadily converted into heat given up to the gas and are then included in the terms of (57) depending on  $\theta$  and  $\theta'$ ; the same remark applies to the parts of  $\dot{f}$  and  $\dot{f}'$  representing thermal energy given up to the diaphone piston. The practical realization of this condition would be to place the resonator-thermometer sufficiently far from the piston that the escaping air is free from eddies. The objection to this procedure lies in the fact that losses of heat into the material of the trumpet are liable to be involved, and also that owing to possible propagation losses the acoustic output is no longer measured at the source of the sound-waves, but becomes a function of the dimensions, shape, &c., of the resonator. It is evident that unless  $\dot{f}'$  can be identified with  $\dot{f}$ , the value of  $w$  calculated from (57) will be an over-estimate (the case  $\dot{f}' < \dot{f}$  is hardly probable).

The temperature differences calculated from the readings of the resistance thermometers, denoted by  $\theta_1$  and  $\theta'_1$ , differ from the true temperature differences  $\theta$  and  $\theta'$  by amounts  $\delta\theta$  and  $\delta\theta'$  respectively, arising from the effect of kinetic heating already mentioned. Although this effect is diminished owing to the fact that differential readings of temperature are taken, the resonator thermometer registered an excess of temperature over the valve thermometer owing to the fact that the former was more exposed to air velocity than the latter. Writing  $\theta_1 = \theta - \delta\theta$  and  $\theta'_1 = \theta' - \delta\theta'$ , equation (57) becomes

$$w = JC_v \dot{M} (\theta_1 - \theta'_1) + JC_v \dot{M} [(\delta\theta - \delta\theta') - (\Delta\theta - \Delta\theta')] - (\dot{f} - \dot{f}'). \dots (58)$$

It is not unreasonable to assume that the Joule-Thomson effect is very approximately the same for steady as for intermittent flow, so that the term  $(\Delta\theta - \Delta\theta')$  in (58) may be neglected.

More serious is the kinetic effect due to the air impinging on the wires of the resistance thermometers. The term  $(\delta\theta - \delta\theta')$  can only be neglected if this effect is approximately the same for steady as for intermittent flow. The effect of the silk insulation on the wires is in favour of reducing this effect by confining periodic temperature changes to the surface in a manner analogous to the well-known skin effect in the electrical conduction of alternating currents. A rough estimate of this source of error may be made as follows:—

According to the experiments of JOULE and THOMSON\* it was found that the rise of temperature due to kinetic heating in a steady air current of velocity  $U$  was proportional to the square of the velocity. In the case of the insulated thermometer wires, we may write for the rise of temperature at the surface of the insulation the expression

$$\theta_s = \kappa U^2. \dots (59)$$

\* JOULE and THOMSON, 'Trans. Roy. Soc.,' June, 1860; KELVIN, 'Collected Works,' vol. I., p. 405.

When the velocity is intermittent we may write for the purpose of the present discussion

$$U = U_0(1 + \epsilon \cos pt) \dots \dots \dots (60)$$

where  $U_0$  is the average velocity of the air, and  $|\dot{\xi}| = \epsilon U_0$  may be taken to represent the velocity amplitude in the sound-wave generated by the intermittent flow. From (59) and (60) we have for the surface temperature the expression

$$\theta_s = \kappa U_0^2 (1 + \frac{1}{2}\epsilon^2 + 2\epsilon \cos pt + \frac{1}{2}\epsilon^2 \cos 2pt).$$

At the surface of the iron thermometer wire (radius of silk insulation = 0.0092 cm., radius of wire = 0.0048 cm.) the periodic terms contribute corresponding fluctuations of much diminished amplitude, which, however, vanish on averaging with regard to the time over a complete period. Thus the average temperature rise due to kinetic heating measured by the thermometer wire is given by

$$\bar{\theta}_i = \kappa U_0^2 (1 + \frac{1}{2}\epsilon^2) \dots \dots \dots (61)$$

Denoting by the suffixes  $v$  and  $r$  temperatures of the valve and resonator thermometers respectively, we notice that  $\delta\theta$  of equation (58) is the difference of the temperature rises due to kinetic heating, so that we may write

$$\delta\theta = \bar{\theta}_{iv} - \bar{\theta}_{ir} = \kappa_v U_{0v}^2 (1 + \frac{1}{2}\epsilon_v^2) - \kappa_r U_{0r}^2 (1 + \frac{1}{2}\epsilon_r^2).$$

When the diaphone is silent and the average flow is the same we have, writing  $\epsilon_v = 0$  and  $\epsilon_r = 0$

$$\delta\theta' = \kappa_v U_{0v}^2 - \kappa_r U_{0r}^2,$$

and thus

$$\delta\theta - \delta\theta' = \frac{1}{2}\kappa_v U_{0v}^2 \epsilon_v^2 - \frac{1}{2}\kappa_r U_{0r}^2 \epsilon_r^2 \dots \dots \dots (62)$$

If we take the value of  $|\dot{\xi}|$  obtained in (64) from the measurements of the acoustic output of the diaphone, we have  $|\dot{\xi}| = 3.02 \times 10^3$  cm./sec. corresponding to an average velocity  $U_0 = 4.18 \times 10^3$  cm./sec., and hence  $\frac{1}{2}\epsilon_r^2 = \frac{1}{2}|\dot{\xi}|^2 / U_{0r}^2 = 0.26$ .

The term  $\kappa_r U_{0r}^2$  represents the kinetic heating effect of a stream of velocity  $U_{0r}$  in the resonator. The experiments of KELVIN and JOULE already quoted give the rise of temperature due to this cause as 1° C. for 180 ft./sec. ( $5.48 \times 10^3$  cm./sec.). Thus the value of the second term on the right-hand side of (62) is given by  $0.26 \times [(4.18)/(5.48)]^2 \times 1^\circ \text{C.} = 0.15^\circ \text{C.}$  As it is probable that the first term on the right-hand side of (62) is of a magnitude not very different from that just calculated, we are justified in supposing the term  $(\delta\theta - \delta\theta')$  in equation (58) to be small compared to the principal term  $(\theta_1 - \theta'_1)$ .

Under the assumptions just made, we may write, finally, in terms of the temperature difference obtained from the readings of the differential resistance thermometers,

$$\dot{w} = JC_v \dot{M} (\theta_1 - \theta'_1) \text{ ergs/sec.} \dots \dots \dots (63)$$

This result enables us to calculate the rate at which energy is being propagated away as sound, and hence, in conjunction with equation (45), gives us a measure of the acoustic efficiency of the diaphone measured at the vertex of the conical resonator. As the method is not entirely free from sources of error inherent in the temperature measurements, the efficiency thus determined will be referred to as the "apparent efficiency." As far as can be judged these sources of error are for the most part eliminated by taking temperature differences with the diaphone sounding and silent, so the apparent efficiency is probably not very different from the true value.

(iii.) *Discussion of the Father Point Tests.*

The observations described under Appendix III. were taken on a diaphone actually in service so that no alterations could be made in the disposition of the apparatus to allow of the realization of the most satisfactory conditions for carrying out the tests. The results derived therefrom must, therefore, be regarded as the best available under the circumstances. The characteristics of the diaphone are shown graphically in figs. (i.) to (iv.) of Appendix III. It is interesting to notice that the acoustic efficiency is at a maximum at an operating pressure of about 20 lbs. per square inch, not very different from that at which fog-signal engineers have found by experiment that the note is most smooth and penetrating. It may be inferred from the trend of the curves that at very low pressures the acoustic efficiency would probably be of the order of one or two parts in a thousand, as has been found by WEBSTER to be the case for musical wind instruments operated by air at a pressure of a few inches of water.

The conditions under which sound-waves are generated by the alternate opening and closing of the ports in the diaphone piston are too complex to allow of an estimate being made of the wave-form in the resonator. This aspect of the subject should, however, be dealt with experimentally by the oscillating valve method. We are unable at the present moment to understand definitely the part played by the formation of the discontinuity in preventing a greater proportion of energy to be propagated to a distance as sound-waves. In its application to fog-signal waves, the problem is greatly complicated by propagation in three dimensions, the divergence tending to retard the tendency to the formation of a discontinuity with the resulting dissipation of energy. The effect of confining the sound-wave to a conical trumpet tends to enhance the formation of a discontinuity. The superiority of the short trumpets employed in practice would seem to be due to the fact that conditions are so adjusted that, while the advantage of resonance is obtained, discontinuity does not form before the wave has emerged into the free atmosphere, when more rapid divergence precludes the further possibility of discontinuity taking place. The fact that in a siren the wave is carried forward by air moving with considerable velocity would tend to retard the formation of the discontinuity and probably increase the

power delivered to the free atmosphere. All these questions are of great importance in practice and constitute a practically unexplored field for future investigation.

Some light may be thrown on the formation of the discontinuity by considering a harmonic plane wave propagated in a cylindrical tube having the cross-section (90 cm.<sup>2</sup>) of the narrowest part of the conical resonator of the diaphone whose acoustic output was measured by the thermodynamical method. It will be noticed from Test 3 that the maximum power output is 2.36 H.P. at a pressure of 19.1 pounds per sq. in.\* The air consumption is 13.3 cubic ft. per sec., which gives for the mean velocity of air over the 90 cm.<sup>2</sup> cross-section of the resonator the value  $4.18 \times 10^3$  cm./sec. at the frequency  $n = 175$ . If we assume that the wave is initially harmonic (an assumption which sets a lower limit to the maximum compression) we may estimate the numerical characteristics of the equivalent sine-wave from the formulæ of § 1. We have  $[dW/dt] = 2.36 \times 746 \times 10^7 / 90 = 1.95 \times 10^8$  ergs cm.<sup>-2</sup> sec.<sup>-1</sup>. Taking  $a = 3.32 \times 10^4$  cm./sec.,  $\rho_0 = 1.29 \times 10^{-3}$  gr./cm.<sup>3</sup>, we obtain  $a\rho_0 = 42.8$ .

In terms of the pressure amplitude we have from formulæ (7)  $|\delta p|^2 = 2a\rho_0 [dW/dt]$ , giving

$$\left. \begin{aligned} |\delta p| &= 1.29 \times 10^5 \text{ dynes/cm.}^2, & |\dot{\xi}| &= 3.02 \times 10^3 \text{ cm./sec.} \\ |\dot{\xi}| &= 2.74 \text{ cm.} & |\delta\rho|/\rho_0 = |s| &= 0.091 \end{aligned} \right\} \quad (64)$$

According to formula (23) we are enabled to calculate that the distance  $x_1$  which the wave will travel before discontinuity sets in, by identifying  $U$  of that formula with the above value of  $|\dot{\xi}|$ . We thus find, for  $\gamma = 1.40$ ,

$$296 \text{ cm.} < x_1 < 327 \text{ cm.}$$

The estimate just derived leads the writer to believe that in actual fog-alarms the tendency to the formation of a discontinuity in a distance comparable to the wave-length and to the axial length of the resonator plays an important part in determining the output of sound which is eventually transmitted to a distance.

#### § 14. SUMMARY AND CONCLUSIONS.

The tests described in the present paper have demonstrated the successful use of the Webster phonometer as a simple and practical instrument for the measurement of the characteristics of pure-toned sound-waves of ordinary intensity. By carrying out acoustic surveys with this instrument, the propagation of fog-signal waves under varying conditions of wind and weather has been studied. The observations show that the wind is by far the most important factor affecting sound propagation. Many of these results may be interpreted in terms of TAYLOR'S theory of extinction of sound by the eddy structure of the atmosphere. From this point of view it may

\* [Added February 14, 1919.—From phonodeik records taken during the 1917 tests at 860 feet distance it was estimated that 25 per cent. of the total acoustic output is contained in the master tone of pitch 174. See footnote, p. 247.]

be expected that further work with the Webster phonometer will contribute materially to our knowledge of atmospheric structure.

By examining the distribution of sound along circular arcs at different distances from the source it is concluded that the greater part of the atmospheric losses occur within half-a-mile, and very probably within a few hundred feet of the siren trumpet. To measure the very intense sound-waves at this close range a less sensitive phonometer without a resonator is recommended for future work. The acoustic wave-form within the trumpet itself should be studied in connection with the theory of the propagation of waves of large amplitude. Theory shows that, in an ideal medium, plane sound-waves transmitting only a small fraction (from 5 to 8 per cent.) of the energy available as compressed air across the area of the narrowest part of the trumpet could only travel about 10 feet before discontinuity sets in. In reality, the tendency to form a discontinuity will be retarded owing to the effect of viscosity and thermal conductivity and owing to the divergence of the waves in three dimensions. It is suggested, however, that the serious energy losses known to exist in the conversion of energy of compressed air into sound may be closely associated with phenomena of finite wave propagation. The experimental solution of this problem will be necessary before we are able to ascertain whether there is any limit (as in the case of ordinary heat engines) to the proportion of power capable of being converted into sound.

In order to obtain some preliminary information on this question, of considerable practical importance in the design of fog-signal generators, the acoustic output of the diaphone was estimated by measuring the difference of temperature of the air on the high- and low-pressure side. Specially wound resistance thermometers of minimum heat capacity enabled temperature differences to be measured to  $1/100^{\circ}$  C. This temperature difference is a measure of the external work done by the compressed air, propagated away as sound. By means of a few simple thermodynamical formulæ the acoustic output may be calculated in terms of this temperature difference. It was found that under the best conditions nearly two and a-half horse-power may be delivered by the diaphone as sound. In rating the efficiency of the diaphone it was necessary to adopt a standard of comparison. That chosen was an ideal siren operating on an adiabatic cycle and capable of converting (in some way as yet undiscovered) *all* the energy of compressed air into sound. In these terms the acoustic efficiency of the diaphone under the best conditions came out to be a little over 8 per cent. It is probable that the larger and more modern types of diaphones have acoustic efficiencies considerably greater than the above figure. The estimates of acoustic output obtained in these experiments must, therefore, be regarded as provisional, pending further work on the subject.

There remains the pleasant duty of acknowledging valuable assistance and co-operation from many quarters. The writer is much indebted to Prof. A. G. WEBSTER, of Clark University, for his kindness in undertaking to supervise the construction of a "phonometer" specially designed for the Father Point tests, and

also for placing at the writer's disposal the manuscript of a memoir dealing with the mathematical theory of his sound-measuring instruments. To the Postmaster-General of Canada, the Hon. L. P. PELLETIER, the writer is indebted for permission to take up permanent quarters on board the mail tender, "Lady Evelyn," stationed at Rimouski, and to make use of this ship in carrying out acoustic surveys in the neighbourhood of the Father Point signal station a few miles away. The writer wishes to testify to the unfailing courtesy of Capt. J. B. POULIOT and officers of the "Lady Evelyn" in carrying out these tests, and their willingness to co-operate in bringing them to a successful conclusion. For the loan of surveying instruments and valuable assistance in constructing charts of the locality, the writer wishes to thank Commander C. SAVARY of the Hydrographical Survey Ship "Cartier." To Mr. H. H. HEMMING the writer is indebted for invaluable assistance in taking observations during the entire month during which the experiments lasted.

Finally, the writer wishes to express his deep obligation to Prof. H. T. BARNES, F.R.S., Director of the Macdonald Physics Building, not only for placing the resources of the laboratory at his disposal for the work, but in kindly offering to bring to the attention of the Canadian Government the importance of this field of research. As a result, facilities for carrying out the tests at Father Point were generously provided for on a very liberal scale by the Department of Marine and Fisheries.

[*Note added February 14, 1919.*—Fog-signal tests were carried out at Father Point in September and October, 1917, under the auspices of the Canadian Honorary Advisory Council for Scientific and Industrial Research. A detailed account of the results obtained is to be published in a Report, copies of which may be obtained from the Secretary of the above Council, Department of Trade and Commerce, Ottawa, Ontario.

In the course of these tests a thorough investigation was made of the thermal method of measuring the acoustic output of a small diaphone sounding a continuous blast. Temperature differences were measured by means of a pair of thermoelements inserted, one on the high-pressure side of the vibrating piston, the other on the low-pressure side. Almost continuous temperature readings were recorded as the air-pressure was allowed to fall gradually from 29 to 6 pounds per square inch; the corresponding acoustic outputs were found to be 350 and 100 watts respectively, while the acoustic efficiencies were eight per cent. at the higher pressure and 24 per cent. at the lower pressure. Several series of observations with and without the trumpet confirmed these results which, taken in conjunction with those obtained from the 1913 tests on a large diaphone, indicate that higher efficiency and greater atmospheric penetration in fog-signal apparatus may be predicted by the utilization of low air-pressures and by the separation of a single source of sound into a number of small synchronized units.

With the co-operation of Prof. DAYTON C. MILLER of the Case School of Applied Science, Cleveland, Ohio, U.S.A., notes from the large and small diaphones were recorded in permanent form as sinuous lines on photographic films, making use of the "phonodeik," a description of which will be found in the inventor's recent book "The Science of Musical Sounds," (Macmillan & Co., New York, 1916). Records were obtained to distances of nearly three miles, and their analysis brought out a number of interesting and important facts. It was found that the sound from the small diaphone, provided with a detachable trumpet, was extremely complex. From records taken with and without the trumpet, it was inferred that the effect of a resonator of correct design would be to concentrate a greater proportion of the total acoustic output into the master tone. The records obtained at various distances from the large diaphone indicate that the high overtones do not travel far, but are filtered out by the scattering action of atmospheric eddies. As the master tone alone survives to an appreciable extent at distances greater than two miles, it is obvious that the object of the designer of fog-signal apparatus should be to concentrate the greatest possible amount of energy into the master tone. From the harmonic analysis of the phonodeik records it is now possible to obtain accurate data as to the relative proportions of energy contained in the master tone and in the overtones.]

## APPENDIX I.—ON THE ACOUSTIC CHARACTERISTICS OF THE WEBSTER PHONOMETER AS EMPLOYED IN THE MEASUREMENT OF SOUND FROM THE DIAPHONE.

## (i.) DETERMINATION OF PHONOMETER CONSTANTS.

The detailed construction of the Webster phonometer employed during the Father Point tests is briefly described in § 11 and 15 illustrated in fig. 2.

After the instrument had been employed in carrying out the measurements of sound from the diaphone as described in the present paper, the constants of the instrument were kindly determined by Prof. WEBSTER himself at Clark University. Without going very far into the mathematical theory of the phonometer, which is to be considered by Prof. WEBSTER elsewhere, it may be remarked that the free vibrations of the diaphragm may be represented by the differential equation

$$m\ddot{x} + \kappa\dot{x} + fx = 0, \quad \dots \dots \dots (i.)$$

where  $m$  is the effective mass of the loaded diaphragm,  $\kappa$  is the effective damping constant, and  $f$  is the effective stiffness of the diaphragm. According to the determination of Prof. WEBSTER

$$m = 0.891 \text{ grs.}, \quad \kappa = 14.0 \text{ dynes/(cm. per sec.)},$$

and

$$f = 5.67 \times 10^6 \text{ dynes/cm.}$$

The frequency  $n$  of the fundamental, given by

$$2\pi n = [f/m - (\kappa/2m)^2]^{\frac{1}{2}} \quad \dots \dots \dots (ii.)$$

gives  $n = 401$  complete vibrations per second.

The magnification of the optical system was determined by mounting an interferometer on the resonator side of the mica diaphragm, and by means of a stroboscopic arrangement measuring the displacement of the centre in terms of a wave-length of light while in actual vibration at frequency 175. At the same time the breadth of the luminous band in which the filament was drawn out was read in the usual way. In this way it was found that 1-scale division of the microscope eye-piece (1 mm.) corresponded to 0.000120 cm. diaphragm displacement.

The pressure amplitude in a sound-wave,  $|\delta p|$ , is connected with the diaphragm displacement and resonator constants by formulæ which have been developed theoretically (and verified experimentally) by Prof. WEBSTER. According to his determinations, with the resonator in position 8,  $|\delta p|$  (expressed in dynes/cm.<sup>2</sup>), is connected with the diaphragm amplitude  $|\delta x|$  (expressed in cm.) by the relation

$$|\delta x| = 8.48 \times 10^{-5} |\delta p| \quad \dots \dots \dots (iii.)$$

Hence if  $d$  is the phonometer scale reading (double amplitude in mm.) we have  $\frac{1}{2}d \times 0.000120 = |\delta x|$ , from which it follows that

$$|\delta p| = 0.708 \times d \text{ dynes/cm.}^2 \quad \dots \dots \dots (iv.)$$

Prof. WEBSTER states that the constants from which (iii.) was derived were tested by measuring in the open air the sound from a standard "phone" or sound generator at pitch 256. Agreements were obtained to within less than one per cent.

There are difficulties in the way of applying (iv.), as determined for small intensities, to convert the larger readings (greater than 5 mm.) to pressure amplitudes, owing to the fact that in the latter case noticeable eddies are set up in the neighbourhood of the resonator aperture. For this reason it would be necessary to carry out a special series of experiments to determine the limits of error (if any) involved in measuring very powerful fog-signal waves by means of the phonometer. As the pressure amplitudes in



the immediate neighbourhood of a fog-signal generator are very large, there is no need for the magnifying effect of a resonator. In future experiments the difficulty just mentioned may be dispensed with by making use of a phonometer consisting only of a suitable diaphragm together with the optical system for determining its vibration amplitude. On account of these uncertainties the phonometer readings obtained on the various acoustic surveys are not reduced to pressure amplitudes. The recorded readings are, however, comparable among themselves for an instrument built to the exact dimensions of that employed in the present tests. While the phonometer readings at a distance may be accurately converted into pressure amplitudes, the variability of atmospheric conditions, even on a calm day, and the absence of any definite law of propagation make it impossible to utilize absolute readings except to a limited extent. In the tabulation of the observations obtained on the acoustic surveys described in Appendix II., and in their graphic representation in the accompanying charts, the results are given in terms of the phonometer readings, which may be reduced, if required, to pressure amplitudes by formula (iv.).

A glance at the tabulated results of the acoustic surveys show that a phonometer reading of 0.1 mm. corresponds to a signal which is feeble, but still sufficiently distinct to serve as a warning under ordinary conditions prevailing at sea. According to formula (iv.) this corresponds to a pressure amplitude,

$$|\delta p| = 0.071 \text{ dynes/cm.}^2 = 7.0 \times 10^{-8} \text{ atmosphere.}$$

It is interesting to note that this is not far removed from the estimate  $|\delta p| = 9.2 \times 10^{-8}$  atmosphere for a just audible note of pitch 181 as determined by TÖPLER and BOLTZMANN.\* The sensitivity of the phonometer was thus very suitably adjusted for the purpose of fog-signal testing at great distances.

#### (ii.) CALIBRATION OF PHONOMETER RESONATOR FOR PITCH.

In order to employ the Webster phonometer in the measurement of sound, it is necessary to tune the resonator to the pitch of the note emitted by the diaphone. This is accomplished by pulling out the inner of the two telescoping cylinders shown in fig. 2, whose position with reference to the outer cylinder is indicated by means of a centimetre scale engraved on the former. Each "resonator position," as defined by the scale reading, corresponds to a definite fundamental pitch. This was determined experimentally by running a small laboratory siren of the usual type by means of compressed air stored up in the tanks of the fog-signal apparatus.† By keeping a finger dipped in oil pressed against the revolving spindle of the siren the speed could be regulated and kept constant over a sufficient length of time to permit the speed of rotation to be accurately determined by means of a stop-watch. At each position of the resonator the siren was allowed to gain in speed while the image of the filament was carefully observed. Resonance was at once observed by widening of the image into a broad band. The siren was then held at this speed and the pitch determined in the usual way. As the pitch was allowed to increase to a value in the neighbourhood of 2000, a whole series of resonance frequencies was observed. There was no difficulty in selecting those corresponding to the fundamental frequencies of the resonator ( $n$  complete vibrations per second). It was found that resonance was obtained for frequencies of  $\frac{1}{2}n$ ; this was evidently due to the first harmonic of the complex note emitted by the siren. More difficult to explain were a series of several resonance frequencies unconnected with the resonator pitch in any simple way, but showing evidence of simple numerical relationships among themselves. As it was

\* TÖPLER and BOLTZMANN 'Ann. Phys. Chem.,' 141, 1870, pp. 321-352. BOLTZMANN's estimate is probably a little too great. For a note of pitch 200 WIEN gives  $|\delta p| = 1.0 \times 10^{-9}$  atmosphere (quoted by RAYLEIGH, 'Phil. Mag.,' 14, 1907, pp. 596-604, 'Scientific Papers,' vol. v., p. 420). For a note of pitch 256 WEBSTER gives  $|\delta p| = 8.9 \times 10^{-9}$ , agreeing fairly well with the value  $|\delta p| = 6.0 \times 10^{-9}$  obtained by RAYLEIGH for a note of the same pitch.

† The siren is very unsatisfactory for the purpose of this determination owing to the presence in the note emitted of a very large number of high harmonics, whose frequencies may coincide with those of the high-pitched overtones of the diaphragm or of the resonator itself, giving rise to numerous spurious resonances.

suspected that these were in some way connected with the free periods of vibration of the mica diaphragm (loaded at the centre) the resonator chamber and back of the phonometer were entirely removed. It was then found that resonance occurred at the following frequencies :

297, 381, 582, 1141, 2060.

Numbers differing but slightly from these or their sub-multiples could be recognized among the resonance frequencies observed with the resonator in position.\* Any note having among its harmonies one of the free periods of the mica diaphragm would show resonance. As the frequencies of these spurious resonances were far removed from that of the diaphone note when sounded over the normal range of air-pressures, the matter was left aside as of subsidiary importance to the main work on hand. In the following table are given the final results of the determinations of resonance frequencies corresponding to the various resonator positions (denoted by *h* and expressed in centimetres).

TABLE I.

Resonator position. <i>h</i> (cm.).	Frequency. <i>n</i> .	$n^2 \times (h + 10 \cdot 8 \text{ cm.})$ .	Resonator position. <i>h</i> (cm.).	Frequency. <i>n</i> .	$n^2 \times (h + 10 \cdot 8 \text{ cm.})$ .
0·0	232	$5 \cdot 72 \times 10^5$	6·0	185·5	$5 \cdot 78 \times 10^5$
1·0	224	5·93	7·0	177	5·67
2·0	217·5	6·04	8·0	174·8	5·72
3·0	206	5·85	9·0	168·5	5·62
4·0	200	5·92	10·0	166	5·75
5·0	193	5·88			
				Mean . . .	$5 \cdot 81 \times 10^5$

According to the elementary theory, the resonance frequency of a resonator of volume *Q* is given by the formula†

$$n = (c/2\pi) \sqrt{(K/Q)}, \dots \dots \dots (v.)$$

*c* being the velocity of sound at the temperature of the experiment given by

$$c = c_0(1 + \frac{1}{2}\alpha t) = (33130 + 61t) \text{ cm./sec.}, \dots \dots \dots (vi.)$$

where  $\alpha = 0 \cdot 00367$  and *t* is the temperature in degrees C.

*K* is the "inertia coefficient" or "conductivity" of the aperture; for a circular aperture of radius *R* in an infinitely extended thin wall  $K = 2R$ .

We may write  $Q = \frac{1}{4}\pi d^2(h + h_0)$ , where *d* is the diameter of the resonator and *h*<sub>0</sub> is the mean length of the cylindrical chamber at position 0.

By taking *h*<sub>0</sub> = 10·8 cm., we notice from Table I. that the product  $n^2(h + h_0)$  is constant within the limits of observational errors, as required by theory. Formula (v.) may then be written

$$n^2(h + 10 \cdot 8) = \pi^{-2}Kc^2/d^2 = 5 \cdot 81 \times 10^5 \dots \dots \dots (vii.)$$

Taking  $c = 3 \cdot 40 \times 10^4$  cm./sec. at  $t = 15^\circ$  C.,  $d = 11 \cdot 7$  cm., we derive for *K* in (vii.) the value  $K = 2 \cdot 12$  cm. The diameter of the aperture of the phonometer resonator was  $2R = 2 \cdot 50$  cm.

The exact theoretical calculation of *K* for the aperture of a resonator of the type under consideration has not yet been carried out as far as the writer is aware; the above experimental determination shows

\* The resonance frequencies of free edge-clamped diaphragms have been carefully studied by MILLER, D. C., 'The Science of Musical Sounds,' Macmillan and Co., New York, 1916, pp. 148, *et seq.*

† RAYLEIGH, 'Sound' (1896), vol. ii., p. 304.

that it agrees roughly with the value  $K = 2.50$  cm. for an aperture of diameter 2.50 cm. in an infinitely extended thin plate. Reference to fig. 2 of § 11 shows that the length of the resonator at position 0 is not determinate owing to the fact that the face opposite the aperture is not plane. The distance from the mica diaphragm to the aperture is 11.5 cm., not very different from the value of  $h_0$  required to satisfy the theoretical formula (i.). For purposes of approximating to the pitch of such resonators for purposes of design, the theoretical formula (v.) may be employed.

It should be noted that, according to the theoretical formula (v.), the resonance frequency exhibits the same temperature coefficient as the velocity of sound as given by (vi.). In designing an instrument for use in connection with fog-signals, where the temperature is liable to large fluctuations, the resonance should not be too sharp.

The results of Table I. are shown graphically in fig. (i.). The continuous curve drawn through the observed points is calculated according to formula (v.).

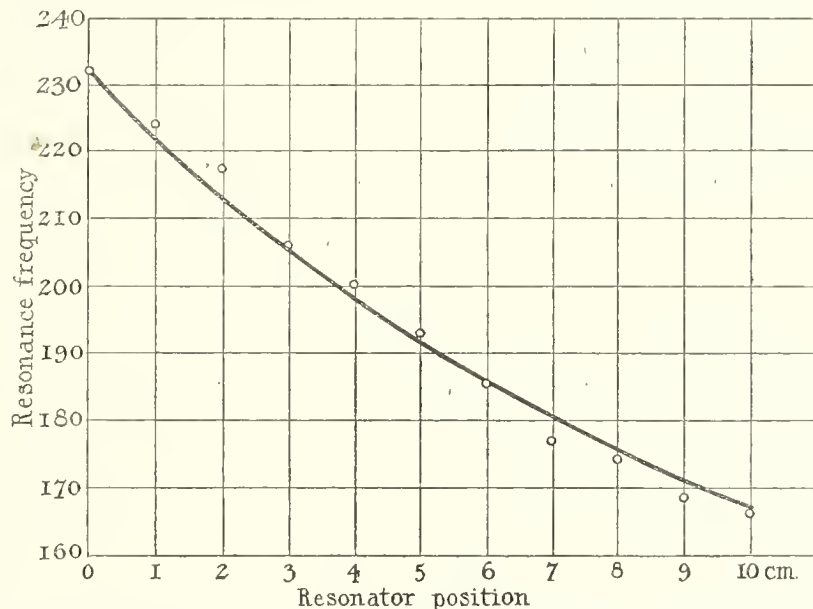


Fig. (i.). Pitch calibration curve of adjustable resonator of Webster phonometer.

(iii.) DETERMINATION OF PHONOMETER RESONANCE CURVE WITH RESPECT TO SOUND-WAVES GENERATED BY THE DIAPHONE.

At distances from the fog-signal greater than 1000 feet the note of the diaphone appeared to be remarkably pure as far as could be judged by the unaided ear.\* At lesser distances, especially within the angle of the resonator, the note was somewhat rougher, while close at hand (50 to 100 feet) a curious crackling sound, somewhat like that emitted when a large sheet of paper is being crumpled up, might be heard at the same time. Behind the resonator, in the acoustic shadow of the fog-signal buildings, the note, while still very loud, was comparatively pure. In order to study the behaviour of the phonometer, with respect to the intense waves emitted by the diaphone, a series of readings was taken at a control station behind the resonator at a corner of the balcony of the fog-signal engineer's residence (marked S in Chart 1 of Appendix II.). The end of the diaphone trumpet was just visible from the phonometer. A few preliminary observations indicated that the diaphone note seemed to have the best quality at a mean pressure (between the beginning and end of the two 3-second blasts) of 19.7 lbs./sq. in. During the entire test the pressure fluctuated very slightly from this value. Readings were taken with the resonator in different positions. In the following table the mean of observations taken on several blasts are given. The maximum readings occurred at resonator position 8.0. According to Table I. the pitch of the diaphone note at the above pressure may be taken at 175 complete vibrations per second. The entire set

\* See footnote, p. 247.

of readings at this position are given to demonstrate the remarkable uniformity of intensity of the successive blasts. The results are shown graphically in fig. (ii).



Fig. (ii). Resonance curve of Webster phonometer with reference to sound-waves generated by the diaphone.

TABLE II.

Resonator position.	No. of observations.	Mean phonometer observations.	Resonator position.	No. of observations.	Mean phonometer observations.	Resonator position.	No. of observations.	Mean phonometer observations.	
0.0	1	0.9	6.9	1	3.8	8.4	2	6.0	
1.0	1	0.9	7.0	5	4.3	8.5	3	5.6	
2.0	1	1.0	7.1	1	4.3	8.8	2	5.6	
3.0	2	1.05	7.2	1	4.6	9.0	3	5.0	
4.0	3	1.3	7.4	3	5.2	9.2	1	4.4	
5.0	4	1.55	7.5	4	5.4	9.4	1	4.2	
6.0	4	2.7	7.6	1	5.9	9.6	1	3.7	
6.5	1	3.2	7.8	2	5.8	10.0	3	3.1	
6.6	1	3.2	8.0	26	5.5				
6.8	1	3.6	8.2	2	5.9				
Successive readings of phonometer with resonator at position 8.0									
		}	5.4	5.3	5.2	5.4	6.3	6.2	5.7
			5.4	5.5	5.5	5.4	5.2	6.2	5.5
			5.6	5.7	5.7	5.5	5.2	5.3	
			5.5	5.6	5.5	5.4	5.0	5.1	
AIR Pressures Operating Diaphone.									
<i>Beginning of Test.</i>					<i>End of Test.</i>				
104.5 cm. mercury, falling to 96.5 cm. at end of blast.					106.5 cm. mercury, falling to 98.5 cm. at end of blast.				
Mean pressure between blasts, 19.4 lbs./sq. in. above atmospheric.					Mean pressure between blasts, 19.7 lbs./sq. in. above atmospheric.				

According to theory resonance curves obtained in this way for the same frequency, but for signals of different intensities should have their ordinates proportional. It would seem at first sight that for very intense waves the sensitivity of the phonometer could be reduced in the ratio of 6 to 1 by taking readings

with the resonator set at a position far removed from that giving resonance. On testing this conclusion for the purpose of employing the phonometer to measure very loud blasts giving readings far off the scale of the instrument when tuned to the exact frequency of the diaphone note, it was found that the proportional relationship did not hold with any approach to accuracy. Although it was surmised that the reason for this discrepancy was connected with the fact that the sound-waves were very much more intense than any which had been hitherto dealt with by means of the phonometer, it was some time before a definite clue was obtained as to the exact nature of the difficulty. While carrying out observations at the control station on a specially calm day, the writer happened to make a slight adjustment of the resonator while a blast was being sounded by the diaphone. A current of air could be distinctly felt blowing outwards from the aperture of the resonator. The phenomenon was investigated with a lighted match which was easily extinguished when held a couple of inches from the resonator. The writer attributes the phenomenon to the formation of a rapid succession of vortex rings set up at the edge of the resonator aperture by the pulsations of air due to the very intense sound-waves (the scale-reading of the phonometer was about 7 mm.). A "vortex stream" is thus set up on both sides of the aperture, that moving into the resonator being broken up and supplying air which issues outwards from the orifice. The phenomenon of jets issuing from resonators has been observed by Lord RAYLEIGH, who has utilized the effect in the design of a "vibration indicator" to measure the powerful sound-waves generated by portable forms of fog-signal apparatus.\* It will be evident that for very intense sounds the theory of the absolute phonometer is invalidated to an extent which requires further investigation.

A few tests were carried out to make certain that the readings of the phonometer were unaffected by the direction in which the instrument was pointed with respect to the source of sound. Readings were taken behind the diaphone trumpet at the control station already mentioned, and also at a position about 130 feet from the trumpet on Line VIII. (Chart 1, Appendix II.). Successive readings at intervals of 45 degrees, measured in the direction N.-E.-S.-W., commencing at 0 degrees with the aperture of the phonometer resonator pointed at the diaphone trumpet, are given below.

	0°.	45°.	90°.	135°.	180°.	225°.	270°.	315°.
Control station . . . . .	6.25	6.3	6.5	6.5	6.5	6.8	6.5	6.5
Position on Line VIII. . .	5.5	5.3	5.75	5.6	5.5	—	—	—

The above readings are constant within the limits of accidental fluctuations of amplitude, indicating that neither the azimuth of the resonator axis with respect to the wave-front or the effect of the observer's head has a noticeable effect on the phonometer readings. According to acoustic theory this result is to be expected, as the wave-length (in this case a little over 6 feet) is large compared to the dimensions of the resonator and of the obstacle formed by the observer's head. The result was also verified by similar tests carried out at a distance in a ship's boat as well as from the deck of the "Lady Evelyn," provided in each case the fog-signal station could be directly viewed from the phonometer. This conclusion is of considerable practical importance in the measurement of sound in the open air, as the phonometer may be turned in such a direction as to eliminate the effect of wind which is liable to set up sound vibrations within the resonator when blowing into or across the aperture. Except on very windy days (wind greater than 30 miles an hour) it was found possible to take phonometer readings without difficulty.

(iv.) DETERMINATION OF THE PITCH REGULATION OF THE DIAPHONE.

It has long been known that one of the important features of the diaphone is its extremely good pitch regulation—that is, the remarkably small variation of pitch within wide limits of operating air pressure. In

\* RAYLEIGH, 'Sound' (1896), vol. II., pp. 216-217; 'Phil. Mag.,' VI., 1908, pp. 289-305; 'Scientific Papers,' vol. v., p. 132.

order to obtain an idea of the extent to which the phonometer readings might be affected by variation of pitch, a series of resonance-curves, of the type shown in fig. (ii.), was obtained for a series of operating pressures from 11.7 to 30.5 lbs./sq. in. The phonometer was mounted on a theodolite tripod at position 2, line VII., Chart 1, 100 feet from the diaphone. Here the note of the diaphone was still somewhat rough, indicating the existence of harmonics. While one observer (H. H. H.) operated the fog-signal at the required pressures, the writer took a number of phonometer observations with the resonator at different positions, with a view to determining that giving the maximum reading. As in the tests described in (i.), some cases of spurious resonances were observed, probably due to harmonics coinciding with an upper partial of the resonator or of the diaphragm. There was no difficulty in picking out the particular position of the resonator corresponding to the fundamental frequency of the diaphone note. The final results only are given in Table III. below, and are shown graphically in figs. (i.) and (iii.) of Appendix III. The mean of the pressures at the beginning and end of each 6-second blast is recorded. The position of the resonator corresponding to the maximum phonometer reading was determined from curves corresponding to that shown in fig. (ii.). The pitch of the diaphone note was taken to be that of the phonometer resonator as given by Table I. and the curve of fig. (i.).

TABLE III.

Mean pressure.	Maximum phonometer reading.	Position of resonator at maximum.	Pitch.
lbs./sq. in.	mm.	cm.	
11.7	4.8	9.0	169
15.5	5.3	8.5	171
19.1	8.2	7.7	174
26.9	5.5	6.5	182
30.5	6.3	4.0	200

In carrying out the acoustic surveys described in Appendix II., it was decided to set the phonometer at position 8, corresponding to pitch 175, and to keep the average operating pressure as closely as possible to 20 lbs./sq. in., corresponding to this frequency. From the resonance curve of fig. (ii.), it will be seen that a variation of 1 cm. in the setting of the phonometer resonator between 7.5 and 8.5 cm. will alter the scale-reading by 0.5 mm., from 5.5 to 6.0 mm., which represents, roughly, the limits of variations due to accidental fluctuations in the note emitted by the diaphone. Reference to fig. (i.) shows that this variation of resonator position corresponds to a variation of pitch between 171 and 176. From Table III. above, it will be seen that the pressure operating the diaphone may vary between 16 and 22 lbs./sq. in. before the pitch is altered to this extent. Furthermore, a reference to the results of Appendix III., tests 1 and 3, indicates that the acoustic output, as measured in the diaphone trumpet, does not vary much more than 10 per cent. between 18 and 23 lbs./sq. in. We conclude, finally, that between these limits of pressure the phonometer, with the resonator set in position 8, will give relative measurements of pressure amplitude from day to day to an accuracy within the accidental fluctuations of the signal sounded by the diaphone. Also, provided the phonometer readings are not too large (not greater than 5 mm.), they may be reduced to pressure amplitudes in C.G.S. units by formula (iv.).

## (v.) NOTE ON THE QUALITY OF THE SOUND EMITTED BY THE DIAPHONE.

In the Father Point tests of 1913, means were not available for studying the quality of the note emitted by the diaphone. It is evident from the remarks already made that overtones probably exist to some extent in the sound-waves close to the trumpet. Owing to the complex conditions of finite-wave propagation,

it is difficult to forecast the relative intensities of the overtones produced in the trumpet from data relating to the characteristics of conical resonators tested in the laboratory.\* The form of trumpet actually used (for dimensions see under fig. 1, § 9) was that giving the greatest atmospheric penetration as determined by a large number of trials carried out at Father Point in 1903 under the direction of Lieut.-Colonel W. P. ANDERSON, Chief Engineer of the Canadian Department of Marine and Fisheries. As is well known, the energy of the sound-waves is dissipated largely owing to the effect of eddies in the atmosphere. According to the mathematical theory developed by TAYLOR (discussed in Section 12), the coefficient of extinction is proportional to the square of the frequency. It follows that overtones in the diaphone note will be much more rapidly extinguished than the fundamental. It is thus important in fog-signal apparatus that as much of the acoustic output as possible be concentrated in the fundamental, or "master tone."

The rapid extinction of overtones with increasing distance from the diaphone was repeatedly observed during the tests carried out by the writer. At a distance of about 1000 feet the note was, as far as could be judged by ear, very nearly a pure tone.

The phonometer, when correctly tuned, enables us to measure in C.G.S. units the pressure amplitude in the fundamental, and the readings given in Appendix II. must be interpreted in this way. As regards the carrying power of the signals it is the energy contained in the fundamental which is by far the most important.

It is highly desirable in fog-signal tests that the dependence of attenuation on wave-length be studied in the light of TAYLOR'S theory, and that observations be carried out on the quality of the note at varying distances, as is now possible by the use of MILLER'S "phonodeik."†

## APPENDIX II.—ACOUSTIC SURVEYS IN THE NEIGHBOURHOOD OF THE FATHER POINT FOG-SIGNAL STATION.

### (i.) GENERAL PROCEDURE IN TAKING OBSERVATIONS.

The object of the acoustic surveys carried out at Father Point was to obtain on different days and under varying meteorological conditions a permanent record of the distribution of sound in the neighbourhood of the same fog-signal station. For this purpose the Webster phonometer described in Appendix I., was found to satisfy the exacting conditions required of a robust and portable instrument sufficiently sensitive to respond to the minute changes of pressure occurring in sound-waves of ordinary loudness.

Through the courtesy of the Department of Marine and Fisheries, permission was given to operate the diaphone at will for the purpose of the tests. Through the kindness of the Postmaster-General, the writer was authorised to take up permanent quarters on the mail tender, "Lady Evelyn," stationed at Rimouski, and to make use of this ship in carrying out acoustic surveys in the neighbourhood of the Father Point signal, a few miles away. Mr. H. H. HEMMING,‡ B.A., assisted in the tests and proved himself invaluable in taking observations. As a matter of regular routine an acoustic survey was carried out whenever possible during the forenoon. The ship was skilfully navigated over a series of courses under the guidance of her commanding officer, Captain J. B. POULIOT. Although the usual weather records were kept at the Father Point meteorological station, it was found necessary, as far as available instruments allowed, to take independent observations from the ship, as air temperatures, wind velocities and directions even half a mile from shore were observed to differ considerably from those on land.

\* As determined by MILLER, D. C., in connection with the development of the "phonodeik." ('The Science of Musical Sounds,' 1916, p. 156, *et seq.*)

† See footnote, p. 247.

‡ Now Capt. H. H. HEMMING, of the Third Field Survey Company, on active service in France.

Air temperature was measured by means of a self-registering thermometer. With the kind permission of Dr. H. T. BARNES, Director of the Macdonald Physics Building, one of his self-recording marine thermometers was installed for the purpose of taking sea temperatures. No direct effect of sea temperatures on sound transmission could be detected, however, so that it has not been thought necessary to reproduce these records. Mr. HEMMING took charge of wind observations with the only apparatus available, a small anemometer consisting of a fan whose revolutions could be timed by means of a stop-watch. With this instrument the velocity of the wind relative to the ship was obtained. The direction of the wind relative to the ship was observed from the direction of the ship's smoke. The ship's speed and the magnetic bearing of the course was noted at the same time. By the usual graphical construction the velocity and direction of the wind relative to the earth's surface was determined. In each of the Charts 1 to 14, the wind velocities at the positions where they were observed are shown in magnitude and direction by arrows, the numbers beside them indicating velocities in statute miles per hour. In future observations of this kind the use of self-registering instruments for wind velocity and direction is recommended.

While phonometer readings were taken at intervals of one minute by the writer, the position of the ship was determined by Mr. HEMMING from sextant observations of the angles subtended by landmarks of known position on shore. Both sets of observations were carefully timed so that the position of the ship at each signal could be plotted down with fair accuracy on a chart of the locality. At each position thus determined an ordinate was drawn perpendicular to the line representing the ship's course, proportional to the phonometer reading, and hence to the pressure amplitude in the wave. In this way is obtained a graphical representation of the variation of sound amplitude along various courses in the neighbourhood of the fog-signal station. It must be kept in mind that the results thus obtained do not represent the state of affairs existing at the same instant, but show variations of amplitude in sequence of time. Each phonometer reading was identified by a position number entered on each of the Charts 1 to 14, opposite the position of the ship at the instant of observation. The corresponding phonometer observations are entered in Tables 1 to 14, together with meteorological observations and remarks.

#### (ii.) DESCRIPTION OF TABLES AND CHARTS.

##### *No. 1.—Short Range Acoustic Survey, September 3, 1913. Table 1 and Chart 1.*

A preliminary survey of conditions of sound propagation in the immediate neighbourhood of the fog-signal station was carried out by means of the Webster phonometer, with a view to obtaining some light on the extent of the large atmospheric losses believed to occur in this region. As a first step, observation stations were marked out at intervals of 50 feet along eight lines radiating from the resonator of the diaphone, making angles of approximately 45 degrees with one another. At the same time topographical observations were carried out, from which a map of the locality could be drawn giving the positions of the various buildings and of the shore line on the seaward side. Observations from which the contour lines of the beach were drawn were carried out by Mr. HEMMING. These are shown in Chart 1 drawn from the data thus obtained. The contour line 1 is the high tide level of September 2, 1913, and is 14 feet below the level of the diaphone resonator. Successive contour lines 1, 2, 3, 4, &c., represent differences of level of 1 foot.

Observations were carried out on September 2, 1913, the day having been chosen on account of the comparatively calm conditions then prevailing. The phonometer was mounted on a theodolite tripod as shown in Plate 1 and tuned to resonator position 8 throughout. The observations were taken almost continuously between 10.30 a.m. and 4 p.m., and are entered in Table 1 in chronological order. Along each of the lines (numbered I. to VIII.) phonometer readings were taken at each observation station and numbered, commencing with No. 1, 50 feet distant from the diaphone: the readings were repeated at each station on the way back. No difficulty was experienced in setting up the phonometer at each



station in the 1-minute interval between the blasts. As a rule each of the two 3-second blasts was measured and the mean of the two readings entered. In some cases the readings were repeated for successive blasts. When more than one signal was measured the suffix indicates the number of readings of which the result entered is the mean.

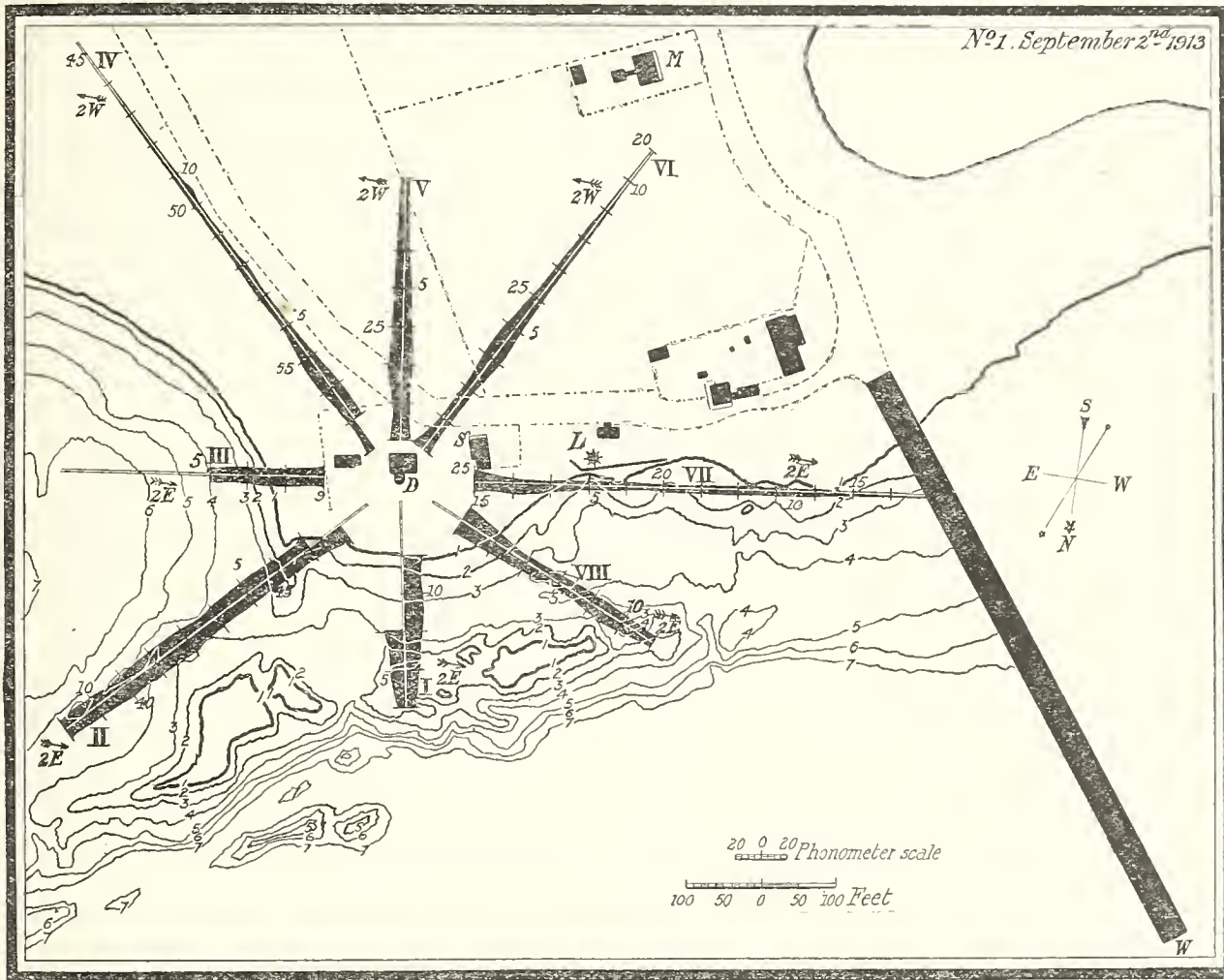


Chart 1. Short range acoustic survey, September 2, 1913. The more important features of the chart referred to in the text are: D, position of the diaphone trumpet; L, Father Point lighthouse; S, control station near engineer's residence; M, meteorological station; W, control station at end of wharf.

The pressure amplitude in the sound-waves was found to be so great within a radius of 100 feet that the phonometer readings were thrown completely off the scale. The readings could be brought on the scale by untuning the resonator. It was found, however, that the resonance curves obtained by plotting phonometer readings against resonator positions (as in fig. (ii.), Appendix I.) did not have proportional ordinates. As the intensity increased, the curves became relatively flatter. A phonometer reading taken with the resonator at any position other than 8 cm., could be expressed in terms of the reading which would be obtained at resonance by a rough interpolation from the series of resonance curves. Such readings, when entered in Table 1, are enclosed in brackets, and are in defect of the true resonance reading if it could have been obtained. As already mentioned under Appendix I., the conversion of the phonometer readings to pressure amplitudes by making use of the constant determined for moderately loud sounds is subject to some uncertainty owing to the existence of eddies in the resonator. Values thus obtained will, however, be in defect of the true pressure amplitude.

The phonometer readings are shown graphically in Chart 1. It will be noticed that although the weather was comparatively calm, atmospheric conditions varied so rapidly that the inward and outward readings taken along each line at intervals of a few minutes are only in rough agreement. There is

some reason to believe that a large proportion of the atmospheric losses take place in the immediate vicinity of the fog signal station. It is of considerable importance that the characteristics of the wave-motion be studied in some detail in this region. The results of the acoustic survey just described may be regarded as giving us some preliminary information of conditions to be met with in the design of apparatus especially suited to determining the wave-form and numerical characteristics of waves of large amplitude.

No. 2.—Short Range Acoustic Survey. September 4 and 5. Table 2 and Chart 2.

The phonometer observations, entered in Table 2 and shown graphically in Chart 2, were taken from a ship's boat (Plate (ii.)). The position of the boat was determined at each signal by measuring the angles between known landmarks by means of a sextant. The observations extended over two days, September 4

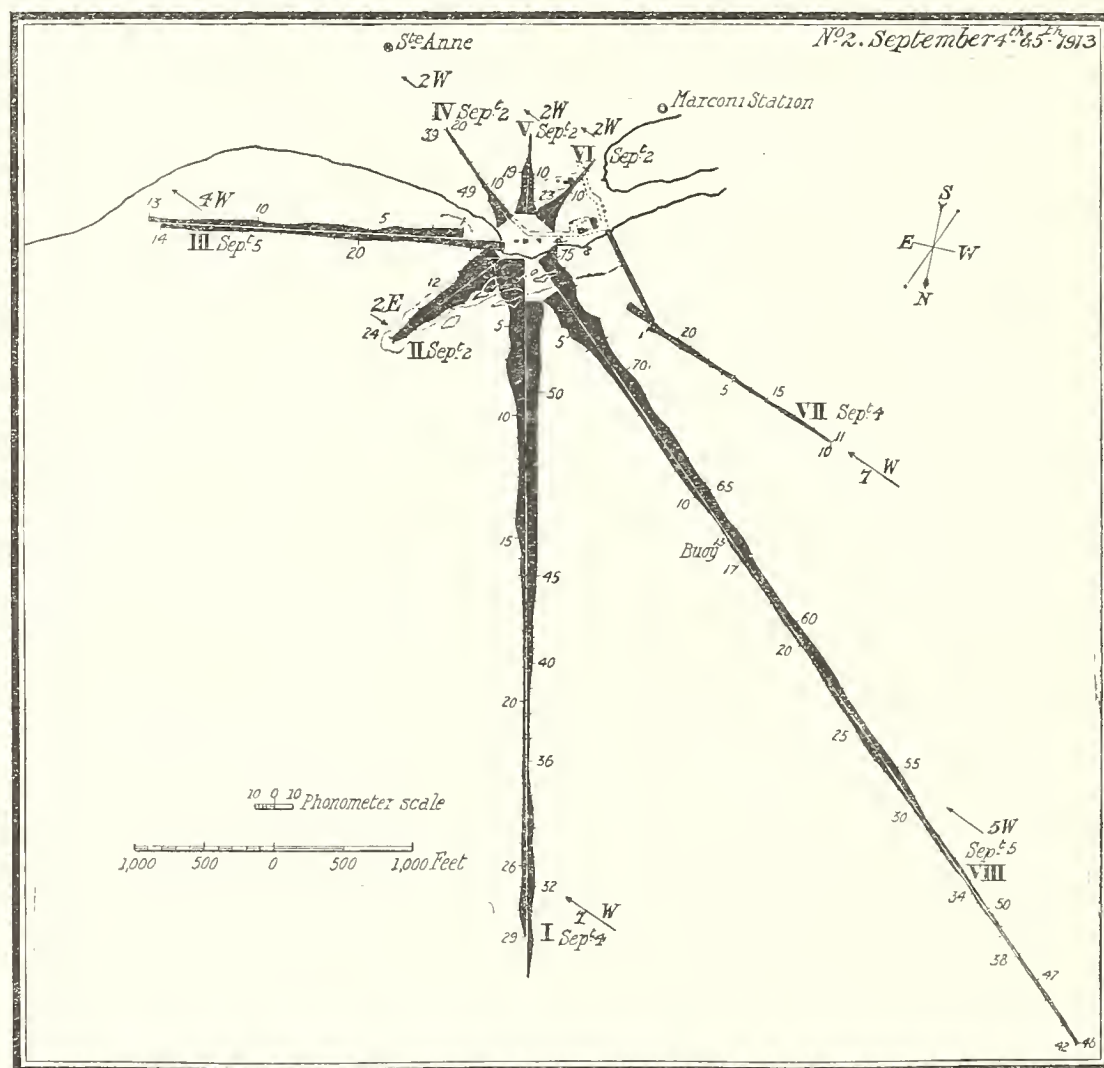
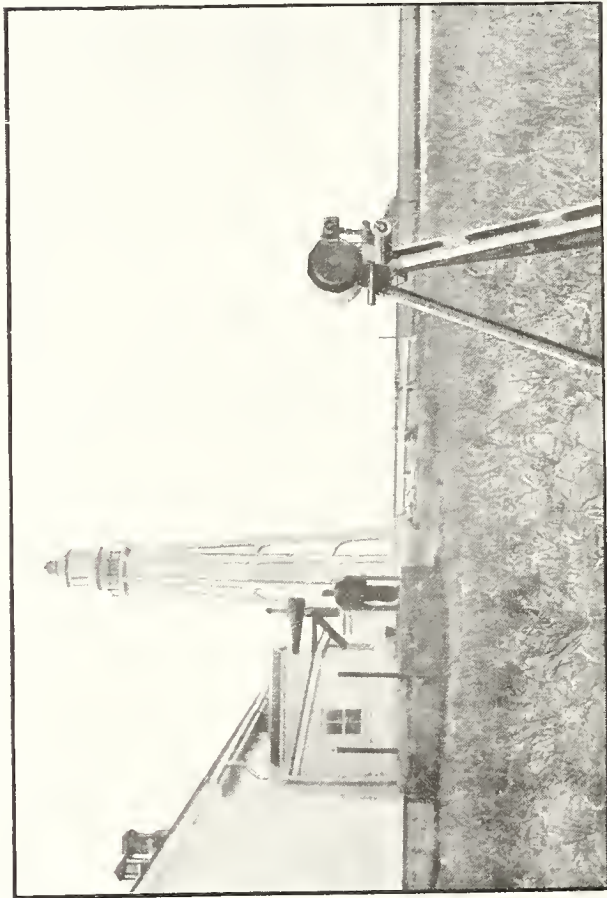


Chart 2. Short range acoustic survey, September 4 and 5, 1913.

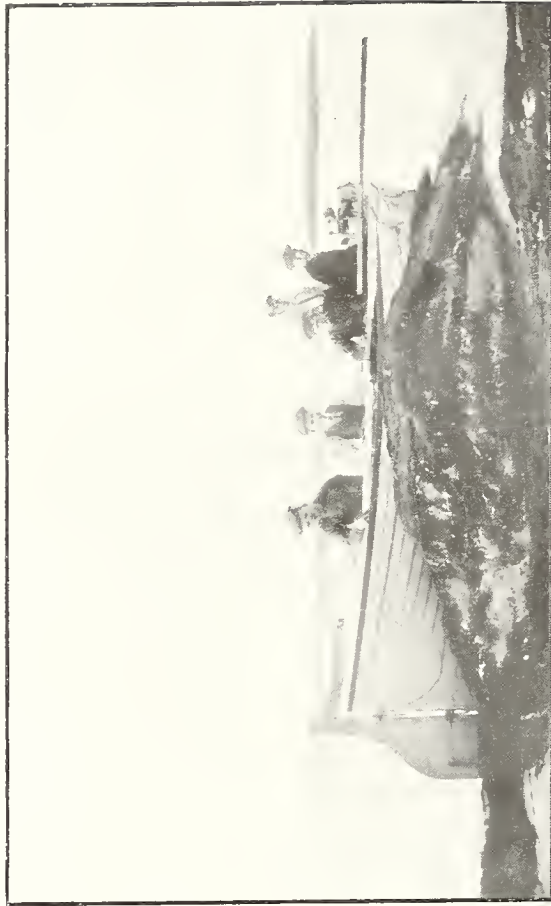
Observations carried out from a ship's boat by means of the Webster phonometer. The position of the ship's boat at each signal (identified by means of the numbers on the chart) was obtained from sextant observations. The phonometer readings at each position are plotted along ordinates at right angles to the inward and outward courses. Wind directions and velocities (represented by arrows) are those registered at the meteorological station.

and 5, 1913. Fortunately, wind and weather conditions did not differ greatly on the two occasions. In order to obtain some idea of the relative amounts of sound propagated over sea and land, the observations of September 2 are graphically represented in Chart 2 on the same scale. Attention is drawn to the fluctuating character of the gradients along lines I. and VIII. In both instances we have examples

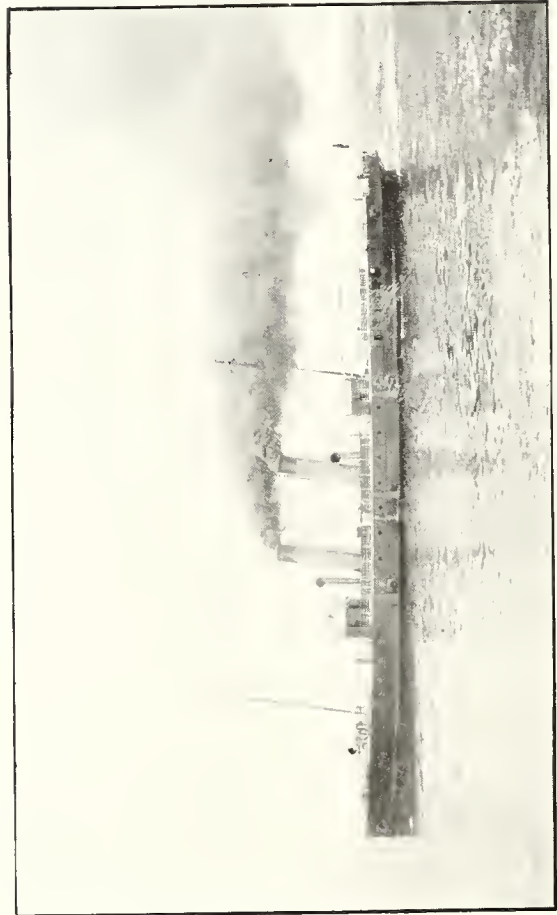




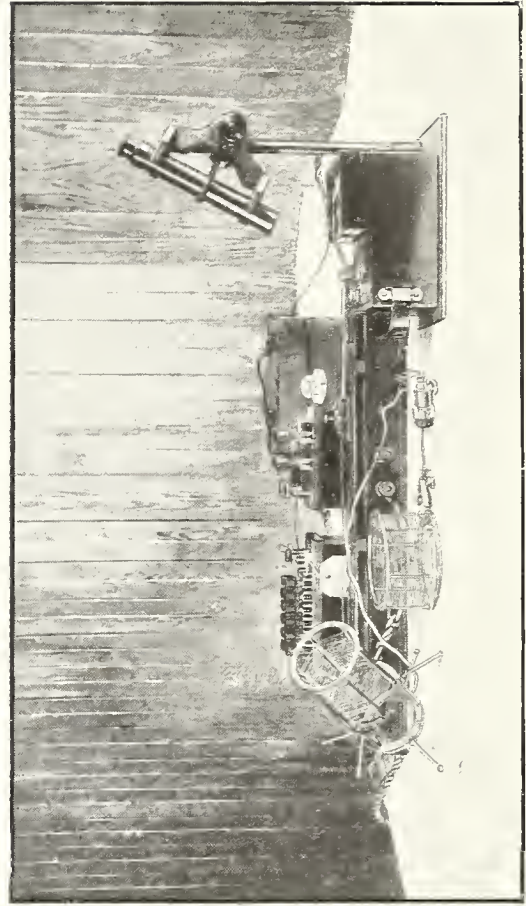
(i.) Webster phonometer mounted on a theodolite tripod. Building on the left is the fog-signal station, showing trumpet of diaphone. Father Point lighthouse in the background. The results obtained are shown graphically in Chart 1.



(ii.) Acoustic survey carried out from a ship's boat. The phonometer is shown mounted at the bow of the boat. The results obtained are shown graphically in Chart 2.



(iii.) C.G.S. "Lady Evelyn." From this ship were taken the phonometer observations for the long range acoustic surveys, the results of which are shown graphically in Charts 3 to 14.



(iv.) Apparatus for the thermal measurement of the acoustic output of diaphone. The skeleton construction of the iron-wire resistance thermometers is clearly shown.

(To face page 259.)

of incipient "silent zones," the amplitude diminishing with distance and increasing again as the distance is further increased. The comparatively small amplitudes along line VII. are due in part to the wind blowing against the direction of sound propagation and in part to the obstructing effect of the wharf.

Nos. 3 to 14. Long Range Acoustic Surveys. (Tables 3 to 14, Charts 3 to 14?)

These observations were taken from the C.G.S. "Lady Evelyn" (Platc (iii)). The phonometer was set up on the main deck in such a position that an unobstructed view of the fog-signal station could be obtained. When the phonometer reading fell to 0.1 mm. the signal was still sufficiently loud for practical purposes. Signals which could still be heard, although incapable of affecting the phonometer, are entered in the tables as 0.0. In the remarks, the intensity of the signal as estimated by ear is entered according to the following scale—*distinct* (between 0.0 and 0.05 on the phonometer), *audible*, *just audible*, *barely audible*, *inaudible*. When a signal was missed or not heard owing to disturbing ship noises *a*— is entered in the table. On landing at Father Point wharf after a series of observations, a number of phonometer readings were taken at this position (W, Chart 1), and a note made of the duration of the echoes. A number of readings were also taken at a control station behind the fog-signal station (S, Chart 1), and observations were made of the air pressure operating the diaphone. It would have been desirable to have had a third observer available to regulate the compressors and keep the pressure constant; it was fortunate, as pointed out in Appendix I., that the pitch of the diaphone varies over a very small range for considerable variations of operating pressure. Also, as may be seen from an inspection of tests 1 and 3 of Appendix III., the acoustic output does not vary between very wide limits over a considerable range of pressures. Thus, although the pressures at the fog-signal station could not be maintained as constant as could be desired, it is concluded that the results of the acoustic survey as shown graphically on Charts 3 to 14 are comparable as regards conditions at the diaphone, and that the extraordinary variations of sound distribution observed from day to day are due for the most part to changes in atmospheric conditions. We proceed to direct attention to some of the outstanding features of the results obtained on these long-range surveys.

No. 3. August 26, 1913. Table 3 and Chart 3.

Wind (as recorded at Father Point meteorological station) very variable. Note effect on sound and the tendency to form regions of inaudibility. Close to the fog-signal station (observations 84 to 89) note the

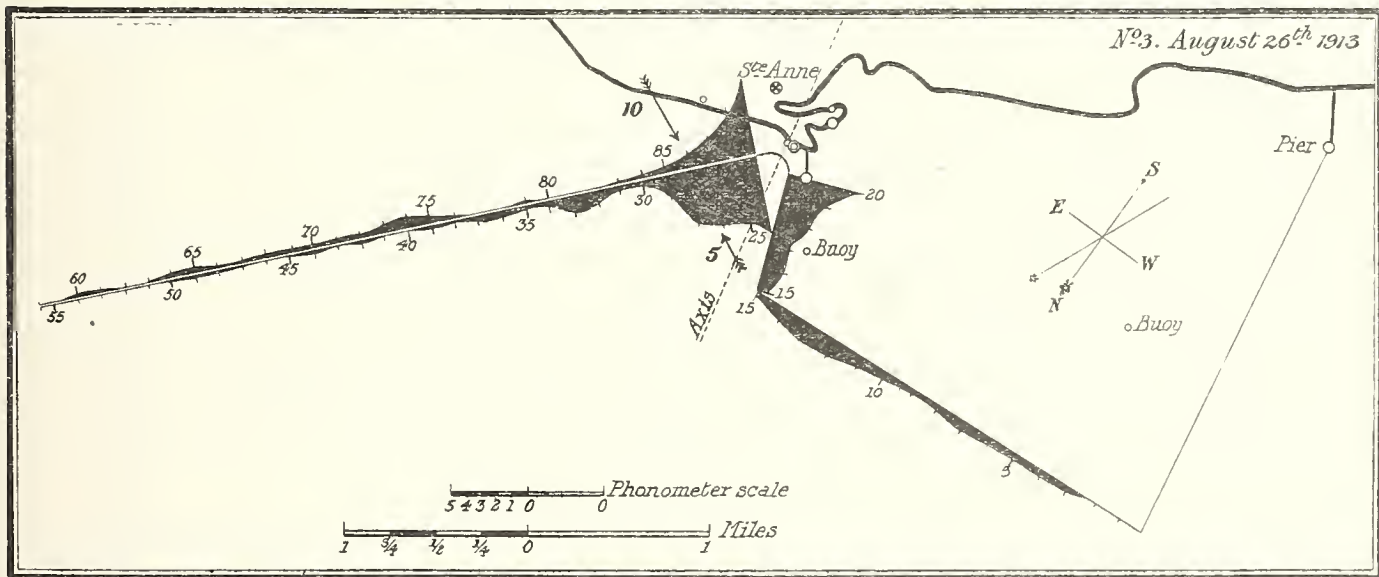


Chart 3. Acoustic survey, August 26, 1913.

deadening effect of a wind blowing from the direction of the shore as compared with the influence of a steadier and more homogeneous wind blowing from the sea (observations 25 to 30). Unfortunately, no anemometer was available for shipboard use at the time these observations were taken.

No. 4. August 30, 1913. Table 4 and Chart 4.

Meteorological conditions unusually favourable to long-distance propagation. Note the fairly regular undulatory character of the gradient. In the writer's opinion this peculiarity affords evidence of some

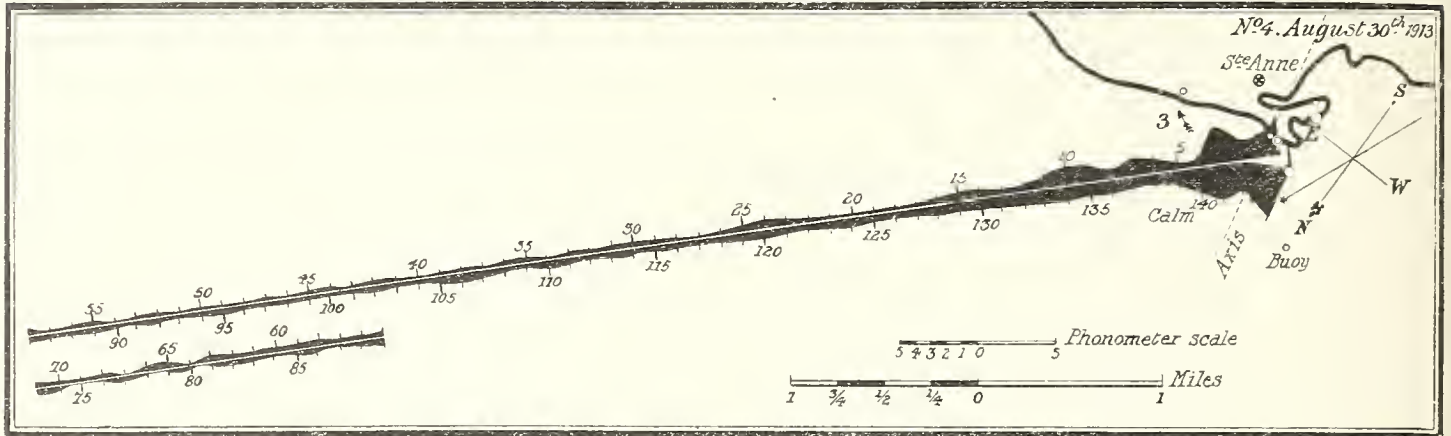


Chart 4. Acoustic survey, August 30, 1913.

sort of regular structure in the wind explained by the existence of large scale eddies according to the theory proposed by TAYLOR and briefly discussed in Section 11. The question is discussed in greater detail in Section (iii.) of the present Appendix.

No. 5. September 3, 1913. Table 4 and Chart 4.

Note the poor propagation against the wind (observations 1 to 6); the signal was first heard from the navigating bridge, about 10 feet above the observer at the phonometer and about 20 feet above sea level,

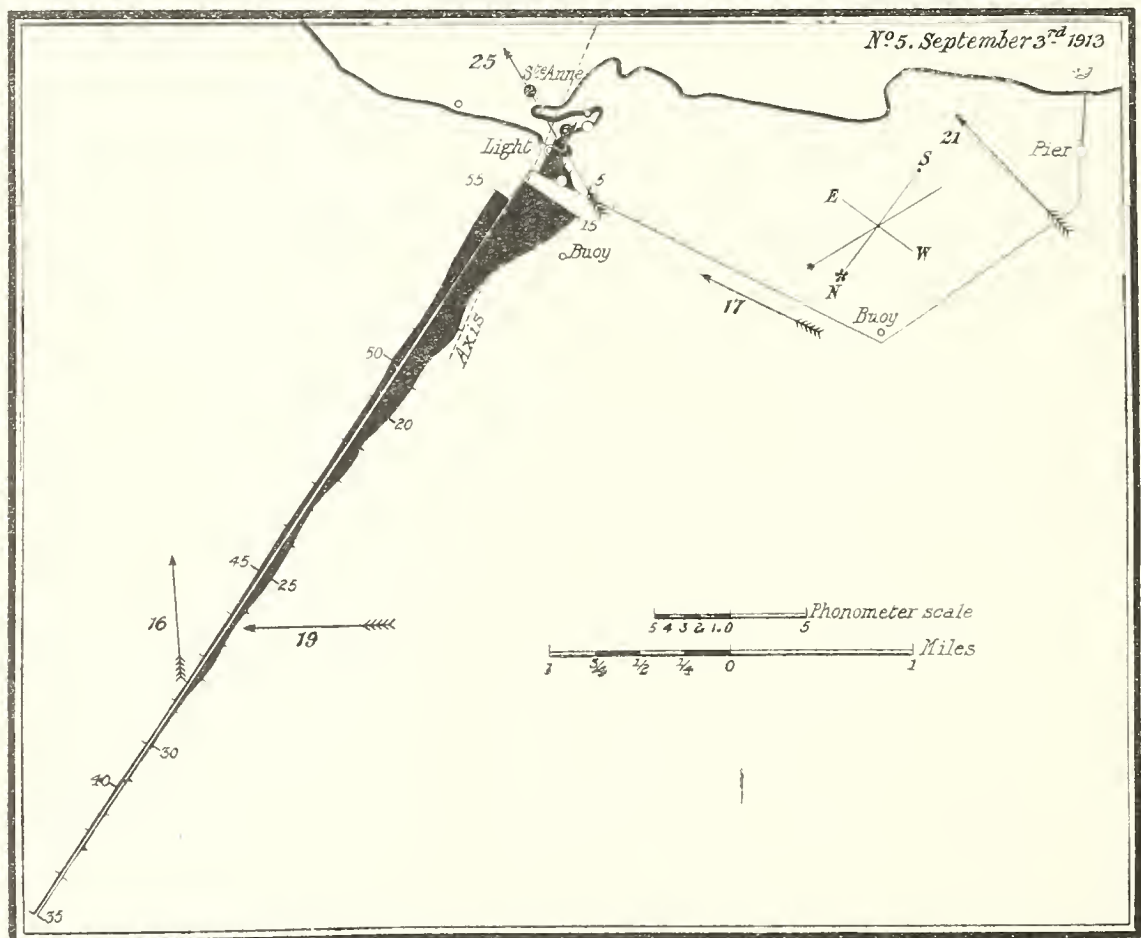


Chart 5. Acoustic survey, September 3, 1913.

thus bearing out the accepted theory of the refraction by an opposing wind of the sound over the observing ship. In spite of the comparatively high velocity of the wind, propagation at right angles to its direction remains fairly good (observations 15 to 35). On the inward course the wind veered to a direction opposite to that of sound propagation; the effect on the gradient is seen to be very marked.

No. 6. September 4, 1913. Table 6 and Chart 6.

The ship was kept to a circular course by navigating so as to keep the Father Point lighthouse directly abeam, and making corrections on the course by keeping the angle subtended by the top and bottom of the lighthouse constant. Note the diminution of intensity on entering the acoustic shadow of the Father

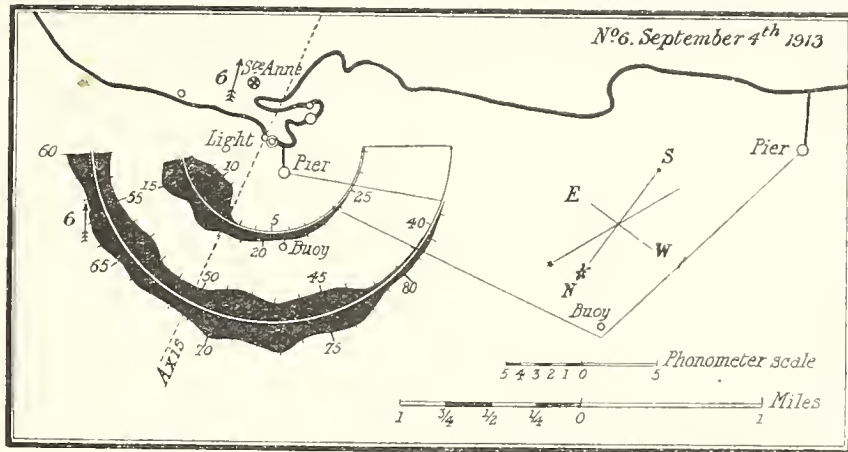


Chart 6. Acoustic survey, September 4, 1913.

Point wharf. The distribution of amplitude along the outer of the two circular courses is much greater than would be expected according to the inverse-square law of propagation, in spite of an opposing wind, indicating reinforcement by refraction from the upper layers of the atmosphere or by sound scattered from eddies. The subject is further discussed in Section (iii.) of the present Appendix.

No. 7. September 5, 1913. Table 7 and Chart 7.

A comparison with Chart 5 shows the deadening effect of an off-shore breeze. Besides containing large

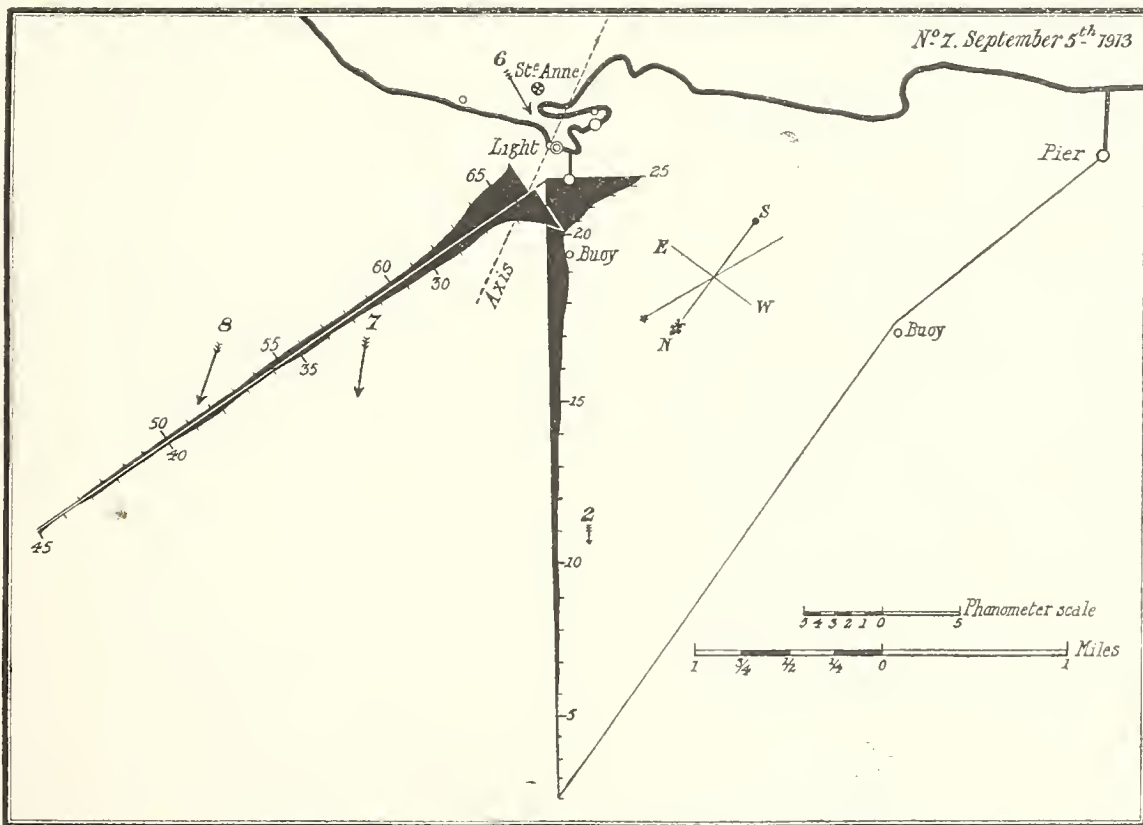


Chart 7. Acoustic survey, September 5, 1913.

temperature inequalities, the eddy-motion character of wind blowing over land is probably accentuated with a marked effect on the attenuation of sound.

No. 8. September 9, 1913. Table 8 and Chart 8.

The transmission of sound is seen to be extremely bad. This is probably due to the fact that the wind was blowing along the direction of the shore and thus contained marked temperature irregularities as well as

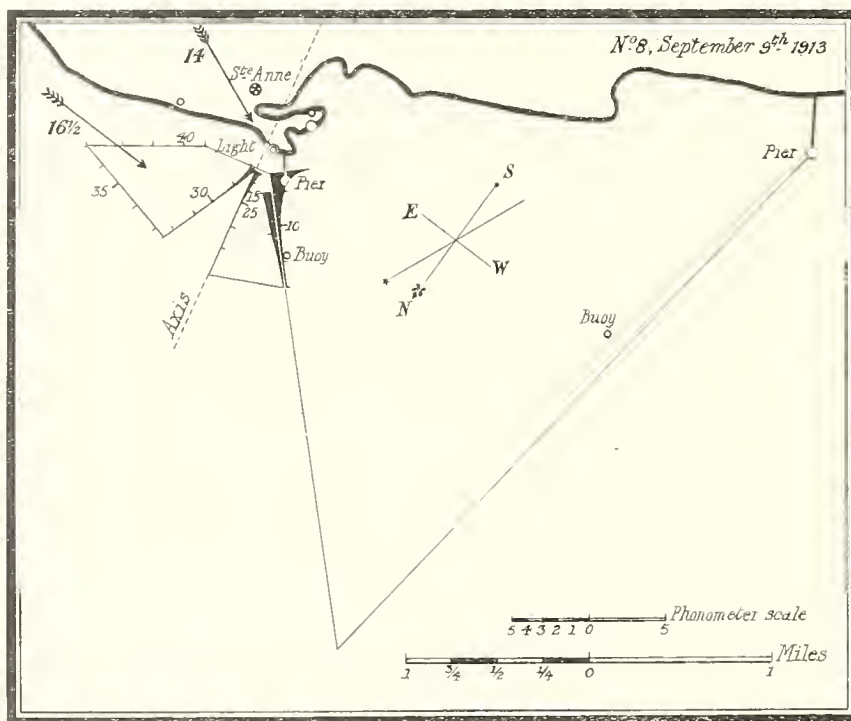


Chart 8. Acoustic survey, September 9, 1913.

more irregular eddy characteristics. On certain occasions with the wind in this quarter the alternations of warm and cool air may be distinctly felt.

No. 9. September 10, 1913. Table 9 and Chart 9.

A comparison with Chart 6 shows the unfavourable conditions for transmission of the signals set up by a wind blowing along the shore or from over the land, confirming conclusions already made.

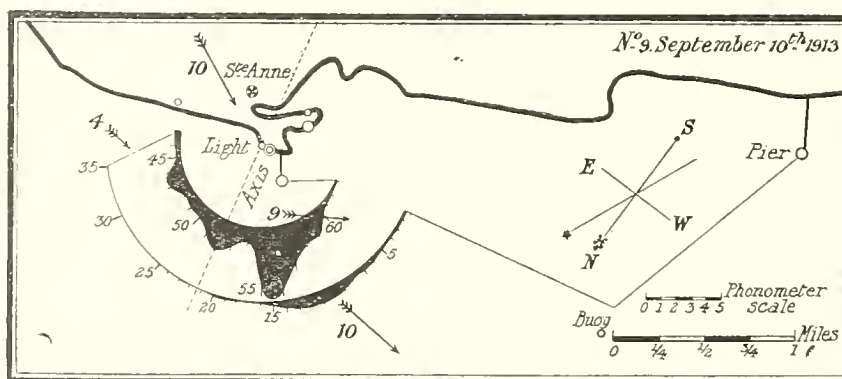


Chart 9. Acoustic survey, September 10, 1913.



No. 10. September 12, 1913. Table 10 and Chart 10.

Note the poor transmissions against the direction of the wind (observations 1 to 11). That the signal was first heard from the bridge confirms the refraction theory. The abnormally low phonometer reading at the control station is difficult to account for except that the wind was in a direction such that the

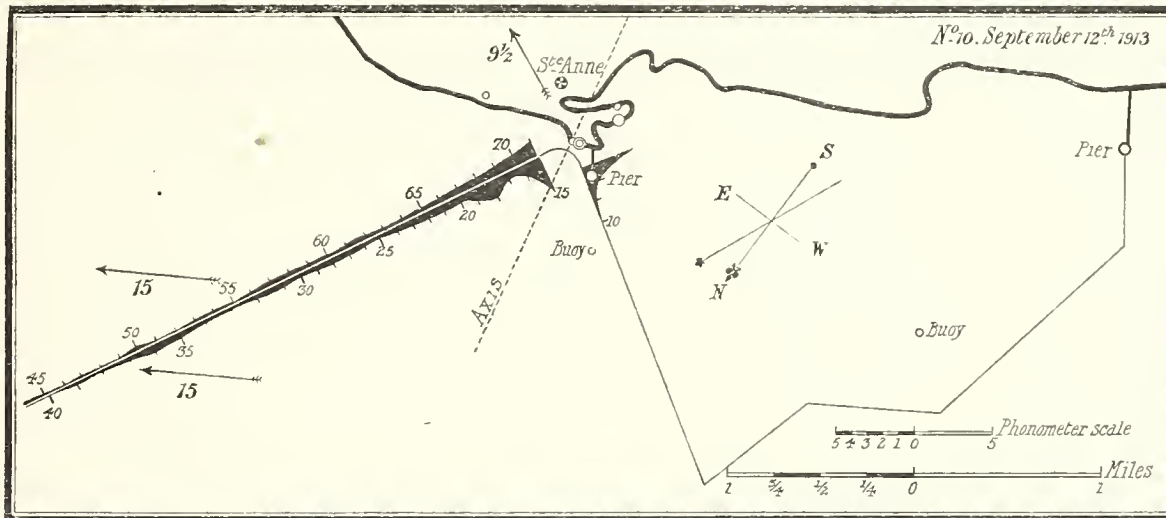


Chart 10. Acoustic survey, September 12, 1913.

influence of the lighthouse and adjoining buildings in creating eddies in the immediate neighbourhood of the diaphone trumpet was greatest. The possibility of eddies in the immediate neighbourhood of a fog-signal apparatus having an abnormally great effect in attenuating sound-waves of large amplitude should be made the subject of a special investigation.

No. 11. September 16, 1913. Table 11 and Chart 11.

Note the very poor transmission against the direction of the wind (observations 1 to 13) with relatively good conditions of propagation in a direction at right angles. In order to see to what an extent the distribution of sound was changed during a short interval of time, the same course inward and outward was

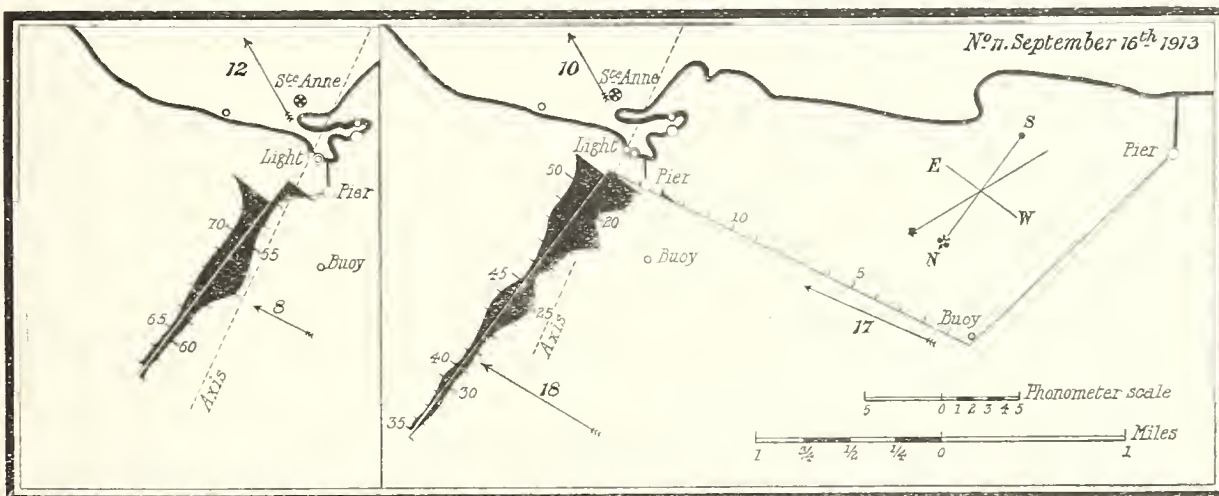


Chart 11. Acoustic survey, September 16, 1913.

repeated (observations 52 to 72). The curves show only a general resemblance. The effect of a wind in a direction opposite to that of the sound is very marked even at a distance as close as the end of Father Point wharf (1150 feet distant).

No. 12. September 17, 1913. Table 12 and Chart 12.

Note the influence of the wind in strengthening the distribution of sound in the direction in which it is blowing.

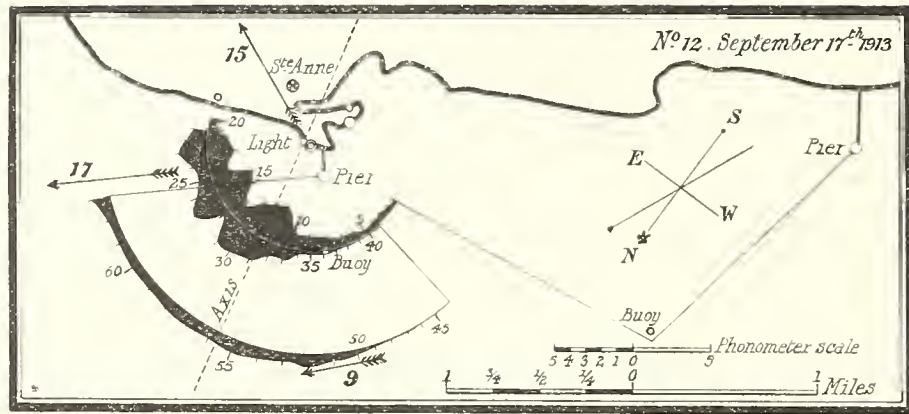


Chart 12. Acoustic survey, September 17, 1913.

No. 13. September 19, 1913. Table 13 and Chart 13.

Weather conditions unusually favourable to transmission of sound. The distribution over the circle of two miles radius is greater than can be accounted for by the inverse-square law of propagation. Note the remarkably uniform distribution over an arc of nearly 180 degrees.

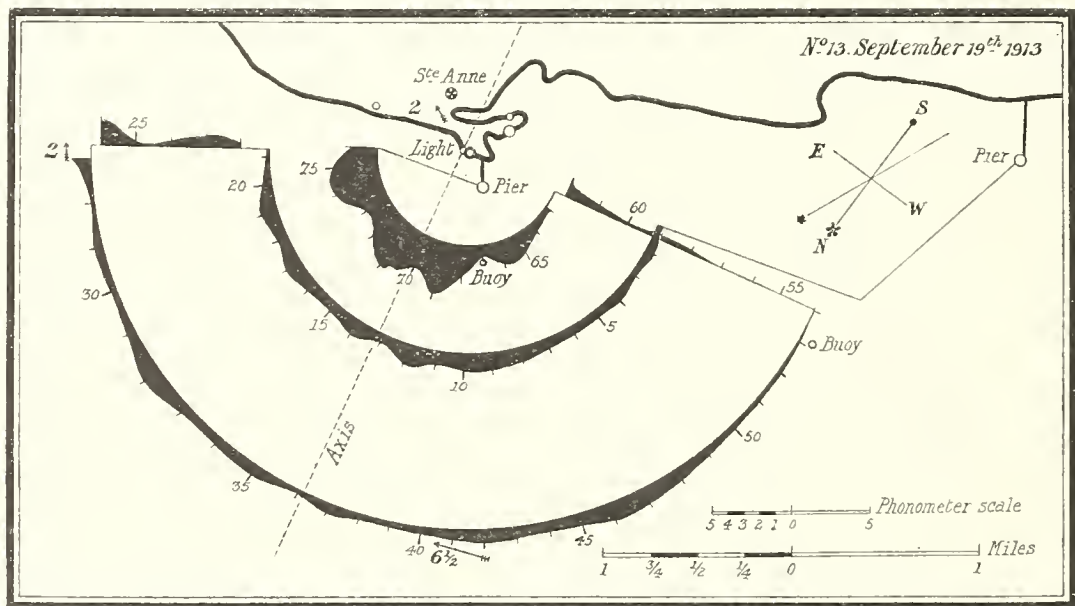


Chart 13. Acoustic survey, September 19, 1913.

No. 14. September 20, 1913. Table 14 and Chart 14.

Note the tendency to the formation of a "silent zone" (observations 30 to 33), and the enormously improved conditions of sound propagation during a temporary calm (observations 48 to 70).

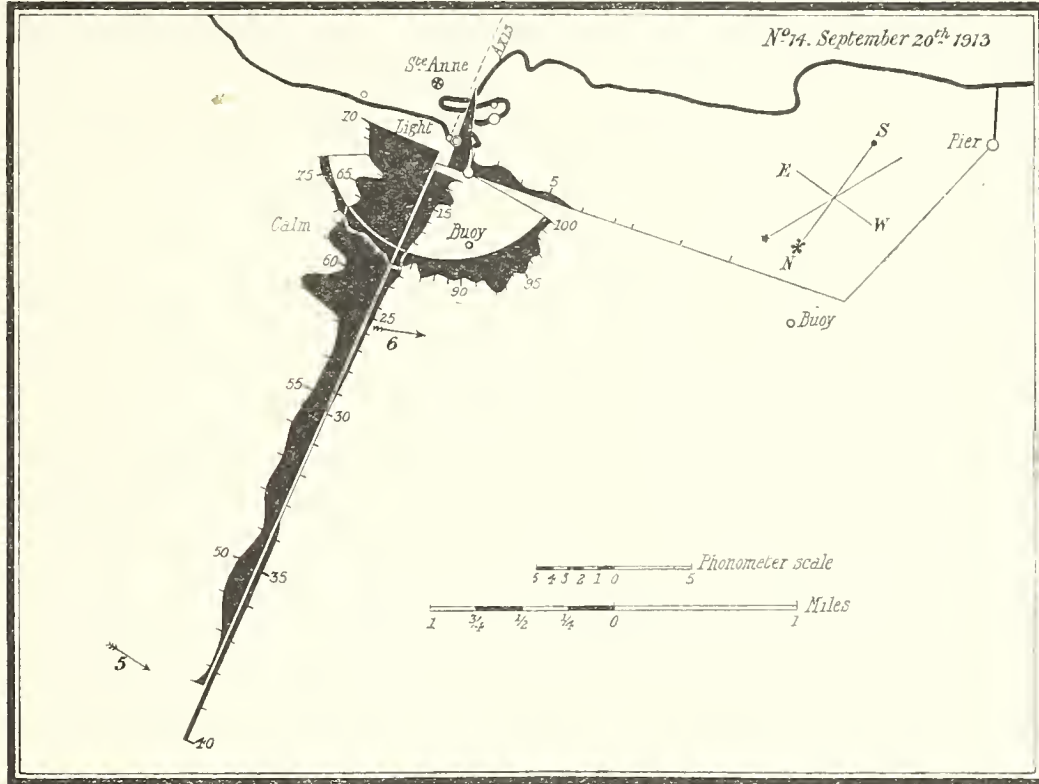


Chart 14. Acoustic survey, September 20, 1913.

(iii.) DISCUSSION OF RESULTS OF ACOUSTIC SURVEYS.

(1) Acoustic Gradients.

It will be evident from an inspection of the charts we have just described that, even on the most favourable days, the atmosphere is so far from homogeneous that the propagation of sound according to the inverse-square law is an approximation of the roughest kind. It is of considerable interest, however, to compare the actual observed gradient of phonometer readings with the theoretical gradient calculated from the acoustic output of the diaphone, assuming ideal conditions of sound propagation. If  $|\delta p|$  be the pressure amplitude at a distance  $r$  sufficiently great compared to a wave-length, the ratio of flow of energy across unit area of wave-front is very approximately given by

$$[dW/dt] = |\delta p|^2 / (2a\rho_0). \dots \dots \dots (i.)$$

Expressing the fact that the entire flow of energy across a hemisphere of radius  $r$  is equal to the acoustic output at the diaphone, we have

$$2\pi r^2 \times |\delta p|^2 / (2a\rho_0) = (\text{acoustic output}). \dots \dots \dots (ii.)$$

If  $d$  is the phonometer reading in mm., we have from the known constant of the instrument

$$|\delta p| = 0.708 d. \dots \dots \dots (iii.)$$

From a knowledge of the pressure of air operating the diaphone, we may obtain a rough estimate of the acoustic output from the results of the thermal tests 1 or 3 described in Appendix III.

In fig. (i.) are drawn on a large scale the gradients of phonometer readings obtained on August 30, 1913. According to test 1 of Appendix III., the acoustic output corresponding to an operating pressure of 19.9 lbs./sq. in. is 1.6 H.P. Expressing the distance R in feet, we obtain for the phonometer reading  $d$  the expression

$$d \text{ (mm.)} \times [R \text{ (feet)}/1000] = 19.4 \dots \dots \dots \text{ (iii.)}$$

from which the theoretical gradient shown in fig. (i.) has been drawn. It will be noticed from the

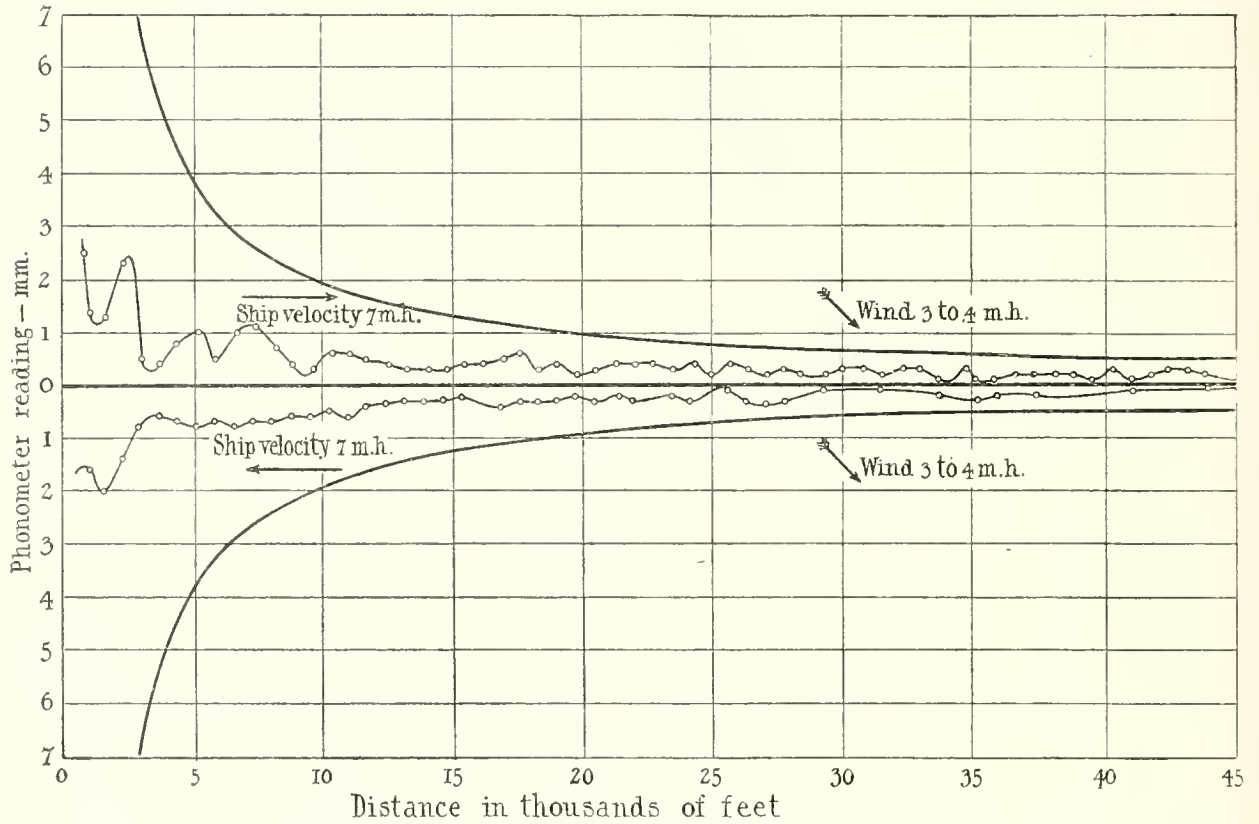


Fig. (i.). Acoustic gradient in the neighbourhood of Father Point diaphone, August 30, 1913.

comparison of the two curves that a very large proportion of the atmospheric losses occur within a radius of  $\frac{1}{2}$  mile. When once a sound-wave has traversed this distance, it is evident from fig. (i.) that on a calm day the subsequent losses are small. This conclusion is supported from an inspection of the acoustic gradients observed on other days.

The curious undulatory character of the gradient is well shown in fig. (i.), and lends support to TAYLOR'S theory respecting the effect of atmospheric eddies on the attenuation of sound. The eddies may be supposed to be travelling with the average speed of the wind (3 to 4 statute miles per hour): the undulations are produced when the observing ship crosses successive eddies. The velocity of the ship was about 7 statute miles per hour. By a simple calculation the diameter of the eddies corresponding to a light breeze of 3.5 statute miles per hour, comes out to be about 700 feet or 230 metres, a result which may not be impossibly large.\* Future observations in this connection should be carried out with a sound-generator (if possible of adjustable pitch) giving a continuous note, preferably from a ship anchored at a considerable distance from the land. Fluctuations of sound amplitude should then be measured by means of a phonometer situated at fixed distances directly to leeward and windward. In addition to obtaining wind-velocity, direction, and other meteorological data by self-registering instruments, means should be taken to observe the velocity gradient of the wind and its gustiness, from which the characteristics of the

\* According to TAYLOR ("Eddy Motion in the Atmosphere," 'Phil. Trans.,' A, 215, 1915, p. 22), the average diameter of an eddy in a wind of velocity 7 metres/sec. (21 statute miles per hour) is given as 40 metres. In light winds the diameter increases. As yet data on the subject are very incomplete.

eddy motion may be deduced.\* The gradient of temperature and water-vapour content should also be observed if possible.

(2) *Distribution of Sound over Circular Courses.*

From the phonometer observations taken over circular courses it is possible to compare at different distances the energy flux across portions of zones of spheres near the surface of the sea, subtending a small angle  $\delta\theta$  (in a vertical plane) at the fog-signal station and a horizontal angle  $\phi$  on either side of the axis of the diaphone trumpet. If  $[dW/dt]$  is the flux of energy across unit area of a spherical wave-front at a distance  $r$ , the total flux of energy across the surface just referred to is given by

$$\iint r^2 [dW/dt] \sin \theta d\theta d\phi. \dots \dots \dots (iv.)$$

Making use of (i.) we have, since  $\sin \theta$  is very nearly unity,

$$\text{energy flux} = \frac{r^2 \delta\theta}{2a\rho_0} \int_{-\phi}^{\phi} |\delta p|^2 d\phi. \dots \dots \dots (v.)$$

Since the phonometer readings were taken at approximately equal intervals over the circular courses, the integral in (v.) may be written  $2\phi [|\delta p|^2]$ , where  $[|\delta p|^2] = (0.708)^2 [d^2]$  is the mean square of the pressure amplitude between the angles  $\pm \phi$ . The value of  $\delta\theta$  is chosen somewhat arbitrarily as the angle subtended by a vertical height of 40 feet at a distance of one nautical mile. Within the solid angle thus constituted is contained the sound which may be serviceable as a warning to ships. Inserting numerical values in (v.), we have, expressing the distance R in feet,

$$\text{energy flux} = 3.47 \times 10^{-3} \cdot (R/1000)^2 \cdot 2\phi \times [d^2] \text{ watts.} \dots \dots \dots (vi.)$$

It is of some interest to compare the energy flux thus observed with the theoretical value calculated from the acoustic output of the diaphone, assuming that the sound is equally distributed in all directions throughout a hemisphere and that conditions of propagation are ideal. In these circumstances we have

$$\text{theoretical energy flux} = \sin \theta \delta\theta (2\phi/2\pi) \times (\text{acoustic output}),$$

or for purposes of numerical calculation, expressing the acoustic output in H.P., we have, inserting the value  $\delta\theta = 40/6080$ ,

$$\text{theoretical energy flux in watts} = (2\phi/2\pi) \times 4.9 \times (\text{acoustic output in H.P.}) \dots \dots (vii.)$$

The acoustic output corresponding to the air pressure operating the diaphone is obtained from the results of the thermal tests tabulated in Appendix III. Before September 13, the acoustic outputs are determined from test 1 and after September 16 from test 3, as the valves admitting air to the diaphone were readjusted in the interval. The results of the acoustic surveys taken over circular courses are tabulated below.

\* The linear hot-wire anemometer, adapted to take continuous records, would appear to be suitable for this purpose (KING, L. V., 'Phil. Mag.' vol. 29, April, 1915, pp. 556-577).

TABLE I.

Date and remarks.	R.	Observation numbers.	$[d^2]$	Energy flux in solid angle.	Theoretical energy flux.
No. 6. September 4, 1913 .	(feet) 3040	3-12 14-22	(mm.) <sup>2</sup> 1·205 0·74	watts. 0·07 0·04	watts.
$\phi = 50^\circ \quad \delta\theta = 40/6080$ .	6080	45-56 62-76	1·73 1·24	0·39 0·28	1·63
Acoustic output = 1·2 H.P. .					
No. 9. September 10, 1913 .	2600	45-60	3·72	0·18	
$\phi = 60^\circ \quad \delta\theta = 40/6080$ .	5100	8-35	0·10	0·02	2·61
Acoustic output = 1·6 H.P. .					
No. 12. September 17, 1913 .	3500	7-17 25-38	3·20 1·27	0·24 0·10	
$\phi = 50^\circ \quad \delta\theta = 40/6080$ .	7000	48-63	0·43	0·13	2·31
Acoustic output = 1·7 H.P. .					
No. 13. September 19, 1913 .	3040	65-75	4·98	0·33	
$\phi = 60^\circ \quad \delta\theta = 40/6080$ .	6080	6-20	0·66	0·18	2·77
Acoustic output = 1·7 H.P. .	12160	28-48	0·46	0·49	
No. 14. September 20, 1913 .	4000	74-96	1·44	0·17	
$\phi = 60^\circ \quad \delta\theta = 40/6080$ .	—	—	—	—	2·77
Acoustic output = 1·7 H.P. .					

The above table shows in several cases that the energy flux in the same solid angle is in some cases greater at 1 mile than at  $\frac{1}{2}$  mile (No. 6), and in one instance (No. 13) considerably greater at 2 miles than at either 1 mile or  $\frac{1}{2}$  mile. According to the inverse-square law of sound propagation, these estimates should be the same. We are obliged to conclude that contributions to the energy flux at these greater distances are made by refraction or by reflection from the upper regions of the atmosphere, and to some extent, possibly, by the sound scattered by atmospheric eddies reaching the observer from all directions.

A comparison of the last two columns of Table I. shows that within the half-mile radius a large proportion of the energy is lost, confirming the conclusion already made as to the comparatively small atmospheric losses beyond this distance.

(iv.) NOTE ON ACOUSTIC SHADOWS.

During the course of the acoustic surveys several opportunities offered of observing the effects of obstacles in giving rise to acoustic shadows.

On September 2, 1913 (see Chart 1), phonometer observations were taken on both sides of the wharf

along line VII. The wharf was 15 feet above the level of the beach and was 37 feet broad, consisting of timber cribwork filled with heavy stones.

The following readings were taken:—

- (1) 5 feet above beach and about 2 feet from nearer vertical wall . . . . . 1·1
- (2) On wharf 15 feet higher on edge nearest to signal . . . . . 2·4
- (3) On wharf at most distant edge. . . . . 1·2
- (4) In acoustic shadow 5 feet above beach and 2 feet from further vertical wall . . . . . 0·2
- (5) 10 feet from foot of wharf in acoustic shadow . . . . . 0·3
- (6) 20 feet from foot of wharf in acoustic shadow . . . . . 1·0

That the reading at position (2) at the higher level is considerably greater than that at position (1) nearer the ground may be attributed to the attenuation of the sound by the rough ground intervening between the wharf and the fog-signal.

On September 19, a few observations were taken in the neighbourhood of the lighthouse (L, Chart 1), built of concrete in the form of an octagonal cylinder about 15 feet in diameter supported by eight flying buttresses (Plate (i)). Phonometer reading on nearer side of lighthouse, 9·0, on opposite side in acoustic shadow, 4·7.

In taking observations from the C.G.S. "Lady Evelyn" it was noticed when manœuvring close to the fog-signal that whenever the fog-signal could not be viewed directly from the phonometer, owing to the interposition of one of the deck structures in the line of sight, the readings were sensibly diminished, indicating the existence of noticeable shadows.

In the case of obstacles of smaller dimensions (*e.g.*, empty sheet-iron gasoline drums, about 2 feet in diameter) no appreciable acoustic shadows could be detected.

TABLE I.—SHORT RANGE ACOUSTIC SURVEY, September 2, 1913.

*Father Point Meteorological Observations.*

Barometer, 30·22. Air temperature: dry bulb, 56° F.; wet bulb, 53° F.

Wind, very light breeze during forenoon. Velocity: 10-11 a.m., 2 miles per hour from E.; 11-12 a.m., 2 miles per hour from E.; 12-1 p.m., 9 miles per hour from E.; 1-2 p.m., 5 miles per hour from E.; 2-3 p.m., 2 miles per hour from W.; 3-4 p.m., 2 miles per hour from W.; 4-5 p.m., 4 miles per hour from W.

Weather during forenoon, clear. Few clouds visible. Sky 10 per cent. overclouded. Sky becomes overcast and wind veers about 2.30 p.m.

PHONOMETER READINGS.

*Note.*—Readings taken at positions 50 feet apart and are entered in chronological order. Position 1 is in each case 50 feet from the resonator of the diaphone. Unless otherwise indicated by a suffix, the entries are the mean of the two readings for each of the 3-second blasts. All readings, other than those enclosed in brackets ( ), were taken with resonator in position 8.

*Line II.*

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	—	11	7·0 <sub>1</sub>	21	2·1	31	3·1	41	10·1 <sub>3</sub>
2	—	12	4·7 <sub>1</sub>	22	1·4	32	2·8 <sub>6</sub>	42	11·3 <sub>3</sub>
3	10·5 <sub>1</sub>	13	4·8 <sub>1</sub>	23	1·5 <sub>1</sub>	33	3·4 <sub>3</sub>	43	8·1 <sub>6</sub>
4	9·7 <sub>1</sub>	14	4·9 <sub>1</sub>	24	1·1	34	5·6 <sub>1</sub>	44	9·2
5	10·0 <sub>1</sub>	15	4·1 <sub>1</sub>	25	1·1	35	4·5 <sub>1</sub>	45	9·7
6	9·4 <sub>1</sub>	16	4·6	26	1·2 <sub>4</sub>	36	4·4 <sub>1</sub>	46	7·9 <sub>3</sub>
7	9·5 <sub>1</sub>	17	4·9	27	1·5	37	6·2 <sub>1</sub>	47	13·8 <sub>3</sub>
8	9·3 <sub>1</sub>	18	4·0 <sub>3</sub>	28	2·9	38	7·2 <sub>1</sub>	48	(> 46)
9	8·2 <sub>1</sub>	19	3·7	29	1·9	39	9·2 <sub>6</sub>		
10	8·0 <sub>1</sub>	20	3·4	30	1·9	40	11·0		

*Remarks.*

Readings plotted on Charts 1 and 2. Wind, 2 miles per hour from E. Observations at control station, 10.27 a.m.: mean of three phonometer readings, 7·7.

1-2. Readings off scale. 24. Most distant station on Line II., 1200 feet; echo audible for 45 seconds. 39. Resonator at positions 6 and 8; readings, 4.2, and 11.0. 40. Resonator at positions 6 and 8; readings, 3.1<sub>3</sub> and 9.2<sub>6</sub>. 47. Resonator at positions 0, 2, 4, 6, and 8; readings, 8.4, 8.2, 8.4, 12.5, and 13.8. 48. Resonator at position 0, reading > 28; entry calculated for position 8 from observation 47 above.

*Line I.*

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	—	4	15.0 <sub>3</sub>	7	6.7	9	13.2	11	17.0
2	—	5	9.9	8	10.6	10	15.0	12	(33.0)
3	—	6	6.7						

*Remarks.*

Readings plotted on Chart 1. Wind, 2 miles per hour from W.

1-3. Resonator at position 0; readings off the scale. 4. Resonator at positions 0, 6, and 8; readings, 5.0, 9.1, and 15.0. 6. Most distant station of Line I., 300 feet. 11. Resonator at positions 4 and 8; readings 10.0 and 17.0. 12. Resonator at position 4; reading, 19.5; entry for position 8 calculated from observation 11 above.

*Line VIII.*

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	(36)	4	7.0	7	6.4	10	6.2	13	4.3
2	(16.0)	5	4.6	8	2.2	11	7.6	14	7.9
3	9.3 <sub>4</sub>	6	7.5	9	2.7	12	6.8	15	12.4
								16	(45)

*Remarks.*

Readings plotted on Chart 1. Wind, 2 miles per hour from E.

1. Resonator at position 4; reading, 21; entry calculated for position 8 from observation 11 of Line I. 2. Resonator at position 4; reading, 9.4; entry calculated for position 8 from observation 11 of Line I. 8. Most distant station, 400 feet. 16. Resonator at position 0; reading, 15; entry calculated for position 8 from observation 4 of Line I. Reading at end of Father Point wharf, distant 1150 feet, 2.6<sub>7</sub>.

*Line VII.*

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	(36)	6	2.5	11	2.0	16	1.75	21	3.4
2	5.4	7	3.0	12	1.6	17	2.2	22	3.9
3	6.8	8	2.4	13	1.1	18	3.2	23	2.2
4	3.8	9	2.5	14	1.0	19	2.0	24	3.0
5	2.6	10	2.8	15	1.05	20	1.9	25	10.5
								26	(37)

*Remarks.*

Readings plotted on Charts 1 and 2. Wind, 2 miles per hour from E. Sky becomes lightly clouded over.

1. Resonator at position 0; reading, 12.0; entry calculated for position 8 from observation 4 of Line I. 13. Most distant station, 650 feet. 26. Resonator at position 0; reading, 12.7; entry calculated for position 8 from observation 4 of Line I.



Line III.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	(22.5)	3	6.2	5	5.2	7	6.5	9	7.6
2	7.8	4	—	6	5.2	8	7.2	10	(19.2)

Remarks.

Readings plotted on Chart 1. Wind, 2 miles per hour from E. Time, 12.02 p.m.

1. Resonator at position 0; reading, 15.0; entry for position 8 calculated from observation 2 below. 2. Resonator at positions 0 and 8; readings, 5.2 and 7.8. 5. Most distant station, 250 feet. 10. Resonator at position 0; reading, 12.8; entry calculated for position 8 from observation 2 above. Observations at control station, 12.25 p.m.; mean of three phonometer readings, 8.0.

Line IV.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	(16.1)	13	0.7	25	0.25	37	0.2	49	1.5
2	5.8 <sub>3</sub>	14	0.4	26	0.2	38	0.2	50	2.8
3	7.8 <sub>3</sub>	15	0.6	27	0.2	39	—	51	2.75
4	4.2	16	0.5	28	0.1	40	0.3	52	3.2
5	3.4 <sub>4</sub>	17	—	29	0.2	41	—	53	3.7
6	2.6 <sub>3</sub>	18	—	30	—	42	0.4	54	—
7	2.2	19	0.25	31	—	43	0.7	55	7.3
8	1.7	20	0.25	32	—	44	0.7	56	7.8
9	1.0	21	0.2	33	—	45	0.9	57	5.0
10	0.8	22	0.25	34	0.25	46	0.7	58	7.1
11	0.7	23	0.2	35	—	47	1.1		
12	0.6	24	0.3	36	—	48	1.8		

Remarks.

Readings plotted on Chart 1. Wind, 2 miles per hour from W., and variable.

1. Resonator at position 0; reading, 5.0; entry for position 8 calculated from observation 2 below. 2. Resonator at positions 0 and 8; readings, 1.8<sub>1</sub> and 5.8<sub>3</sub>. 29. Most distant station, 1450 feet. 45. Wind changes direction. 48. Wind at right angles to direction of sound. 50. Wind along direction of sound. 55. Wind drops to calm.

Line VI.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	5.6	7	3.1	13	0.4	19	0.75	25	4.7
2	5.4 <sub>3</sub>	8	1.9	14	0.7	20	0.65	26	6.8
3	3.4	9	0.6	15	0.4	21	0.9	27	7.8
4	7.0	10	0.9	16	0.3	22	1.2	28	4.9
5	5.6	11	0.5	17	0.7	23	2.2	29	3.3 <sub>3</sub>
6	3.3	12	1.0	18	0.6	24	3.9	30	8.3 <sub>3</sub>

Remarks.

Readings plotted on Charts 1 and 2. Wind, 2 miles per hour from W., and very variable.

15. Most distant station, 750 feet. Wind from W. Thunder clouds moving up from N.W. 20. Time 2.14 p.m. Slight shower of rain commences. 28. Wind dies away completely.

Line V.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	6.4 <sub>3</sub>	7	3.6	13	1.0	19	3.6	25	6.8
2	6.4 <sub>5</sub>	8	3.0	14	0.7	20	3.4	26	9.1
3	7.7	9	2.3	15	0.85	21	3.65	27	3.8
4	7.4	10	2.7	16	0.65	22	3.35	28	7.5
5	5.2	11	1.8	17	0.85	23	4.3		
6	3.4	12	0.6	18	1.45	24	6.2		

Remarks.

Readings plotted on Charts 1 and 2. Wind, 2 miles per hour from W.

14. Most distant station, about 700 feet. Time, 3.43 p.m. Reading at end of Father Point wharf, 4.2.

TABLE 2.—SHORT RANGE ACOUSTIC SURVEY, September 4 and 5, 1913.

Father Point Meteorological Observations, September 4.

Barometer, 30.21. Air temperature: dry bulb, 47° F.; wet bulb, 43° F.

Wind: steady; 3-4 p.m., velocity 7 miles per hour from W.; 4-5 p.m., velocity 7 miles per hour from W.

Weather, clear. Sky unclouded during observations.

PHONOMETER READINGS.

Line VII.

September 4.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	2.5	6	0.6	11	0.2	16	0.3	21	1.1
2	1.4	7	0.4	12	0.4	17	0.6	22	3.5
3	1.0	8	0.4	13	0.3	18	0.7	23	4.2
4	0.8	9	0.2	14	0.4	19	1.8	24	5.0
5	0.8	10	0.2	15	0.3	20	1.0		

Remarks.

Readings plotted on Chart 2. Wind, 7 miles per hour from W. Sea smooth.

1. Time, 3.45 p.m. Boat close to end of Father Point wharf. 10. Turned back along same line. 22. Boat close to end of Father Point wharf.

Line I.

September 4.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	>20	12	3.5	23	1.5	34	3.5	45	5.5
2	17.0	13	3.8	24	1.3	35	2.3	46	5.5
3	15.0	14	5.3	25	2.3	36	1.5	47	6.5
4	10.0	15	4.3	26	1.8	37	1.5	48	5.0
5	9.0	16	2.8	27	2.3	38	1.6	49	6.0
6	8.0	17	3.0	28	3.3	39	2.0	50	7.0
7	10.0	18	1.5	29	1.0	40	3.5	51	7.5
8	8.2	19	1.5	30	3.1	41	3.0	52	7.3
9	5.0	20	1.5	31	2.0	42	3.0	53	8.5
10	5.0	21	1.5	32	3.5	43	3.8	54	9.3
11	5.0	22	1.4	33	3.0	44	4.3	55	8.0

Remarks.

Readings plotted on Chart 2. Wind, 7 miles per hour from W. Sea smooth.

1. Time, 4.18 p.m. Reading off scale. 29. Turned back along same line.

Control station.—Phonometer reading, 5.0.

Mean air-pressure operating diaphone, 19.9 lbs. per sq. inch above atmospheric.

*Father Point Meteorological Observations, September 5.*

Barometer, 29.97. Air temperature: dry bulb, 47° F.; wet bulb, 44° F.

Wind: steady; 3-4 p.m., velocity 5 miles per hour from W.; 4-5 p.m., velocity 4 miles per hour from W.; 5-6 p.m., velocity 4 miles per hour from W. Weather clear. Sky unclouded during observations.

PHONOMETER READINGS.

*Line VIII.*

September 5.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	(10.5)	17	1.7	33	1.7	49	0.6	65	5.8
2	(6.0)	18	1.1	34	1.0	50	0.9	66	5.9
3	8.4	19	1.6	35	1.1	51	1.0	67	6.5
4	6.0	20	1.6	36	1.2	52	1.4	68	6.3
5	7.8	21	1.4	37	0.8	53	1.6	69	6.0
6	4.7	22	1.4	38	0.8	54	2.4	70	6.0
7	3.0	23	2.6	39	0.4	55	2.6	71	6.8
8	2.7	24	2.5	40	0.2	56	3.3	72	9.3
9	3.5	25	3.0	41	0.3	57	3.3	73	9.0
10	2.9 <sub>5</sub>	26	2.7	42	0.7	58	3.6	74	9.6
11	1.6	27	3.3	43	0.1	59	4.3	75	10.0
12	0.9	28	2.3	44	0.3	60	3.6	76	12.5
13	1.3	29	2.3	45	0.4	61	4.4		
14	1.4	30	1.7	46	0.5	62	5.2		
15	1.1	31	1.7	47	0.3	63	4.8		
16	1.1	32	1.9	48	0.3	64	5.8		

*Remarks.*

Readings plotted on Chart 2. Wind, 5 miles per hour from W. Sea smooth.

1. Time, 4.15 p.m. 1-2. Resonator at position 0; readings, 3.5 and 2.0; entries calculated for position 8 from observation 4. Line 1 of Table 1. 44. Time, 5.10 p.m., turned back along same line.

*Line III.*

September 5.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	5.5	7	3.4	13	2.5	19	2.3	25	4.3
2	5.0	8	3.5	14	2.3	20	3.0	26	4.6
3	4.6	9	2.2	15	2.8	21	2.6		
4	4.5	10	3.1	16	1.9	22	2.7		
5	2.6	11	2.3	17	1.9	23	3.0		
6	2.2	12	2.4	18	2.3	24	3.6		

*Remarks.*

Readings plotted on Chart 2. Wind, 4 miles per hour from W. Sea smooth.

13. Turned back along same line. 26. Boat grounded on beach.

Control station.—Mean of two readings, 33.

Mean air-pressure operating diaphone at conclusion of observations, 18.3 lbs. per sq. inch above atmospheric.

TABLE 3.—LONG RANGE ACOUSTIC SURVEY, August 26, 1913.

*Father Point Meteorological Observations.*

Barometer, 30.00. Air temperature: dry bulb, 59° F.; wet bulb, 46° F.

Wind: variable in direction during observations. Velocity: 8-9 a.m. (Position Nos. 0-10), 5 miles per hour from W.; 9-10 a.m. (Position Nos. 10-69), velocity 7 miles per hour to commence with: wind veers by S. and N. to wind from E.; 10-11 a.m. (Position Nos. 69-89), velocity 10 miles per hour from E.

Weather: cloudy; clouds almost stationary. Sky 80 per cent. overcast.

## PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	—	19	2.9	37	0.3	55	—	73	0.6
2	—	20	4.8	38	0.1	56	—	74	0.7
3	0.3	21	3.2	39	0.1	57	—	75	0.5
4	0.3	22	3.4	40	0.0	58	—	76	0.3
5	0.4	23	5.0	41	0.0	59	0.0	77	0.0
6	0.5	24	4.2	42	0.2	60	0.3	78	0.0
7	0.7	25	5.2	43	0.0	61	0.3	79	0.2
8	0.4	26	4.0	44	0.3	62	0.1	80	0.0
9	0.3	27	3.8	45	0.0	63	0.1	81	0.0
10	0.5	28	3.5	46	0.0	64	0.3	82	0.0
11	0.7	29	1.0	47	0.2	65	0.3	83	0.2
12	1.2	30	0.3	48	0.2	66	0.2	84	0.3
13	1.2	31	0.2	49	0.2	67	0.2	85	0.45
14	0.6	32	0.7	50	0.1	68	0.3	86	0.9
15	0.6	33	1.1	51	0.0	69	0.2	87	1.8
16	1.5	34	0.3	52	0.0	70	0.3	88	2.6
17	1.4	35	0.2	53	—	71	0.4	89	5.0
18	2.3	36	0.4	54	—	72	0.3		

*Remarks.*

8.44 a.m. Left Rimouski wharf.

1. Signal first heard. 11. Air temperature, 50° F. 19. Ship just off Father Point wharf. 25. Time, 9.15 a.m. Course set outwards from fog-signal station. 41. Signal audible. 53-56. Escape steam blowing off: signals not heard. 57. Time, 9.47 a.m. Ship turned on course back to Father Point. 63. Air temperature, 51° F. 77. Signal just audible. Air temperature, 52° F. 89. Time, 10.10 a.m. Ship opposite Father Point wharf.

TABLE 4.—LONG RANGE ACOUSTIC SURVEY, August 30, 1913.

*Father Point Meteorological Observations.*

Barometer, 29.65. Air temperature: dry bulb, 48° F.; wet bulb, 47° F.

Wind: very light; velocity: 9-10 a.m., 3 miles per hour; 10-11 a.m., calm. Direction from W. Weather hazy. Clouds moving very slowly from W. Sky completely clouded over.

## PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
0	2.5	30	0.4	60	0.2	90	—	120	0.4
1	1.4	31	0.4	61	0.2	91	0.1	121	—
2	1.3	32	0.3	62	0.2	92	0.2	122	0.2
3	2.3	33	0.4	63	0.3	93	0.1	123	0.3
4	0.5	34	0.2	64	0.0	94	0.2	124	0.3
5	0.4	35	0.4	65	0.3	95	0.3	125	0.3
6	0.8	36	0.3	66	0.3	96	0.1	126	0.35
7	1.0	37	0.2	67	0.0	97	0.2	127	0.4
8	0.5	38	0.3	68	0.1	98	0.1	128	0.6
9	1.0	39	0.2	69	0.1	99	—	129	0.5
10	1.1	40	—	70	0.15	100	0.1	130	0.6
11	0.7	41	0.3	71	0.2	101	0.1	131	0.6
12	0.4	42	0.3	72	0.2	102	0.2	132	0.7
13	0.3	43	0.2	73	0.2	103	0.1	133	0.7
14	0.6	44	0.3	74	0.1	104	0.1	134	0.8
15	0.6	45	0.3	75	0.0	105	0.3	135	0.7
16	0.5	46	0.1	76	0.0	106	0.35	136	0.8
17	0.4	47	0.3	77	0.1	107	0.3	137	0.7
18	0.3	48	0.1	78	0.0	108	0.1	138	0.6
19	0.3	49	0.1	79	0.1	109	0.1	139	0.8
20	0.3	50	0.2	80	0.0	110	0.3	140	1.4
21	0.4	51	0.2	81	0.1	111	0.2	141	2.0
22	0.4	52	0.2	82	0.2	112	0.2	142	1.6
23	0.5	53	0.2	83	0.05	113	0.3	143	2.8
24	0.6	54	0.1	84	0.1	114	0.2	144	3.0
25	0.3	55	0.3	85	0.1	115	0.3	145	4.5
26	0.4	56	0.1	86	0.05	116	0.2		
27	0.2	57	0.2	87	0.1	117	0.3		
28	0.3	58	0.3	88	0.1	118	0.3		
29	0.4	59	0.3	89	0.2	119	0.3		

*Remarks.*

8.28 a.m. Left Rimouski wharf. Light fog over sea. Sea unruffled. Signal just audible. 8.29-8.59 a.m. Course to Father Point wharf. Signal heard over entire course. 8.56 a.m. Ship abeam Father Point wharf. Phonometer reading, 0.9. Echo audible 20 seconds.

0. Time, 9.01 a.m. Started course from fog-signal. 8. Air temperature, 50° F. Echo audible 10 seconds. 9. Sky heavily overcast; light rain. 22. Rain stops. 33. Sky overhead clears, and sun commences to shine. 37. Sun shining brightly; smoke from ship hangs low. 40. Signal not heard. 55. Breeze freshening. 64. Signal barely audible. 67-69. Signals just audible. 71-73. Time, 10.20 a.m. Ship turns at end of course. Distance from fog-signal, 8.64 nautical miles. 75-76. Signals barely audible. Air temperature, 52° F. 77. Signal just audible, but distinct. 80-81. Signal barely audible. Termination of signal distinct. 99. Signal not heard. 102. Noticeable increase in audibility. Air temperature, 50° F. 105-107. Marked increase in audibility. Sky overcast. 133. Echo of signal marked. 144. Echo audible 15 seconds.

*Control Observations.*

*End of Father Point wharf.*—Mean of four phonometer readings, 4.5. Echoes heard for 23, 19, and 21 seconds. Maximum of echo (5 to 6 seconds after termination of second blast) gave phonometer reading about 0.2. Interval between 3-second blasts not detectable in echo.

*Control station.*—Mean of nine phonometer readings, 7.0.

*Mean air pressure* operating diaphone, 19.9 lbs./sq. in. above atmospheric.

TABLE 5.—LONG RANGE ACOUSTIC SURVEY, September 3, 1913.

*Father Point Meteorological Observations.*

Barometer, 30.19. Air temperature: dry bulb, 57° F.; wet bulb, 55° F.

Wind: steady. Velocity: 10-11 a.m., 25 miles per hour; 11-12 a.m., 26 miles per hour. Direction: from W. Clouds strato-cumulus moving from W. Sky 90 per cent. overcast.

## PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	0.0	13	1.55	25	0.5	37	0.1	49	0.45
2	0.0	14	3.5	26	0.3	38	0.0	50	0.6
3	0.0	15	4.0	27	0.4	39	0.1	51	0.5
4	0.0	16	1.8	28	0.4	40	0.1	52	0.55
5	0.0	17	1.2	29	0.25	41	0.1	53	1.0
6	0.7	18	1.6	30	0.2	42	0.15	54	1.2
7	1.0	19	1.2	31	0.15	43	0.15	55	1.25
8	3.8	20	1.0	32	0.1	44	0.2	56	1.0
9	3.0	21	0.6	33	0.1	45	0.25	57	1.5
10	2.0	22	0.6	34	0.0	46	0.35	58	4.0
11	2.0	23	0.3	35	—	47	0.3	59	4.5
12	4.0	24	0.4	36	—	48	0.35	60	2.5

*Remarks.*

1. Time, 10.30 a.m. Air temperature, 58° F. Sky partly overcast by heavy clouds. Sea moderately rough; waves breaking. Slight haze noticeable. Signal first heard from navigating bridge but not on main deck 10 feet lower. 2. Signal just audible. 35. Signal just audible. 36. Time, 11.05 a.m. Sky clearing. Air temperature, 57° F. Ship turns at end of course. Signal just audible. 41. Sky clearing. Sea becomes smoother. Slight haze hanging low. 48-50. Rapid increase in audibility as estimated by ear. 55. Sun shining brightly and clouds clearing. Sea becomes much smoother. 60. Time, 11.30 a.m. Air temperature, 58° F. Ship makes for Father Point wharf.

*Control Observations.*

*End of Father Point wharf.*—Mean of three phonometer readings, 3.7. Echo, 18 seconds; maximum 4 seconds after termination of second blast.

*Control station.*—Phonometer reading, 7.3.

*Mean air pressure* operating diaphone, 18.2 lbs./sq. in. above atmospheric.

TABLE 6.—LONG RANGE ACOUSTIC SURVEY, September 4, 1913

*Father Point Meteorological Observations.*

Barometer, 30.26. Air temperature: dry bulb, 47° F.; wet bulb, 43° F.

Wind: steady. Velocity: 10-11 a.m., 5 miles per hour from N.W. 11-12 a.m., 3 miles per hour from the N.W.

Weather fairly clear. Clouds moving from W. Sky 50 per cent. clouded over.

## PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	0.0	18	0.7	35	0.0	52	1.1	69	0.9
2	0.0	19	0.6	36	0.0	53	1.7	70	1.4
3	0.0	20	0.3	37	0.0	54	1.3	71	1.2
4	0.0	21	0.3	38	0.0	55	0.9	72	1.4
5	0.0	22	0.2	39	0.0	56	0.9	73	1.8
6	0.0	23	0.0	40	0.0	57	1.2	74	1.0
7	—	24	0.0	41	0.1	58	1.2	75	1.1
8	0.6	25	0.0	42	0.15	59	—	76	1.2
9	2.0	26	0.0	43	0.3	60	1.5	77	0.8
10	2.0	27	0.0	44	1.0	61	1.1	78	0.3
11	1.8	28	0.0	45	1.4	62	0.7	79	0.4
12	0.6	29	0.0	46	1.4	63	1.1	80	0.55
13	0.8	30	0.0	47	1.2	64	1.2	81	0.3
14	1.2	31	0.0	48	1.7	65	0.7	82	—
15	1.6	32	0.0	49	1.7	66	0.9	83	—
16	0.6	33	0.0	50	1.1	67	0.8		
17	1.1	34	0.0	51	1.0	68	0.7		

*Remarks.*

9.52 a.m. Left Rimouski wharf. Sea smooth. Sun shining brightly. Air temperature, 50° F.

1. Start of circular course at  $\frac{1}{2}$  mile distance from fog-signal station.

3. No signal heard. 4-6. Signal just audible. 12-13. Time at position 12, 10.21 a.m. Ship turning at end of course. Phonometer in acoustic shadow of deck house. 23. Signal just audible. Father Point wharf obstructing. 24-27. Signals barely audible. 28-37. Time at position 28, 10.38 a.m. Course along radius to 1 mile circular course. No signals heard along this course. 38. Signal just audible. 39. Signal not heard. 40. Signal just audible. 58-59. Time at position 58, 11.09 a.m. Ship turning back along 1 mile circular course. 82. Signal not heard. 83. Time 11.38 a.m. Ship turns back to Father Point wharf. Air temperature, 49° F.

*Control Observations.*

*End of Father Point wharf.*—Mean of six phonometer readings, 4.2. Echoes audible about 8 seconds and faint.

*Control station.*—Phonometer reading, 6.4.

*Mean air pressure* operating diaphone, 17.6 lbs./sq. in. above atmospheric.

TABLE 7.—LONG RANGE ACOUSTIC SURVEY, September 5, 1913.

*Father Point Meteorological Observations.*

Barometer, 29·97. Air temperature: dry bulb, 47° F.; wet bulb, 44° F. Wind: velocity, 10-11 a.m., 6 miles per hour from E.; 11-12 a.m., 3 miles per hour from E.

Weather, partly clear. Clouds moving from W. Sky 80 per cent. clouded over.

## PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	—	15	0·6	29	0·6	43	0·15	57	0·2
2	—	16	0·7	30	0·5	44	0·0	58	0·15
3	—	17	0·8	31	—	45	0·05	59	0·2
4	—	18	1·1	32	0·3	46	0·1	60	0·2
5	0·1	19	1·3	33	0·25	47	0·15	61	0·3
6	0·1	20	1·1	34	0·2	48	0·15	62	0·45
7	0·2	21	2·0	35	0·15	49	0·1	63	0·7
8	0·25	22	2·7	36	0·1	50	0·15	64	1·3
9	0·25	23	4·0	37	0·1	51	0·1	65	1·6
10	0·3	24	5·3	38	0·2	52	0·1	66	2·0
11	0·3	25	6·0	39	0·3	53	0·15		
12	0·3	26	3·0	40	0·1	54	0·25		
13	0·4	27	1·0	41	0·1	55	0·2		
14	0·5	28	0·4	42	0·1	56	0·3		

*Remarks.*

10.23 a.m. Left Rimouski wharf. Sea smooth, showing regions ruffled by variable breezes. Sky overcast by light fleecy clouds. Air temperature, 47° F.

1. Time, 10.53 a.m. Course set towards fog-signal. Signal not heard. Air temperature, 46° F.

2-4. Signals not heard.

14-16. Signals show marked increase in audibility. 25. Time, 11.16 a.m.; ship turning along new course. 44. Signals just audible. 45. Time, 11.38 a.m.; ship turning back along same course; air temperature, 48° F. 66. Time, 11.58 a.m. Ship turns in to Father Point wharf; air temperature, 52° F.

*Control Observations.*

*End of Father Point wharf.*—Mean of four phonometer readings, 4·2.

*Control station.*—Mean of four phonometer readings, 6·8.

*Mean air-pressure* operating diaphone, 18·3 lbs./sq. in. above atmospheric.



TABLE 8.—LONG RANGE ACOUSTIC SURVEY, September 9, 1913.

*Father Point Meteorological Observations.*

Wind : velocity, 10-11 a.m., 14 miles per hour from E. ; 11-12 a.m., 14 miles per hour from E.

Weather partly clear. Clouds moving from N. Sky 80 per cent. clouded over.

## PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	—	7	—	13	1.2	19	—	25	0.0
2	—	8	0.0	14	1.2	20	—	26	0.2
3	—	9	0.0	15	0.4	21	—	27	0.6
4	—	10	0.2	16	0.2	22	—	28	0.5
5	—	11	0.7	17	0.0	23	—	29	0.1
6	—	12	2.3	18	—	24	—	30	0.0

*Remarks.*

10.15 a.m. Left Rimouski wharf. Sea moderate ; waves breaking. Sky overcast by light clouds. Air temperature, 52° F.

4. Signal distinctly heard from bridge but not from deck. 5-6. Inaudible from deck. 7. Signal distinctly heard from bridge but not from deck. 8. Signal first heard from deck. 9. Audible. 12. Time, 10.56 a.m. ; ship turning back along same course. 13-14. Phonometer in acoustic shadow of deck house. 17-19. Inaudible. 20. Barely audible. 21. Inaudible. 22. Time, 11.06 a.m. ; course back to fog-signal ; signal barely audible. 23-24. Just audible. 25. Audible. 27. Time, 11.11 a.m. ; course outwards from fog-signal. 30. Signal just audible. 31. Signal not heard. 32. Time, 11.17 a.m., course changed ; signal not heard. 33-34. Inaudible. 35. Barely audible. 36. Time, 11.21 a.m. ; course changed towards fog-signal ; signal inaudible. 37. Inaudible. 38. Barely audible. 39-40. Just audible. 41. Time, 11.26 a.m. ; air temperature, 53° F.

*Control Observations.*

*End of Father Point wharf.*—Mean of six phonometer readings, 2.5. No echoes heard.

*Control station.*—Mean of four phonometer readings, 7.5.

*Mean air pressure* operating diaphone, 18.3 lbs./sq. in. above atmospheric.

TABLE 9.—LONG RANGE ACOUSTIC SURVEY, September 10, 1913.

*Father Point Meteorological Observations.*

Wind: 10-11 a.m., velocity, 4 miles per hour from E. 11-12 a.m., 10 miles per hour from E.

Weather, clear. Clouds, none.

## PHONOMETER READINGS.

Position No.	Phono- meter.	Position No.	Phono- meter.	Position No.	Phono- meter.	Position No.	Phono- meter.	Position No.	Phono- meter.
1	0·15	14	0·3	27	0·0	40	—	53	1·3
2	0·15	15	0·2	28	0·0	41	—	54	1·0
3	0·06	16	0·1	29	—	42	—	55	4·0
4	0·1	17	0·1	30	—	43	—	56	4·2
5	0·1	18	0·1	31	—	44	0·3	57	2·6
6	0·3	19	0·05	32	—	45	0·3	58	1·6
7	0·35	20	0·15	33	—	46	1·0	59	1·6
8	0·25	21	0·0	34	—	47	1·2	60	0·9
9	0·6	22	0·0	35	—	48	0·6	61	0·4
10	0·7	23	0·05	36	—	49	0·9	62	0·3
11	0·7	24	0·0	37	—	50	0·8	63	0·1
12	0·7	25	0·0	38	—	51	1·5		
13	0·6	26	0·0	39	0·15	52	2·0		

*Remarks.*

10.38 a.m. Left Rimouski wharf. Sea smooth. Sky unclouded. Air temperature, 50° F.

1. Time, 10.51 a.m. Commencement of circular course at 1 mile. 6. Air temperature, 47° F. 9. Fog-signal in line with end of Father Point wharf. 26. Audible. 29-32. Barely audible. 33-34. Audible. 35. Time, 11.29 a.m. Course altered. Signal barely audible. 43. Time, 11.37 a.m. Commencement of circular course at  $\frac{1}{2}$  mile. 58. Ship enters acoustic shadow of wharf. 59. Wind drops to a light breeze. 63. Time, 11.56 a.m. End of circular course. Ship turns to Father Point wharf. Air temperature, 50° F.

*Control Observations.**End of Father Point wharf.*—Phonometer reading, 5·0. Slight echo audible.*Control station.*—Phonometer reading, 9·3.

TABLE 10.—LONG RANGE ACOUSTIC SURVEY, September 12, 1913.

*Father Point Meteorological Observations.*

Wind: velocity, 10-11 a.m., 10 miles per hour from W.; 11-12 a.m., 9 miles per hour from W.

Weather, cloudy. Clouds almost stationary. Sky completely overcast.

## PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	—	16	0·7	31	0·2	46	0·0	61	0·2
2	0·0	17	0·3	32	0·1	47	0·1	62	0·2
3	0·0	18	0·9	33	0·1	48	0·1	63	0·15
4	0·0	19	0·6	34	0·05	49	0·1	64	0·2
5	0·0	20	0·3	35	0·2	50	0·2	65	0·3
6	0·0	21	0·4	36	0·3	51	0·1	66	0·3
7	0·0	22	0·3	37	0·1	52	0·1	67	0·4
8	—	23	0·3	38	0·05	53	0·15	68	0·4
9	—	24	0·2	39	0·1	54	0·2	69	0·6
10	0·0	25	0·1	40	0·0	55	0·1	70	0·8
11	0·1	26	0·2	41	0·0	56	0·15	71	1·0
12	0·7	27	0·2	42	0·0	57	0·3	72	1·4
13	3·3	28	0·2	43	0·0	58	0·3	73	2·0
14	1·5	29	0·2	44	0·1	59	0·2		
15	2·1	30	0·1	45	0·1	60	0·15		

*Remarks.*

10.42 a.m. Left Rimouski wharf. Sea smooth. Sky completely overcast by heavy clouds. Air temperature, 52° F.

1. Time, 11.0 a.m. Signal first heard from deck. 2-3. Just audible. 4. Audible. 5-7. Just audible. 8. Inaudible. 9. Barely audible. 10. Audible. 14. Phonometer in acoustic shadow of deck house. 15. Time, 11.14 a.m. Ship turns to take up course away from fog-signal. 16-17. Phonometer in acoustic shadow of deck house. Echo audible for about 6 seconds. 41. Time, 11.43 a.m. Ship turns back along same course. 71. Ship turns into Father Point wharf. Air temperature, 51° F.

*Control Observations.*

*End of Father Point wharf.*—Mean of five phonometer readings, 1·0.

*Control station.*—Phonometer reading, 3·9.

*Mean air pressure* operating diaphone, 22·6 lbs./sq. in. above atmospheric.

TABLE 11.—LONG RANGE ACOUSTIC SURVEY, September 16, 1913.

*Father Point Meteorological Observations.*

Barometer, 30.49. Air temperature: dry bulb, 52° F.; wet bulb, 48° F.

Wind: 9-10 a.m., velocity, 12 miles per hour from W.; 10-11 a.m., 13 miles per hour from W.

Weather, clear. Clouds, none.

## PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	—	16	3.5	31	0.3	46	0.3	61	0.2
2	—	17	5.0	32	0.1	47	0.6	62	0.3
3	—	18	2.0	33	0.0	48	1.1	63	0.3
4	—	19	2.0	34	0.0	49	1.3	64	0.3
5	—	20	1.0	35	0.1	50	1.4	65	0.2
6	—	21	2.3	36	0.2	51	2.3	66	0.4
7	—	22	0.9	37	0.1	52	2.0	67	0.6
8	—	23	0.7	38	0.2	53	0.3	68	0.8
9	—	24	0.4	39	0.5	54	0.5	69	0.8
10	—	25	1.2	40	0.3	55	0.8	70	0.9
11	—	26	0.8	41	0.3	56	1.5	71	1.2
12	—	27	0.3	42	0.4	57	1.6	72	2.6
13	0.2	28	0.2	43	0.8	58	0.6		
14	1.0	29	0.3	44	0.8	59	0.3		
15	4.0	30	0.2	45	0.3	60	0.3		

*Remarks.*

9.27 a.m. Left Rimouski wharf. Sea moderate; waves breaking. Sky perfectly clear. Air temperature, 54° F.

1. Time, 9.42 a.m. Signal first heard. 2-10. Signals barely audible. 11. Just audible. 12. Audible. 18. Time, 9.59 a.m. Ship starts on course away from fog-signal. 33. Time, 10.17 a.m. Ship turns back along the same course. 45. Sky becomes slightly overcast. 51. Time, 10.35 a.m. Ship turns back along same course. 53. Phonometer in acoustic shadow of deck house. 62. Time, 10.47 a.m. Ship turns back towards fog-signal. 72. Ship turns into Father Point wharf. Air temperature, 54° F.

*Control Observations.**End of Father Point wharf.*—Mean of four phonometer readings, 1.5.*Control station.*—Mean of four phonometer readings, 6.5.*Mean air pressure* operating diaphone, 19.7 lbs./sq. in. above atmospheric.

TABLE 12.—LONG RANGE ACOUSTIC SURVEY, September 17, 1913.

*Father Point Meteorological Observations.*

Barometer, 30·14. Air temperature: dry bulb, 54° F.; wet bulb, 52° F.  
 Wind: 10-11 a.m., velocity, 11 miles per hour from W.; 11-12 a.m., 15 miles per hour from W.  
 Weather, cloudy. Clouds moving from W. Sky completely clouded over.

PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	0·2	14	0·8	27	2·0	40	0·0	53	0·6
2	0·2	15	2·0	28	0·5	41	—	54	0·7
3	0·3	16	2·3	29	1·8	42	—	55	0·8
4	0·2	17	0·9	30	1·8	43	—	56	0·7
5	0·1	18	1·6	31	1·6	44	0·0	57	0·8
6	0·3	19	1·0	32	0·9	45	0·0	58	0·7
7	0·35	20	0·6	33	0·9	46	0·0	59	0·6
8	0·5	21	0·6	34	0·3	47	0·0	60	0·6
9	0·7	22	—	35	0·3	48	0·0	61	0·5
10	0·8	23	1·6	36	0·3	49	0·1	62	0·6
11	2·3	24	0·9	37	0·2	50	0·3	63	1·2
12	2·1	25	0·8	38	0·0	51	0·5		
13	1·8	26	1·4	39	0·0	52	0·8		

*Remarks.*

10.29 a.m. Left Rimouski wharf. Sea smooth. Sky completely overcast. Smoke from ship hangs low. Air temperature, 56° F.

1. Time, 10.48 a.m. Ship commences circular course at ½-mile radius. 6. Ship clear of acoustic shadow of wharf. 12. Echoes marked, audible for 10 seconds. 21. Time, 11.08 a.m. Ship turns back along same course. 38-39. Signals audible. 40. Signal barely audible. 41-43. Ship turns outward from fog-signal to take up circular course at 1 mile radius. Signals inaudible. 44. Time, 11.32 a.m. Ship commences circular course. Signal inaudible. 45-46. Signals just audible. 47. Signal audible. 63. Time, 11.51 a.m. Ship turns into Father Point wharf. Air temperature, 54° F.

*Control Observations.*

*End of Father Point wharf.*—Mean of three phonometer readings, 1·8.  
*Control station.*—Phonometer reading, 4·9.  
*Mean air pressure* operating diaphone, 24·7 lbs./sq. in. above atmospheric.

TABLE 13.—LONG RANGE ACOUSTIC SURVEY, September 19, 1913.

*Father Point Meteorological Observations.*

Wind : 8-10 a.m., average velocity 2 miles per hour from W.

Weather, clear. No clouds.

## PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	0.2	17	1.0	33	0.7	49	0.5	65	1.3
2	0.4	18	0.7	34	0.6	50	0.2	66	1.4
3	0.3	19	1.0	35	0.7	51	0.2	67	0.8
4	0.5	20	—	36	0.2	52	0.1	68	1.8
5	0.4	21	0.3	37	0.6	53	0.1	69	3.2
6	0.5	22	0.3	38	0.3	54	—	70	2.0
7	0.5	23	0.7	39	0.3	55	—	71	3.2
8	0.8	24	0.3	40	0.4	56	0.0	72	2.2
9	0.9	25	0.2	41	0.6	57	0.0	73	1.6
10	1.0	26	1.6	42	0.8	58	0.3	74	3.1
11	0.7	27	1.2	43	0.7	59	0.2	75	2.8
12	1.2	28	0.3	44	0.6	60	0.2	76	1.7
13	0.5	29	0.6	45	0.7	61	0.5		
14	0.9	30	0.4	46	1.1	62	1.0		
15	0.6	31	0.6	47	1.0	63	—		
16	—	32	1.3	48	0.6	64	0.6		

*Remarks.*

8.40 a.m., left Rimouski wharf. Sea smooth. Sky unclouded. Very light breeze. Air temperature, 59° F.

1. Time, 8.55 a.m. Commencement of circular course at 1 mile radius. 21. Time, 9.12 a.m. Course away from fog-signal. 26. Time, 9.18 a.m. Commencement of circular course at 2 miles radius. 54. Time, 9.48 a.m. Course towards fog-signal. Signal barely audible. 56. Signal just audible. 57. Audible. 63. Time, 9.58 a.m. Commencement of circular course at  $\frac{1}{2}$  mile radius. 68. Marked echo : audible for 10 seconds. 76. Time, 10 11 a.m. Course set towards Father Point wharf. Air temperature, 53° F.

*Control Observations.**End of Father Point wharf.*—Mean of four phonometer readings, 5.0. Echoes audible for 20 seconds.*Control station.*—Phonometer reading, 6.8.*Mean air pressure* operating diaphone, 24.7 lbs./sq. in. above atmospheric.

TABLE 14.—LONG RANGE ACOUSTIC SURVEY, September 20, 1913.

PHONOMETER READINGS.

Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.	Position No.	Phono-meter.
1	—	21	0.7	41	0.4	61	3.2	81	0.3
2	0.0	22	0.4	42	0.2	62	3.0	82	0.5
3	0.0	23	0.3	43	0.25	63	3.0	83	0.6
4	0.05	24	0.3	44	0.15	64	2.4	84	1.0
5	0.6	25	0.2	45	0.2	65	3.2	85	0.9
6	0.5	26	0.3	46	0.5	66	2.6	86	0.5
7	1.0	27	0.2	47	0.1	67	4.0	87	1.2
8	1.0	28	0.1	48	0.25	68	4.5	88	0.9
9	5.5	29	0.1	49	1.1	69	4.7	89	1.2
10	—	30	0.05	50	1.2	70	5.0	90	1.2
11	2.3	31	0.0	51	0.6	71	1.2	91	1.6
12	2.0	32	0.0	52	1.4	72	0.6	92	2.4
13	1.2	33	0.0	53	1.2	73	—	93	2.4
14	2.0	34	0.3	54	1.6	74	0.6	94	1.8
15	0.9	35	0.3	55	1.2	75	0.6	95	2.0
16	1.0	36	0.3	56	1.0	76	0.3	96	1.6
17	0.9	37	0.2	57	1.4	77	0.6	97	1.6
18	0.7	38	0.2	58	3.2	78	0.4	98	0.6
19	0.4	39	0.15	59	2.9	79	0.7	99	—
20	0.4	40	0.2	60	2.5	80	0.3	100	0.6

Remarks.

10.13 a.m. Left Rimouski wharf. Sea smooth. Sky unclouded. Slight breeze from E. Air temperature, 52° F.

1. Signal first heard from bridge. 2. Signal first heard from deck: barely audible. 3. Audible. 12. Time, 10.35 a.m. Start of course away from fog-signal. 17. Echo audible about 25 seconds. 31-32. Audible. 33. Just audible. 40. Time, 11.06 a.m. Ship turns back along same course. 42. Ship stopped; fog-signal on port side. 43. Ship stopped; fog-signal straight ahead. 44. Ship stopped; fog-signal on starboard side. 45. Ship stopped; fog-signal straight ahead. 46. Ship starts in course towards Father Point. 67. Air temperature, 56° F. 70. Time, 11.40 a.m. Course altered to take up circular course at ½ mile radius. 71-73. Phonometer in acoustic shadow of deck house. 74. Time, 11.43 a.m. Commencement of circular course at ½ mile. 98. Ship enters acoustic shadow of wharf. 100. Time, 12.09 p.m. Course set for Father Point wharf. Air temperature 58° F.

Control Observations.

End of Father Point wharf.—Mean of two phonometer readings, 3.75.

Control station.—Mean of two phonometer readings, 7.1.

Mean air-pressure operating at conclusion of observations, 24.6 lbs./sq. in. above atmospheric.

NOTE.—Observations 42-45 were taken with a view to determining whether the effect of the ship's hull when presented broadside and bow-on was noticeable on the intensity of the sound as measured at the phonometer. It was concluded that within the limits of variation due to changing atmospheric conditions such an effect is not noticeable.

## APPENDIX III.—ON THE THERMODYNAMIC MEASUREMENT OF ACOUSTIC EFFICIENCY.

## (i.) GENERAL PROCEDURE IN TAKING OBSERVATIONS.

The construction of the open-wound resistance thermometers employed in measuring temperature differences is clearly shown in the Plate (iv.). That on the low-pressure side of the diaphone ( $S_0$ ) was situated about 5 inches from the edge of the piston, while that on the high-pressure side (R) was situated in the large valve admitting the "sounding air," as shown diagrammatically in fig. 3. Electrical connection to the Wheatstone bridge was made through an automobile spark-plug inserted in the cover plate of the valve. At the beginning and end of a series of observations a test was made of the insulation of the wire grids. It was found that after a long series of observations the high-pressure thermometer became slightly damp if left in position over night, owing to the accumulation in the large valve, in which it was situated, of moisture brought over with the air from the storage tanks. It was thus necessary on commencing a test to thoroughly dry out the high-pressure thermometer; the insulation then remained satisfactory during the entire series of observations occupying about three hours.

During the series of observations the gas-engine operating the compressors were kept running continuously until the highest pressure to be employed in the tests had been attained. During this interval the mercury manometer connected to the storage tanks was read at known intervals, so that the rate of pressure increase could be determined at each pressure. The small relay-valve connected to the large valves admitting the "driving" and "sounding" air to the diaphone was operated by one of the observers (H. H. H.) to give a 6-second blast as determined by an accurate stop-watch. The same observer also noted accurately the fall of the mercury manometer in this interval. At the same time the writer noted the deflection of the galvanometer of the Wheatstone bridge to which the differential thermometers were connected. Each observation was repeated, the battery current of the Wheatstone bridge being reversed in the interval. The mean pressure fall in the 6-second interval is entered in the accompanying tables together with the difference of resistances of the differential thermometers corresponding to the observed galvanometer deflections.

After a series of observations with the diaphone sounding has been taken, the diaphone piston was removed and three small pieces of rubber packing inserted between the down-stream face of the driving head and the opposite face of the cylinder. By means of a set-screw inserted in the centre of the cover-plate the piston as a whole was not only prevented from vibrating but could be moved forward slightly against the pressure of the rubber cushions until the opposing ports were in such a position that the pressure-fall of the manometer in 6 seconds was the same at a given pressure as when the diaphone was allowed to sound, indicating that the air consumption in the two cases was the same. This adjustment was made at about 20 lbs. pressure (atmospheric); an inspection of the series of pressures recorded in the accompanying tables shows that, except at some of the higher pressures, the two series agree fairly well throughout. Test No. 1 was carried out without any alteration of the existing adjustments. Test No. 2 was carried out with the large valve admitting sounding air set so that the air consumption was roughly halved. Before commencing Test No. 2, the diaphone piston was removed and carefully cleaned and lubricated. The sounding-valve was then adjusted until the diaphone emitted its clearest and smoothest note as judged by the ear. A comparison of the data given in Tests 1 and 3 shows that at the same pressure the rate of air consumption is somewhat greater in the latter. The acoustic efficiency is considerably improved in Test 3. Test 4 was carried out with the rate of air consumption about halved. In Test 5 the supply of sounding-air was turned off and the compressors stopped. The air from the storage tanks was then allowed to reciprocate the piston only. The fall of the pressure manometer in known intervals of time enables the rate of air consumption to be calculated. It will be noticed that only a comparatively small proportion of air is required to operate the diaphone piston. Unfortunately, temperature readings were not taken during this test. An upper limit to the rate at which energy is consumed in driving the piston may be made from the results of Test 4.



(ii.) MEASUREMENT OF PRESSURE AND AIR CONSUMPTION.

Pressure was measured by a mercury gauge connected to the storage tanks. During the 6-second blast required for the resistance thermometers to take up their final temperatures, the mercury column fell through a measured distance from which the air consumption could be calculated. Let the pressure fall from  $p_1$  to  $p'_1$ . If  $\rho_1$  and  $\rho'_1$  be the corresponding densities, we have by BOYLE'S law

$$p_1 - p'_1 = (\rho_1 - \rho'_1) R\Theta_1, \dots \dots \dots (i.)$$

$\Theta_1$  being the temperature of the air in the storage-tanks and  $R$  the gas constant. If we denote by  $\dot{M}$  the rate of mass-flow of air during a blast of  $t$  seconds, and by  $V$  the total value of the storage tanks, we have

$$\dot{M}t = V (\rho_1 - \rho'_1). \dots \dots \dots (ii.)$$

Under standard conditions of pressure and temperature we have

$$p_0 = \rho_0 R\Theta_0, \dots \dots \dots (iii.)$$

so that from (i.), (ii.), and (iii.) we have for the rate of air consumption

$$\frac{\dot{M}\Theta_1}{\rho_0} = \frac{(p_1 - p'_1)}{p_0} \frac{V\Theta_0}{t}. \dots \dots \dots (iv.)$$

The volume of each of the storage tanks was calculated to be 282 cubic ft., so that

$$V = 846 \text{ cubic ft.} = 2.39 \times 10^6 \text{ cm.}^3.$$

Throughout all the observations the duration of blast was  $t = 6$  seconds. The pressure drop varied from 4 to 12 cms., and could be read with ease to half a millimetre. Allowance was made at each observation for the rate at which the pressure was increasing during the 6 seconds owing to the continuous operation of the compressors. The temperature of the air in the tanks was taken at  $15^\circ \text{ C.}$  throughout, a value observed during one of the tests by the resistance thermometers. The air consumption in cubic feet per second under standard conditions of pressure and temperature is then given by (iv.) in the form

$$\frac{\dot{M}}{\rho_0} = \frac{(p_1 - p'_1)}{76} \times \frac{846}{6} \times \frac{273^0}{288^0} = 1.76 \times (p_1 - p'_1) \text{ cubic ft./sec.} \dots \dots \dots (v.)$$

The output of a siren of unit efficiency as determined by formula (45) is given by

$$\dot{W} = JC_v \dot{M}\Theta_1 \left[ 1 - (p_0/p_1)^{\frac{\gamma-1}{\gamma}} \right]. \dots \dots \dots (vi.)$$

Remembering that  $JC_v(\gamma - 1) = R = p_0/(\rho_0\Theta_0)$ , and making use of (iv.), we may write equation (vi.) in the form

$$\dot{W} = \frac{(p_1 - p'_1)}{t} \cdot \frac{V}{\gamma - 1} \left[ 1 - (p_0/p_1)^{\frac{\gamma-1}{\gamma}} \right].$$

If  $(p_1 - p'_1)$  be measured in centimetres of mercury, we have for numerical reduction

$$\dot{W} = \frac{(p_1 - p'_1) \times 13.6 \times 981}{6 \times 0.4} \times \frac{2.39 \times 10^6}{7.46 \times 10^9} \left[ 1 - (p_0/p_1)^{\frac{\gamma-1}{\gamma}} \right] \text{ H.P.}$$

$$\dot{W} = 17.8 \times (p_1 - p'_1) \times \left[ 1 - (p_0/p_1)^{\frac{\gamma-1}{\gamma}} \right] \text{ H.P.} \dots \dots \dots (vii.)$$

In calculating the last factor we write for  $p_1$  the mean pressure (above vacuum) between the beginning and end of the 6-second blast.

(ii.) ON THE MEASUREMENT OF TEMPERATURES.

The construction of the resistance thermometers employed in measuring the fall of air temperatures passing through the diaphone is briefly described in § 12. Although an attempt was made to make the high-pressure thermometer (of resistance  $R_0$  at  $0^\circ$  C.) of exactly the same resistance as the low-pressure instrument (of resistance  $S_0$  at  $0^\circ$  C.) it was found on making a careful measurement that

$$R_0 = 85.044 \text{ ohms,} \quad S_0 = 82.095 \text{ ohms.}$$

The temperature coefficient of the iron wire employed as determined by Mr. A. A. SCOTT\* was  $\alpha = 0.004964$ . The thermometers  $R_0$  and  $S_0$  were connected by leads of heavy copper wire, of resistances 0.15 and 0.25 ohms respectively, so as to form two arms of a Wheatstone bridge. The ratio coils of the bridge were of resistances 100.84 and 100.81 ohms, sufficiently close together in value as to be considered equal. In series with  $S_0$  was inserted a magnanin resistance box subdivided into tenths of an ohm. A portable Weston galvanometer of 217 ohms resistance and sensitivity of  $10^{-6}$  amperes was employed to determine the balance of the Wheatstone bridge. In taking readings of temperature differences with the diaphone sounding and silent, a rough balance was obtained by adjusting the resistance box to the nearest tenth ohm and interpolating from the galvanometer deflection. If  $\delta\theta$  be the temperature difference between the thermometer wires when the diaphone is sounding, and  $\delta\theta'$  that when the diaphone is silent, corresponding to resistances  $s$  and  $s'$  required to balance the bridge in each case, we easily prove that

$$\delta\theta - \delta\theta' = -\frac{(R_0 - S_0)}{S_0} (\theta_1 - \theta'_1) + \frac{s - s'}{\alpha s_0}, \dots \dots \dots \text{(viii.)}$$

$\theta_1$  and  $\theta'_1$  being the temperatures of the thermometer  $R_0$  when sounding and silent respectively. The first term represents the small correction arising from the inequality of resistance of the two thermometers. As the series of observations with the diaphone sounding and silent were taken immediately following one another,  $\theta_1$  and  $\theta'_1$  are assumed to be so nearly equal that this correction term may be neglected. We thus calculate the difference of the temperature differences of the two thermometers under conditions "sounding" and "silent" from the formula

$$\delta\theta - \delta\theta' = \frac{s - s'}{82.095 \times 0.004964} = 2.46 (s - s'). \dots \dots \dots \text{(ix.)}$$

From formula (44) we may calculate the acoustic output of the diaphone from the formula

$$\begin{aligned} \dot{w} &= JC_v \dot{M} (\Theta_1 - \Theta) \\ &= \frac{(p_1 - p'_1)}{t} \frac{V}{\gamma - 1} \frac{(\Theta_1 - \Theta)}{\Theta_1} \dots \dots \dots \text{(x.)} \end{aligned}$$

We have seen from the discussion of § 12 that to a tolerable order of accuracy we may identify the actual temperature drop  $(\Theta_1 - \Theta)$  in the diaphone when sounding with the observed difference of temperature differences of the thermometer wires  $(\delta\theta - \delta\theta')$ , (following the notation of (viii.) above). Inserting numerical values in (x.) we may thus write for purposes of computation, taking  $\Theta_1 = 288^\circ$  A.,

$$\dot{w} = 17.8 \times (p_1 - p'_1) \frac{(\delta\theta - \delta\theta')}{288^\circ} \text{ H.P.} \dots \dots \dots \text{(xi)}$$

In the diaphone actually tested the exhaust from the "driving head" passed into the resonator so that the estimate (xi.) includes the work required to operate the diaphone piston. This includes not only the work required to overcome friction but also a small portion of energy converted into sound. The former is

\* SCOTT, A. A., "A Study of Iron Wire for Electrical Resistance Thermometers," 'Trans. Roy. Soc. of Canada,' vol. VII., Third Series, 1913.

converted into heat, a large part of which is returned to the air, passing through the piston, and therefore does not contribute to the temperature drop of formula (xi). As has already been mentioned, the frequency does not alter very greatly with the operating pressure, while the amplitude of vibration cannot vary between very wide limits if the valve-system of the driving head is to produce reciprocating motion at all. A reference to observation 1 of Test 4, at reduced air consumption, gives for the total power consumed in driving the piston and emitting sound the value 0.06 H.P. We are thus justified in estimating that throughout the entire range of operating pressures not more than 1/10 H.P. is required to reciprocate the diaphone piston. To this order of accuracy the power expenditure  $\dot{w}$  calculated from (xi) may be attributed to external work being propagated away in the form of sound-waves.

TEST No. 1. September 13, 1913.

No. of observation.	Mean pressure above atmosphere. cm. mercury.	Pressure drop in 6 seconds.		Pressure increase in 6 seconds due to compressors. cm. mercury.	Mean pressure drop in 6 seconds. cm. mercury ( $p_1 - p'_1$ ).	Resistance change of differential thermometers, sounding and silent. ( $s - s'$ ). ohms.
		Sounding. cm. mercury.	Silent. cm. mercury.			
1	50.8	3.7	3.35	1.0	4.5	0.57
2	60.5	4.2	4.1	0.95	5.1	0.80
3	70.1	4.5	4.85	0.9	5.6	0.95
4	79.8	5.2	5.55	0.85	6.2	1.05
5	89.7	5.55	5.8	0.8	6.5	1.20
6	99.1	6.3	6.9	0.8	7.4	1.40
7	103.0	6.5	7.1	0.75	7.55	1.40
8	109.0	7.1	7.35	0.75	8.0	1.31
9	118.6	7.5	8.1	0.75	8.55	1.28
10	128.2	7.9	8.9	0.75	9.15	1.23
11	137.5	9.1	10.15	0.75	10.4	1.14

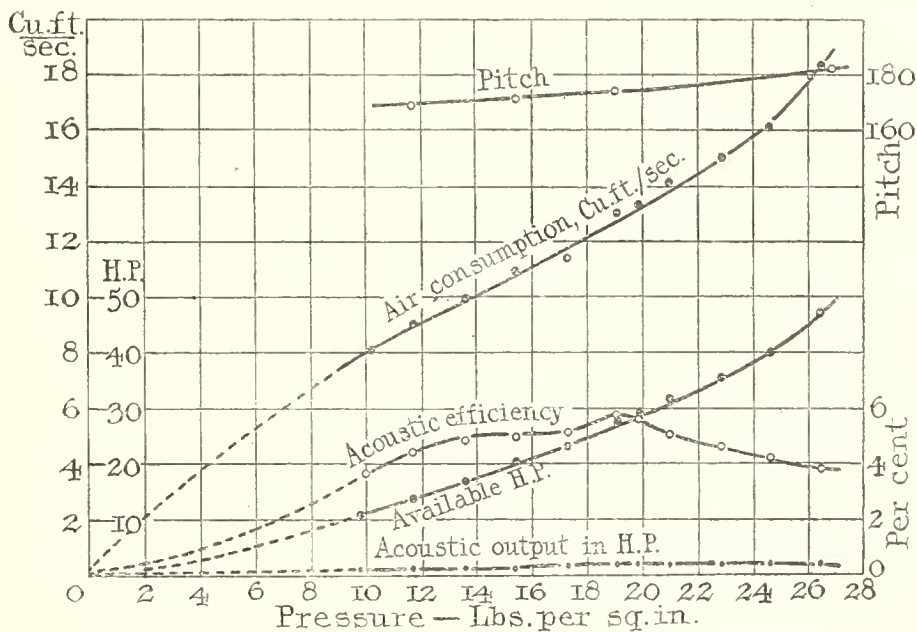


Fig. (i). Characteristics of the diaphone.  
Results of Test 1, September 13, 1913. Air consumption normal.

TEST No. 1 (continued).

No. of observation.	Mean pressure above atmosphere. lbs./sq. in.	Air consumption in cubic feet per second.	Maximum power possible in H.P. (W).	Temperature differences, sounding and silent ( $\delta\theta - \delta\theta'$ ).	Power emitted as sound and consumed in driving piston in H.P. (w).	Acoustic efficiency ( $\eta = w/W$ ).
				° C.		
1	9.8	7.9	10.9	1.40	0.39	0.036
2	11.7	9.0	13.9	1.97	0.62	0.044
3	13.6	9.9	16.9	2.34	0.81	0.048
4	15.4	10.9	20.5	2.58	0.99	0.049
5	17.3	11.4	23.1	2.95	1.19	0.051
6	19.1	13.0	27.9	3.44	1.57	0.057
7	19.9	13.3	29.2	3.44	1.60	0.056
8	21.0	14.1	31.9	3.22	1.66	0.050
9	22.9	15.0	35.8	3.15	1.66	0.046
10	24.7	16.1	40.0	3.03	1.70	0.042
11	26.5	18.3	47.3	2.80	1.80	0.038

TEST No. 2. September 15, 1913.

No. of observations.	Mean pressure above atmosphere. cm. mercury.	Pressure drop in 6 seconds.		Pressure increase in 6 seconds due to compressors. cm. mercury.	Mean pressure drop in 6 seconds. cm. mercury. ( $p_1 - p'_1$ ).	Resistance change of differential thermometers, sounding and silent. ( $s - s'$ ). ohms.
		Sounding. cm. mercury.	Silent. cm. mercury.			
1	51.6	1.75	1.45	1.05	2.1	0.40
2	61.5	2.0	1.8	1.0	2.9	0.63
3	71.5	2.2	2.25	0.9	3.1	0.70
4	81.2	2.8	2.7	0.9	3.6	1.03
5	91.1	2.65	2.95	0.9	3.6	0.96
6	100.8	3.1	3.25	0.85	4.0	1.04
7	110.7	3.8	3.7	0.8	4.6	1.00
8	120.5	4.2	3.8	0.7	4.7	0.67
9	130.4	4.5	4.25	0.7	5.1	0.71
10	140.1	5.1	4.8	0.7	5.7	0.72

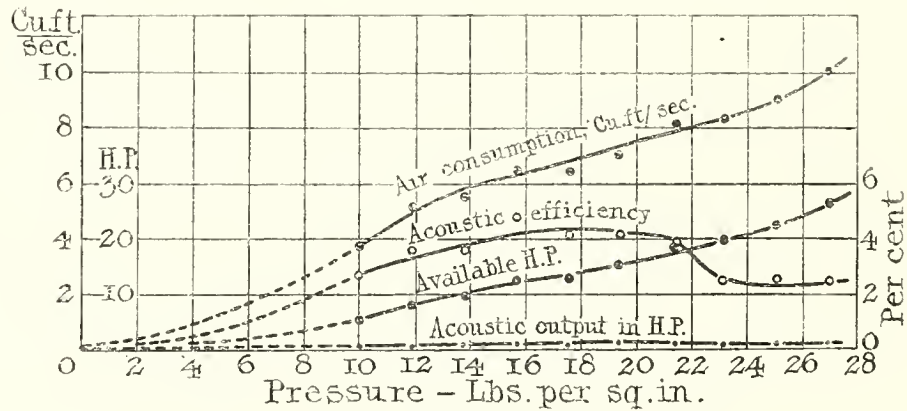


Fig. (ii.). Characteristics of the diaphone.

Results of Test 2, September 15, 1913. Air consumption halved by throttling.

TEST No. 2 (continued).

No. of observations.	Mean pressure above atmosphere. lbs./sq. in.	Air consumption in cubic feet per second.	Maximum power possible in H.P. (W).	Temperature differences, sounding and silent. ( $\delta\theta - \delta\theta'$ ).	Power emitted as sound and consumed in driving piston in H.P. ( $w$ ).	Acoustic efficiency. ( $\eta = w/W$ ).
1	10.0	3.7	5.1	° C. 0.98	0.13	0.026
2	11.9	5.1	8.0	1.55	0.28	0.035
3	13.8	5.5	9.5	1.72	0.33	0.035
4	15.7	6.4	12.2	2.53	0.57	0.047
5	17.6	6.4	12.9	2.36	0.53	0.041
6	19.4	7.0	15.3	2.56	0.63	0.041
7	21.4	8.1	18.7	2.46	0.71	0.038
8	23.2	8.3	19.9	1.65	0.48	0.024
9	25.1	9.0	22.4	1.75	0.55	0.025
10	27.0	10.0	26.4	1.77	0.62	0.024

TEST No. 3. September 16, 1913.

No. of observations.	Mean pressure above atmosphere. cm. mercury.	Pressure drop in 6 seconds.		Pressure increase in 6 seconds due to compressors. cm. mercury.	Mean pressure drop in 6 seconds. ( $p_1 - p'_1$ ).	Resistance change of differential thermometers, sounding and silent. ( $s - s'$ ). ohms.
		Sounding. cm. mercury.	Silent. cm. mercury.			
1	38.5	3.7	3.7	1.1	4.9	0.58
2	50.5	4.0	4.0	1.0	5.1	1.16
3	60.3	4.4	4.2	0.9	5.3	1.31
4	70.0	5.0	4.9	0.9	5.85	1.46
5	79.8	5.6	5.6	0.8	6.5	1.59
6	89.6	6.0	6.0	0.8	6.8	1.83
7	99.3	6.7	6.8	0.8	7.55	2.05
8	109.0	7.1	6.9	0.8	7.8	1.90
9	118.8	7.7	7.5	0.8	8.4	1.66
10	128.6	8.0	8.2	0.7	8.9	1.25
11	138.2	8.8	9.0	0.7	9.7	0.82
12	148.0	9.3	10.3	0.7	10.5	0.64

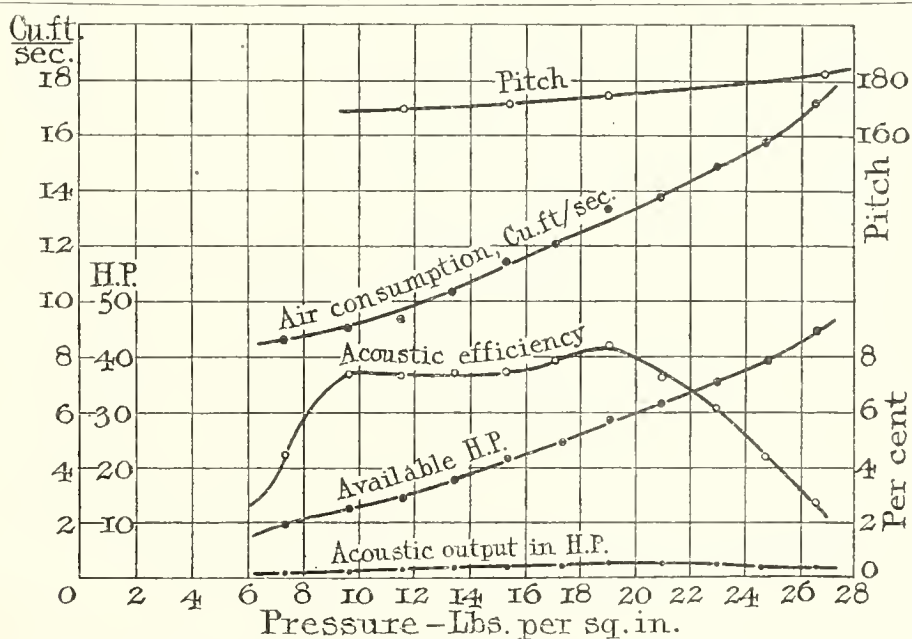


Fig. (iii). Characteristics of the diaphone.

Results of Test 3, September 16, 1913. Valves admitting sounding and driving air re-adjusted.

TEST No. 3 (continued).

No. of observations.	Mean pressure above atmosphere. lbs./sq. in.	Air consumption in cubic feet per second.	Maximum power possible in H.P. (W).	Temperature difference, sounding and silent. ( $\delta\theta - \delta\theta'$ ).	Power emitted as sound and consumed in driving piston in H.P. ( $w$ ).	Acoustic efficiency. ( $\eta = w/W$ ).
				° C.		
1	7.4	8.6	9.7	1.43	0.43	0.044
2	9.7	9.0	12.3	2.85	0.90	0.073
3	11.6	9.3	14.5	3.22	1.06	0.073
4	13.5	10.3	17.7	3.59	1.30	0.074
5	15.4	11.4	21.4	3.91	1.57	0.074
6	17.2	12.0	24.2	4.50	1.88	0.078
7	19.1	13.3	28.5	5.04	2.36	0.083
8	21.0	13.7	31.1	4.67	2.25	0.072
9	23.0	14.8	35.2	4.08	2.11	0.061
10	24.8	15.7	39.0	3.08	1.69	0.043
11	26.6	17.1	44.3	2.02	1.21	0.027
12	28.6	18.5	49.5	1.57	1.01	0.020

TEST No. 4. September 16, 1918.

No. of observation.	Mean pressure above atmosphere. cm. mercury.	Pressure drop in 6 seconds.		Pressure increase in 6 seconds due to compressors. cm. mercury.	Mean pressure drop in 6 seconds cm. mercury. ( $p_1 - p'_1$ ).	Resistance change of differential thermometers, sounding and silent. ( $s - s'$ ) ohms.
		Sounding. cm. mercury.	Silent. cm. mercury.			
1	40.0	0.85	0.65	1.05	1.8	0.22
2	51.7	1.6	1.6	1.0	2.6	0.62
3	61.6	1.85	1.95	0.9	2.8	0.94
4	71.4	2.3	2.25	0.9	3.2	1.08
5	81.3	2.55	2.55	0.8	3.35	1.25
6	91.1	2.9	3.0	0.8	3.75	1.35
7	100.8	3.6	3.55	0.8	4.40	1.44
8	110.7	3.8	3.7	0.8	4.55	1.49
9	120.5	4.25	4.0	0.75	4.85	1.08
10	130.4	4.6	4.3	0.7	5.15	0.89
11	140.1	5.05	5.0	0.7	5.75	0.87
12	149.6	(6.1)	5.9	0.7	6.7	0.84
13	159.1	7.1	6.8	0.7	7.65	0.99

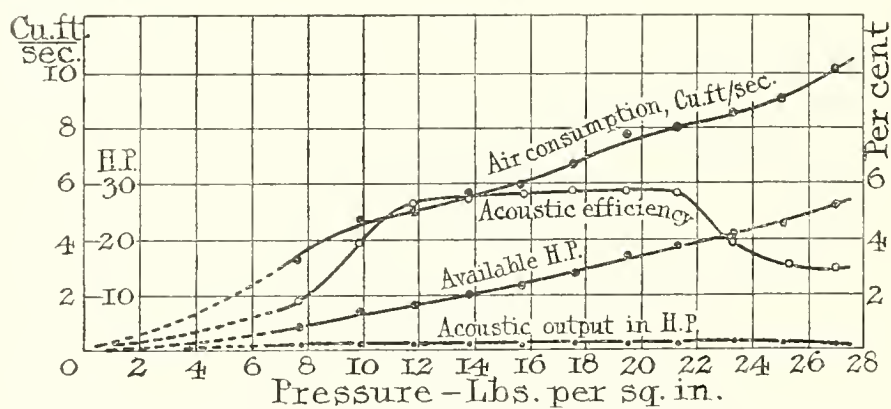


Fig. (iv.). Characteristics of the diaphone.

Results of Test 4, September 16, 1913. Conditions as in Test 3, with air consumption halved by throttling.

## TEST NO. 4 (continued).

No. of observation.	Mean pressure above atmosphere. lbs./sq. in.	Air consumption in cubic feet per second.	Maximum power possible in H.P. (W).	Temperature difference, sounding and silent ( $\delta\theta - \delta\theta'$ ).	Power emitted as sound and consumed in driving piston in H.P. (w).	Acoustic efficiency ( $\eta = w/W$ ).
				° C.		
1	7.7	3.2	3.6	0.54	0.06	0.017
2	9.9	4.6	6.3	1.52	0.24	0.038
3	11.8	4.9	7.7	2.31	0.40	0.052
4	13.8	5.6	9.8	2.66	0.53	0.054
5	15.7	5.9	11.2	3.08	0.63	0.056
6	17.6	6.6	13.5	3.32	0.77	0.057
7	19.5	7.7	16.8	3.54	0.96	0.057
8	21.3	8.0	18.3	3.66	1.03	0.056
9	23.3	8.5	20.5	2.66	0.80	0.039
10	25.1	9.0	22.8	2.19	0.70	0.031
11	27.0	10.1	26.3	2.14	0.76	0.029
12	28.9	11.8	31.9	2.07	0.86	0.027
13	30.7	13.4	37.6	2.44	1.15	0.031

## TEST NO. 5. AIR CONSUMED IN DRIVING CYLINDER.

No. of observations.	Mean pressure above atmosphere. cm. mercury.	Pressure drop in time $t$ . ( $p_1 - p_2$ ). cm. mercury.	$t$ . seconds.	Mean pressure above atmosphere. lbs./sq. in.	Air consumption. cubic feet/seconds.
1	47.0	12.0	260.6	9.1	0.48
2	58.2	10.3	183.4	11.2	0.59
3	68.3	10.0	161.4	13.1	0.65
4	78.1	9.7	142.6	15.1	0.72
5	88.0	10.0	129.8	17.0	0.81
6	98.0	10.0	118.2	18.9	0.89
7	108.0	10.0	109.6	20.8	0.96
8	118.0	10.0	93.2	22.8	1.13
9	128.1	9.8	93.4	24.7	1.11
10	138.0	10.0	78.0	26.6	1.36
11	148.0	9.5	63.2	28.6	1.58
12	157.9	10.2	58.2	30.5	1.81







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E. G. J. HARTLEY, B.A. (OXON), AND C. V. BURTON, B.Sc. (LONDON).

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V. *On Osmotic Pressures Derived from Vapour-Pressure Measurements :  
Aqueous Solutions of Cane Sugar and Methyl Glucoside.*

*By The Earl of BERKELEY, F.R.S. ; E. G. J. HARTLEY, B.A. (Oxon); and  
C. V. BURTON, B.Sc. (London).*

Received February 3,—Read March 1, 1917.

INTRODUCTORY.

SINCE our previous communications on cane sugar ('Roy. Soc. Proc.,' A, vol. 77, 1906) and on calcium ferrocyanide ('Phil. Trans.,' A, vol. 209) we have endeavoured to improve the apparatus and method therein described. In these endeavours, two objects, besides that of determining osmotic pressures, have been in view : (1) to find out what are the best conditions for making the method both accurate and of general applicability ; (2) to obtain data for the construction of suitable apparatus for the determination of the absolute vapour density of liquids in air or other gas.

As far as accuracy is concerned, the close agreement between osmotic pressures observed directly, and those here calculated from the vapour pressures, shows that, for solutions at 0° C. the method is susceptible of considerable precision. The experiments at 30° C., however, are on the whole not quite so concordant ; this is probably because the quantity of water vapour in the air stream is some six times the amount carried at 0° C., so that small variations in conditions which would be without effect at the lower temperature, now make themselves apparent. This, indeed, is shown clearly in the magnitude of the correction to be applied for the expansion of the air between the solution and water vessels (see p. 316). In the early stages of the work (at 0° C.) our results indicated that the successful application of the method depends largely on the control of the experimental conditions ; accordingly we made as many changes as possible, but as each experiment takes several days to complete, a long time is required to determine the effect of any one change. The departure of Mr. HARTLEY for the front prevented a further investigation of the question but we think that no new changes will alter substantially the results now presented.

The importance of measurements of the absolute vapour density of water vapour in air has been realized generally for some time past ; the differences between REGNAULT'S values for air and for a vacuum (at 0° C., especially) require

re-determination, the more so in that his air values seem in themselves not very satisfactory, and it is just the air values which are wanted in the majority of researches. The experimental error of our results is now reduced sufficiently to warrant the belief that in absolute measurements the chief difficulty will lie in the determination of the quantity of air passed, rather than in the amount of water vapour it carries.

The research is divided into two parts. In Part I. are given the measurements of the compressibilities of the solutions; these were carried out with the aid of Dr. BURTON. Part II. embodies the experiments on the vapour pressures of solutions of cane sugar and  $\alpha$ -methyl glucoside at 0° C. and 30° C., also some determinations of the vapour pressures of dilute sulphuric acid. All the experiments, except a few dating later than January 22, 1916, were done in conjunction with Mr. HARTLEY.

As both these gentlemen have left the laboratory and are not within reach, the other author should be held responsible for all mistakes in presentation of fact or theory.

## PART I.\*

### THE COMPRESSIBILITIES. (BERKELEY and BURTON.)

In a previous communication we have given the results of our measurements on the compressibilities of calcium ferrocyanide solutions. These results were not very satisfactory because the experiments had to be carried out as rapidly as possible, otherwise the prolonged strain on the outer glass tube† (through which the readings on the piezometer stem were taken) soon caused it to collapse.

*New Apparatus.*—To obviate this, a new apparatus, A, was designed in which the glass tube was replaced by a metal casting pierced for windows. With this apparatus some of the experiments here recorded were made; but as the main features of A are embodied in yet another apparatus, B, the former will not be described.

Fig. 1 shows B in elevation. The apparatus is divided into two main pieces, A and B, which are joined "pressure tight" by means of a dermatine ring as shown; this method is similar to that described by us in 'Phil. Mag.,' vol. 32, 1916, p. 157. The upper part A (called the dome) is furnished with a pair of windows, C (the use of which will be described later), and is joined to the pressure system by a nut fitted with differential threads, by means of which the steel pressure tubing, E, can be forced home into its conical seating at D. The part B which is closed at the bottom by a nickel-steel plank (made "pressure tight" by dermatine), carries five pairs of windows, F, spaced at regular intervals for observing the level of the mercury in the stem of the

\* This part of the research was completed in 1911.

† See 'Phil. Trans.,' A, vol. 209, p. 192.

piezometer. The windows are tapered plugs cut from one-inch plate glass; they were inserted into dermatine washers moulded inside and outside to the same taper. The openings for the windows in the casting having been machined to this taper (large end inwards), the glass together with its dermatine wrappers was placed in position from the inside and pushed home as well as could be by means of wedges. On putting a high hydrostatic pressure on the apparatus a final "leak-tight" seating was secured.

*The Bath.*—The whole apparatus (about two feet high) is immersed in a water-bath, which is furnished with a thermostat and stirrer; submerged electric lamps supply heat, and two of the lamps are under the control of the thermostat. The front of the bath is fitted with a plate-glass window, so that the graduations on the piezometer stem are seen clearly when a small 4-volt lamp is placed behind the apparatus.

The same bath, divided into two compartments by a loosely fitting vertical partition, was used for the observations at  $0^{\circ}\text{C}$ . One of these compartments contained ice, and a constant stream of cold water was pumped from this compartment into the other. During an experiment, which took some hours, care was taken that the ice reached nearly to the bottom of the bath, and the supply was maintained by hand. The temperature variations were observed by means of a Beckmann thermometer reading to  $0^{\circ}\cdot 01\text{ C}$ . (estimating to  $0^{\circ}\cdot 001\text{ C}$ .) in the bath, and another reading to  $0^{\circ}\cdot 02\text{ C}$ . in the dome of the apparatus.

*Piezometers.*—Piezometers similar to those of our earlier research were used in apparatus A, but in the course of the work we found that there were two drawbacks to this form: (1) the somewhat large bulb took a very considerable time to return to the temperature of the bath after having been heated or cooled by the alterations in pressure (at  $0^{\circ}\text{C}$ . this effect is small); (2) it was found that for a given pressure on the

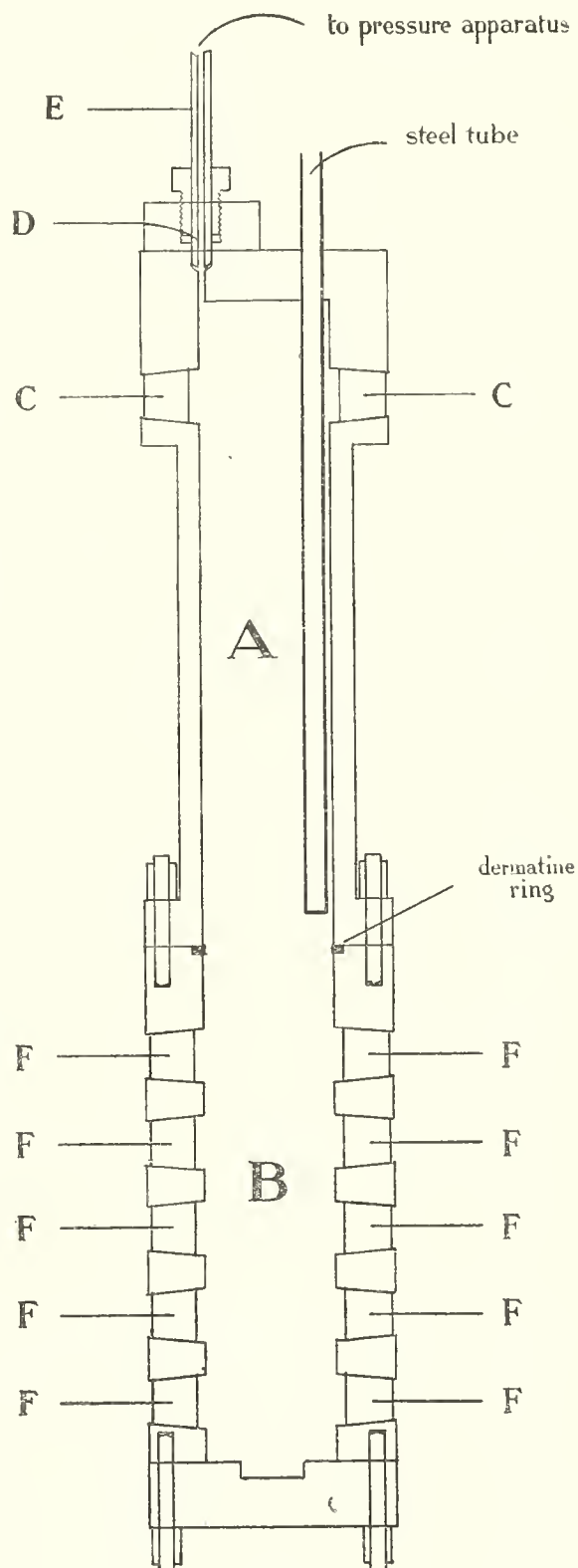


Fig. 1.

apparatus, there was a difference in the final\* position of the mercury level in the stem according as the pressure had previously been rising or falling. In all cases the falling pressure gave the higher reading. The cause of this was eventually traced to the lubricant† surrounding the tap key at the top of the piezometer.

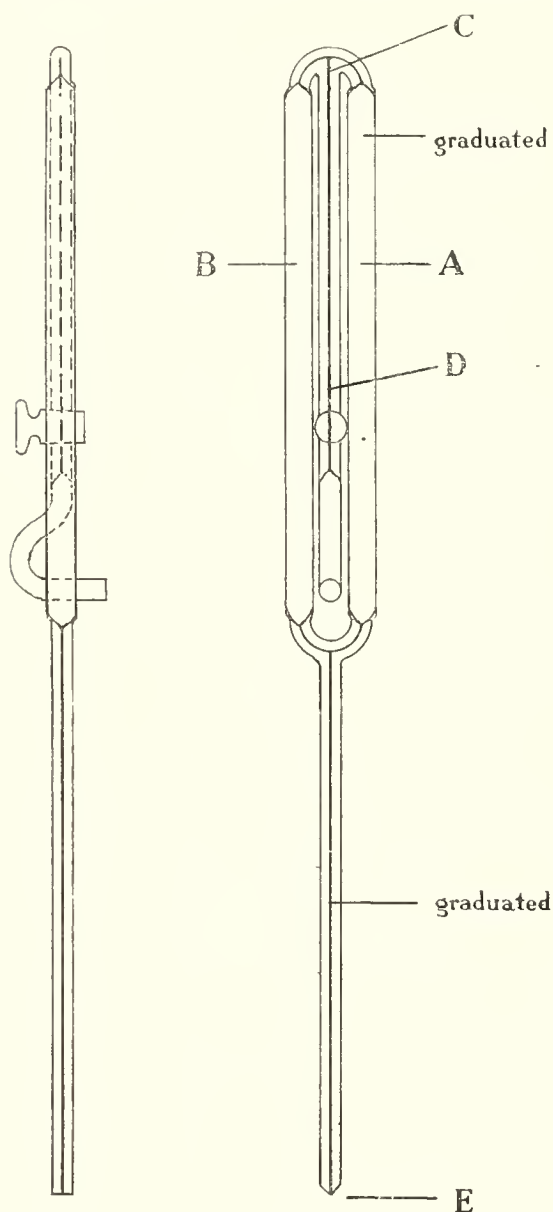


Fig. 2.

The piezometer shown in fig. 2 seems to meet both troubles. The bulb (total volume about 32 c.c.) is divided into two branches, A and B, thus giving a larger cooling surface. The tap is now placed at the end of a graduated capillary, CD, so that by careful manipulation the latter can be filled with mercury to a level which will be in the field of view of window C, of fig. 1.

The remainder of the piezometer contains the solution, except for a centimetre or two of mercury at the bottom of the stem. Thus the solution is confined between two surfaces of mercury, and although the mercury meniscus near the tap will move slightly, if this movement be noted the real change in volume of the solution can be calculated.

*The Pressures.*—The apparatus used is one of Schäffer and Budenberg's dead-weight gauges, delivering a maximum pressure of 140 atmospheres.‡ The pressure was transmitted by castor oil from the screw plunger to a mercury U-tube; and by water from the latter to the compressibility apparatus.

In the course of the research it was noticed that rapid changes of pressure, especially when on the up grade, caused some uncertainties in

\* That is when the temperature is constant again after the effects of changing the pressure have disappeared. Constancy of temperature is indicated by the fact that there is no further movement in the mercury; indeed, the piezometer is in effect a very sensitive thermometer.

† For, on increasing the pressure, the lubricant is compressed, and as there is a slight difference in pressure due to the unbalanced height of the mercury in the stem, the key may move slightly into its seating; this movement obviously is not reversible. Occasionally, another source of trouble was encountered, namely, that caused by a small bubble of air left in the key of the tap when filling the piezometer; this bubble could be seen easily, but it was found to be there sometimes even in the new form about to be described. The presence of this trace of air would give quite fallacious results for the lower measurements.

‡ The same apparatus as was used for the determination of direct osmotic pressure, see 'Phil. Trans.,' A, vol. 206, 1906, p. 485.



the reading of the mercury level in the piezometer. Direct observation showed that when a certain rate of increase of pressure was exceeded, the mercury thread might move rapidly enough to leave some of the solution behind clinging to the walls of the capillary, and this was the more marked the stronger the solution.\* To decide the maximum rate of change of pressure that would be safe, experiments (which are not detailed) were made with the most viscous solution (960 gr. of cane sugar per litre) about to be examined. Judging by the information thus obtained, the method of changing the pressure described below seems free from objection.

A light metal cup was placed on the top of the floating weights of the Schäffer and Budenberg gauge. Above this was suspended a hollow cylinder with a conical end truncated so as to leave a horizontal opening of about 0.8 cm. in diameter. When it was desired to increase the pressure, a quantity of small lead shot equivalent in weight to one of the large weights supplied with the pressure apparatus was run into the cylinder. On opening the orifice the shot were delivered at a constant rate into the metal cup below.†

When all the shot had run through, a needle valve, situated so as to cut off the compressibility vessel from the pressure apparatus, was closed; and the metal cup with its contents was replaced rapidly by one of the weights, after which the needle valve was opened. This process was repeated until the mercury in the piezometer stem showed in the field of view of the adjacent window above. It was found that the pressure could be lowered slowly enough by means of two needle valves in series.

*Method Followed in the Determinations of the Compressibilities.*—In the present research no attempt was made to get air-free solution. In our work on calcium ferrocyanide we found that this precaution was unnecessary.

The method followed was to fill the piezometer by gentle suction, taking care that no visible bubbles of air were left behind. When full, the piezometer was inverted and some mercury run into the open tube above the tap, which, when cautiously opened, allowed a thread to flow downwards into the capillary (CD of fig. 2), the flow being stopped when the meniscus reached a part of the capillary known to be visible through the upper window (C of fig. 1).

If the determinations were to be made at 0° C., the piezometer when full was placed with its stem immersed in the solution, and the twin bulbs were then cooled by an ice pack until a temperature slightly above that of the bath had been reached;

\* This effect is partly dependent on viscosity; for where some solution has been left in the annular space between the mercury and the walls, this annular space is in effect a capillary tube through which the liquid has to be forced by the hydrostatic pressure of the mercury acting at the bottom of the enclosed solution.

† The rate at which the shot fall is independent of the head of shot and depends on the diameter of the orifice. The correct diameter was found by trial, and was such as to cause the mercury in the stem of the more sensitive piezometer to rise 1 mm. in 25 seconds.

further cooling with the stem in mercury, caused the latter to rise to a suitable level. The piezometer was then quickly transferred to its position in the lower half of the compressibility apparatus which was already in the bath, and, with luck, the mercury thread carried in the stem joined the mercury already in place at the bottom of the apparatus.

It was found that a satisfactory junction was greatly facilitated by chamfering off the bottom of the piezometer stem as shown at E in fig. 2.\*

A very similar procedure was followed for the experiments at 30° C. The piezometer being in place, the upper half of the apparatus was passed over the projecting bulbs and secured both to the lower half and to the pressure system.

Supposing these operations to have been carried out successfully, the mercury meniscus should stand, when the bath temperature had been regained, slightly below the lowest window; then a small increase of pressure will bring it opposite the window.

On the other hand, should the meniscus be above this window, the apparatus has to be taken apart, the mercury driven out so as to replace some of it by solution, and after cooling, &c., replaced in the bath.

When a steady state had been reached, the pressure on the apparatus, the level of the meniscus showing in the lower window and that in the topmost window (C of fig. 1), and the temperature both of the bath and of the interior of the apparatus were noted. The pressure was then increased until the meniscus showed in the second window; this increase of pressure caused a development of heat which was dissipated in about three-quarters of an hour, as indicated by the constancy of the position of the meniscus; when steady, the five quantities were again noted, and so on.

Having taken the readings for the fifth window, the pressure was reduced and the process just described was precisely reversed until the initial phase was reached.

It is to be noted, on the assumption that there is no hysteresis in the glass of the piezometer,† that the same readings (corrected for small displacements of the upper meniscus and for any change in the temperature of the bath) should be obtained whether going up or going down the scale of pressures. When these readings are noticeably divergent we have generally found that a pellet of solution has formed across the mercury thread and therefore such experiments should be viewed with suspicion. On the other hand even if the readings are the same it is no proof of a

\* In later work this difficulty is overcome by fastening a small capsule containing mercury to the bottom of the stem.

† We would draw attention to a source of error which has been observed in one of the Jena-glass piezometers. This error lies in the fact that some of the air bubbles usually present in capillary tubing (as long hair-like lines) communicate with the bore of the tube; when under pressure minute threads of mercury can be seen to be moving in these capillaries.

good experiment; there may have been liquid left behind on the capillary walls which is picked up again when the meniscus reaches it on its downward journey, but we have reason to think that this seldom occurs when changing the pressure slowly as already described.

*Example of Experiments.*—The following experiments are selected from the laboratory note-book as a sample of our work with the twin bulb piezometer:—

EXPERIMENT with a Solution of  $\alpha$ -Methyl Glucoside at  $0^\circ$  C.

(Wt. conc. = 54.692 gr. per 100 gr. water.)

Date.	Time.	Temperatures of		Pressure. Atmo- spheres.	Readings on		Remarks.
		Bath.	Appa- ratus.		Upper capillary.	Lower capillary.	
1911 July 7	6.30 p.m.	—	—	—	—	—	Filled Piezometer VIII. and filled up bath with ice.
„ 8	7.15 a.m.	—	—	—	—	—	Filled up with ice.
	7.45 „	—	—	—	—	—	
	8.0 „	—	—	—	—	—	Ran mercury thread into piezo- meter and placed in bath.
	9.0 „	—	—	—	—	—	Placed piezometer in apparatus (B) and joined up (the dome was previously cooled in ice).
	9.40 „	5.383	6.960	17.01	26.1 <sub>5</sub>	410.8	
	9.55 „	5.381	6.920	17.01	—	408.1	Note that $5^\circ.490$ on the bath Beckmann = $0^\circ.23$ C.
	10.5 „	5.382	6.917	17.01	—	408.0	
	10.15 „	5.382	6.916	17.01	—	407.8	
	10.25 „	5.384	6.916	17.01	26.2	407.8	
	10.53 „	5.382	6.912	57.83	26.2 <sub>5</sub>	251.0	
	11.3 „	5.382	6.912	57.83	26.2 <sub>5</sub>	251.0	
	11.16 „	5.384	6.914	78.25	26.3	173.0	
	11.26 „	5.385	6.916	78.25	26.3	173.0	
	11.42 „	5.386	6.917	102.06	26.3 <sub>5</sub>	83.0	
	11.52 „	5.385	6.916	102.06	26.3 <sub>5</sub>	83.0	
	12.1 „	5.383	6.914	57.83	26.2 <sub>5</sub>	251.0	
	12.11 „	5.385	6.915	57.83	—	251.2	
	12.21 „	5.385	6.915	57.83	26.25	251.2	
	12.31 „	5.388	6.919	17.01	26.2	408.0	
	12.41 „	5.388	6.919	17.01	26.2	408.0	
	12.51 „	5.388	6.919	17.01	26.2	408.0	

## EXPERIMENT with a Solution of Cane Sugar at 30° C.

(Wt. conc. = 111.89 gr. per 100 gr. water.)

Date.	Time.	Temperatures of		Pressure. Atmo- spheres.	Readings on		Remarks.
		Bath.	Appa- ratus.		Upper capillary.	Lower capillary.	
1911							
June 12	12.20 p.m.	—	—	—	—	—	Filled Piezometer VII. with the solution on 10th, adjusted upper meniscus.
	2.30 "	—	—	17.01	26.4	—	Placed piezometer in position and screwed dome on.
June 13	11.40 "	3.444	7.344	17.01	27.2	209.5	Note that 3°.44 on Beckmann thermometer of bath = 29°.99 C.
	9.3 a.m.	3.444	7.344	17.01	27.2	209.5	
	9.25 "	—	—	51.03	—	—	
	9.27 "	3.444	7.359	51.03	27.2	132.7	
	9.37 "	3.444	7.350	51.03	27.2	132.2	
	9.48 "	3.444	7.350	51.03	27.2	132.0	
	9.58 "	3.444	7.345	51.03	27.2	132.0	
	10.19 "	3.444	7.359	85.05	27.25	55.9	
	10.29 "	3.444	7.354	85.05	—	55.2	
	10.39 "	3.444	7.350	85.05	—	55.0	
	10.50 "	3.444	7.344	85.05	27.2	55.0	
	11.0 "	3.444	7.320	51.03	27.2	130.5	
	11.10 "	3.444	7.332	51.03	—	131.5	
	11.20 "	3.444	7.338	51.03	—	131.65	
	11.30 "	3.444	7.340	51.03	—	131.85	
	11.40 "	3.444	7.340	51.03	—	131.9	
	11.50 "	3.444	7.340	51.03	27.2	131.9	
	12.3 p.m.	3.444	7.323	17.01	27.15	208.0	
	12.18 "	3.444	7.336	17.01	—	209.1	
	12.35 "	3.444	7.340	17.01	—	209.2	
12.48 "	3.444	7.340	17.01	27.2	209.25		
1.1 "	3.444	7.340	17.01	—	209.3		
2.25 "	—	—	—	—	—	Found temperature had fallen owing to failure in relay—adjusted.	
	3.21 "	3.443	7.334	—	—	208.7	
	3.42 "	3.444	7.340	—	—	209.2	
	3.54 "	3.443	7.340	—	27.2	209.2	
	4.7 "	3.444	7.344	—	27.2	209.2	
	10.0 "	3.444	7.343	—	27.25	209.2	

NOTE.—The apparent constancy of the bath is partly fictitious. The thermometer ought to have been tapped before each reading.

*The Corrections.*—As already mentioned, a correction has to be applied to the observed pressure for the height of mercury in the stem, this correction (A of Table I.) is self-evident and need not detain us, but a further correction (B of Table I.) due to

the same cause has to be applied to the volume of the piezometer, for it is evident that the higher the mercury in the stem, the more the walls of the bulb are caused to come in towards each other.

To obtain this correction a set of separate experiments was made with each piezometer, thus: the piezometer was inverted and filled (up to the graduations in the stem) with recently boiled water. The stem was then connected to a mercury manometer by means of a T-piece, so that by joining the T to an exhaust pump, the pressure on the water could be reduced and the amount of the reduction measured on the manometer. The change in volume caused by the change in pressure is given directly by the difference in readings of the water meniscus. These two corrections (together with others which will be understood readily) as applied to the experiment of June 12, are shown in Table I.

TABLE I.

Observed pressure.	Correction to pressure for excess of external pressure. A.	Corrected pressure.	Observed readings of mercury meniscus in stem.	Volume of solution uncorrected.	Correction to the volume for —			Volume of solution corrected.	Mean relative coefficient of compressibility.	Mean coefficient of compressibility of solution.*	Pressure range above atmospheric pressure.
					Temperature.	Reading of mercury meniscus in upper capillary.	Excess of external pressure B.				
atmospheres. 17·01	-0·00	17·01	209·5	32·42119	0·0	0·0	0·0	32·42119	$10^{-5} \times$	$10^{-5} \times$	atmospheres.
51·03	-0·09	50·94	132·0	32·39319	-0·00001	0·0	-0·00004	32·39314	2·550	2·773	17 to 51
85·05	-0·19	84·86	55·0	32·36541	0·0	0·0	-0·00008	32·36533	2·528	2·751	51 „ 85
51·03	-0·09	50·94	131·9	32·39315	+0·00005	-0·00001	-0·00004	32·39315	2·529	2·751	85 „ 51
17·01	-0	17·01	[209·4] estimated	32·42115	+0·00005	0·0	-0·0	32·42120	2·550	2·773	51 „ 17

\* These values are obtained by adding the coefficient of compressibility of the glass of the piezometer ( $= 0·223 \times 10^{-5}$ ) to the numbers in the preceding column.

## THE RESULTS.

*Compressibility of Mercury.*—The following is a summary of our results with mercury. Five observations were made:—

With Piezometer 1A. The mean relative coefficient at  $0^\circ$  C. between 1 and 101 atmospheres was  $0·169 \times 10^{-5}$ .

With Piezometer 7. The mean relative coefficient at  $1·8^\circ$  C. between 1 and 110 atmospheres was  $0·171 \times 10^{-5}$ .

With Piezometer 1A. The mean relative coefficient at  $29·5^\circ$  C. between 8 and 150 atmospheres was  $0·165 \times 10^{-5}$ .

With Piezometer 3c. The mean relative coefficient at  $29^{\circ}5$  C. between 8 and 89 atmospheres was  $0.163 \times 10^{-5}$ .

With Piezometer 7. The mean relative coefficient at  $30^{\circ}4$  C. between 28 and 117 atmospheres was  $0.169 \times 10^{-5}$ .

All the piezometers, except 7 and 8 which are made of soda-glass, are of Jena No.16<sup>III</sup> glass, we may therefore mean the results for 1A and 3c at  $30^{\circ}$  C.

If we take AMAGAT'S value for the coefficient compressibility of mercury at  $0^{\circ}$  C., namely  $0.392 \times 10^{-5}$  and correct it to  $30^{\circ}$  C. by means of CARNAZZI'S ('Nuovo Cim.,' 5, 1903, pp. 73-89) temperature coefficient, we get

$$0.393 \times 10^{-5}.$$

Then the Jena-glass piezometer at  $0^{\circ}$  C. will have a coefficient of

$$0.392 \times 10^{-5} - 0.169 \times 10^{-5} = 0.223 \times 10^{-5};$$

and at  $30^{\circ}$  C. it will be

$$0.393 \times 10^{-5} - 0.164 \times 10^{-5} = 0.229 \times 10^{-5};$$

whilst the soda-glass piezometers, Nos. 7 and 8, may be taken to have, at  $0^{\circ}$  C. and  $30^{\circ}$  C., the coefficients

$$0.221 \times 10^{-5} \text{ and } 0.224 \times 10^{-5} \text{ respectively.}$$

*The Compressibility of Water.*—For purposes of comparison we give two observations at  $0^{\circ}$  C., which have already been published; these were obtained with piezometer 1A, and the mean relative coefficient was, between 15 and 76 atmospheres,  $4.886 \times 10^{-5}$  in the one case, and in the other  $4.904 \times 10^{-5}$  for a range of 1 to 61 atmospheres. On adding the coefficient of compressibility of the Jena-glass the mean coefficient for water becomes  $5.109 \times 10^{-5}$  and  $5.127 \times 10^{-5}$  respectively. These numbers agree with one another remarkably well and do not differ greatly from AMAGAT'S values. The new results for water at  $0^{\circ}$  C. and  $30^{\circ}$  C. are given in Table II., where the columns tabulate the following:—

(1) Gives the number of the piezometer; (2) the mean temperature to which the results are reduced; (3) the pressure range—in the experiments with piezometers 7 and 8 the range is given both for a rising pressure and a falling one; (4) gives the mean relative coefficient of compressibility; (5) the coefficient for the glass of the particular piezometer in use, derived from the compressibility of mercury; (6) the coefficient of the liquid alone.

TABLE II.—Water at 0° C. and 30° C.

No. of piezometer.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.	No. of piezometer.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.
7	0·12 ° C.	10 to 27	× 10 <sup>-5</sup> 4·864	× 10 <sup>-5</sup> 0·221	× 10 <sup>-5</sup> 5·085	8	· 0·18 ° C.	14 to 41	× 10 <sup>-5</sup> 4·850	× 10 <sup>-5</sup> 0·221	× 10 <sup>-5</sup> 5·071
		27 " 48	4·858	—	4·820			—	5·041		
		48 " 27	4·858	—	4·819			—	5·040		
		27 " 10	4·869	—	4·849			—	5·070		
1A	29·52	0 to 14	4·382	0·229	4·611	3C	29·53	20 to 41	4·282	0·229	4·511
		14 " 27	4·362	—	4·591			—	4·454		
		27 " 41	4·316	—	4·545			—	4·450		
		41 " 54	4·240	—	4·469			—	4·409		
7	29·6	10 to 51	4·263	0·224	4·487	7	30·19	20 to 32	4·262	0·224	4·486
		51 " 10	4·261	—	4·485			—	4·462		
8	30·01	17 to 48	4·234	0·224	4·458	8	30·01	20 to 32	4·238	—	4·486
		48 " 78	4·210	—	4·434			—	4·462		
		78 " 48	4·207	—	4·431			—	4·465		
		48 " 17	4·234	—	4·458			—	4·448		

TABLE III.—Cane Sugar at 0° C.

No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of glass of piezometer.	True mean coefficient of solution.	No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of glass of piezometer.	True mean coefficient of solution.
1A* 180 gr. of sugar per litre at laboratory temperature.	° C. 0·01	0 to 20 20 " 41 41 " 61 61 " 82	× 10 <sup>-5</sup> 4·168 4·178 4·165 4·135	× 10 <sup>-5</sup> 0·223 — — —	× 10 <sup>-5</sup> 4·391 4·401 4·388 4·358	1A* 300 gr. of sugar per litre at laboratory temperature.	° C. 0·00	0 to 20 20 " 41 41 " 61 61 " 82	× 10 <sup>-5</sup> 3·747 3·730 3·700 3·673	× 10 <sup>-5</sup> 0·223 — — —	× 10 <sup>-5</sup> 3·970 3·953 3·923 3·896
1A* 420 gr. of sugar per litre of solution at laboratory temperature.	0·02	0 to 20 20 " 37 37 " 51 51 " 81	3·301 3·303 3·298 3·270	0·223 — — —	3·524 3·526 3·521 3·493	7 56·80 gr. of sugar to 100 gr. of water (420).	0·28	7 to 34 34 " 61 61 " 34 34 " 7	3·257 3·241 3·241 3·257	0·221 — — —	3·478 3·462 3·462 3·478
1A* 540 gr. of sugar per litre at laboratory temperature.	0·01	0 to 20 20 " 41 41 " 61 61 " 81	2·973 2·962 2·925 2·895	0·223 — — —	3·196 3·185 3·148 3·118	3B* 660 gr. of sugar per litre at laboratory temperature.	0·21	0 to 20 20 " 41 41 " 61 61 " 82 82 " 102	2·611 2·577 2·567 2·550 2·509	0·223 — — — —	2·834 2·800 2·790 2·773 2·732

\* These experiments were done with the old apparatus having a glass tube outside.



TABLE III—Cane Sugar at 0° C. (continued).

No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of glass of piezometer.	True mean coefficient of solution.	No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of glass of piezometer.	True mean coefficient of solution.
7 111.9 gr. of sugar to 100 gr. of water (660).	° C. 0.13	7 to 41 41 " 75 75 " 41 41 " 7	× 10 <sup>-5</sup> 2.575 2.556 2.563 2.576	× 10 <sup>-5</sup> 0.221 — — —	× 10 <sup>-5</sup> 2.796 2.777 2.784 2.797	3B* 750 gr. of sugar per litre at laboratory temperature.	° C. 0.03	0 to 20 20 " 41 41 " 61 61 " 82	× 10 <sup>-5</sup> 2.309 2.346 2.340 2.329	× 10 <sup>-5</sup> 0.223 — — —	× 10 <sup>-5</sup> 2.532 2.569 2.563 2.552
3B* 750 gr. of sugar per litre at laboratory temperature.	0.03	0 to 20 20 " 41 41 " 61 61 " 82	2.739 2.302 2.235 2.216	0.223 — — —	2.962 2.525 2.458 2.439	3C 750 gr. of sugar per litre at laboratory temperature.	0.00	14 to 48 48 " 82 82 " 122 122 " 14	2.347 2.323 2.292 2.322	0.223 — — —	2.570 2.546 2.515 2.545
7 141.4 gr. of sugar to 100 gr. of water (750).	0.10	7 to 44 44 " 82 82 " 44 44 " 7	2.343 2.324 2.322 2.341	0.221 — — —	2.564 2.545 2.543 2.562	1A 182.7 gr. of sugar to 100 gr. of water (850).	0.00	0 to 20 20 " 48 48 " 75 75 " 105	2.212 2.160 2.153 2.139	0.223 — — —	2.435 2.383 2.376 2.362
7 183.5 gr. of sugar to 100 gr. of water (850).	0.12	0 to 41 41 " 88 88 " 41 41 " 0	2.123 2.112 2.112 2.125	0.221 — — —	2.344 2.333 2.333 2.346	7 215.4 gr. of sugar to 100 gr. of water (920).	0.20	10 to 27 27 " 48 48 " 95 95 " 48 48 " 10	2.014 2.002 1.995 1.991 2.015	0.221 — — — —	2.235 2.223 2.216 2.212 2.236

\* These experiments were done with the old apparatus having a glass tube inside.

TABLE IV.—Cane Sugar at 30° C.

No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above the atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.	No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above the atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.
3C 420 gr. sugar per litre at laboratory temperature.	° C. 29.52	0 to 27	$\times 10^{-5}$ 3.106	$\times 10^{-5}$ 0.229	$\times 10^{-5}$ 3.335	7 56.7 gr. sugar to 100 gr. of water (540).	° C. 29.84	17 to 41	$\times 10^{-5}$ 3.111	$\times 10^{-5}$ 0.224	$\times 10^{-5}$ 3.335
		27 " 54	3.076	—	3.311						
		54 " 82	3.061	—	3.315						
		82 " 109	3.025	—	3.328						
		0 " 82	3.079	—	—						
3C 540 gr. sugar per litre at laboratory temperature.	29.53	0 to 27	2.824	0.229	3.053	3C 660 gr. sugar per litre at laboratory temperature.	29.83	0 to 27	2.552	0.229	3.781
		27 " 61	2.794	—	3.788						
		61 " 88	2.769	—	3.733						
		88 " 116	2.783	—	3.714						
7 660 gr. sugar per litre at laboratory temperature.	29.55	17 to 34	2.562	0.224	2.786	7 111.9 gr. sugar to 100 gr. of water (660).	29.87	17 to 51	2.550	0.224	2.774
		34 " 51	2.547	—	2.771						
		51 " 68	2.527	—	2.753						
		68 " 88	2.509	—	2.774						
3C 142.1 gr. sugar to 100 gr. of water (750).	29.52	0 to 34	2.370	0.229	2.599	3C 850 gr. sugar per litre at laboratory temperature.	29.52	0 to 34	2.176	0.229	2.405
		34 " 68	2.350	—	2.579						
		68 " 102	2.332	—	2.561						
		102 " 136	2.302	—	2.531						

TABLE IV.—Cane Sugar at 30° C. (continued).

No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above the atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.	No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above the atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.
3C 185.3 gr. sugar to 100 gr. water (850).	° C. 29.53	0 to 34	2.165	0.229	2.394	1A 185.3 gr. sugar to 100 gr. water (850).	° C. 29.53	0 to 27	2.202	0.229	2.431
		34 " 75	2.144	—	2.395						
		75 " 109	2.130	—	2.395						
		109 " 147	2.117	—	2.372						
7 183.6 gr. sugar to 100 gr. of water (850).	29.90	20 to 61	2.189	0.224	2.413	1A 218.5 gr. sugar to 100 gr. water (920).	29.52	0 to 27	2.089	0.229	2.318
		61 " 102	2.138	—	2.362						
		102 " 61	2.140	—	2.364						
		61 " 20	2.186	—	2.410						
1A 920 gr. sugar per litre at laboratory temperature.	29.53	17 to 44	2.130	0.229	2.359	1A 243.0 gr. sugar to 100 gr. of water (960).	29.53	0 to 27	2.019	0.229	2.248
		44 " 71	2.055	—	2.284						
		27 to 71	1.974	0.224	2.198						
		71 " 116	1.919	—	2.143						
7 238.3 gr. sugar to 100 gr. water (960).	29.54	116 " 71	1.920	—	2.144	1A 243.0 gr. sugar to 100 gr. of water (960).	29.53	27 " 61	2.004	—	2.233
		71 " 27	1.975	—	2.199						
		27 " 71	1.983	—	2.207						
		27 " 71	1.983	—	2.207						

TABLE V.— $\alpha$ -Methyl Glucoside at 0° C. and 30° C.

No. of piezometer and weight concentration.	Mean temperature of observation.	Pressure range above the atmospheric pressure in atmospheres.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.	No. of piezometer and weight concentration.	Mean temperature of observation.	Pressure range above the atmospheric pressure in atmospheres.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.
8 23.0 gr. to 100 gr. of water.	° C. 0.12	17 to 48	$\times 10^{-5}$ 3.857	$\times 10^{-5}$ 0.221	$\times 10^{-5}$ 4.078	7 23.0 gr. to 100 gr. of water.	° C. 29.98	20 to 31	$\times 10^{-5}$ 3.624	$\times 10^{-5}$ 0.224	$\times 10^{-5}$ 3.848
		48 " 82	3.843	—	3.859						
		82 " 48	3.834	—	3.829						
		48 " 17	3.866	—	3.736						
		17 to 58	3.110	0.221	3.791						
		58 " 78	3.081	—	3.825						
		78 " 102	3.069	—	3.861						
		102 " 58	3.076	—	3.833						
		58 " 17	3.109	—	—						
		—	—	—	—			—	—	—	—
8 54.7 gr. to 100 gr. of water.	° C. 0.21	20 to 48	2.817	0.221	3.038	7 54.5 gr. to 100 gr. of water.	29.98	20 to 37	3.101	0.224	3.325
		48 " 92	2.798	—	3.331						
		92 " 48	2.800	—	3.286						
		48 " 20	2.817	—	3.327						
		[20 " 0	2.812	—	3.301						
		—	—	—	3.318						
		—	—	—	3.335						
		—	—	—	3.329						
		—	—	—	—						
		—	—	—	—						
8 90.2 gr. to 100 gr. of water.	° C. 0.13	0 to 44	2.672	0.221	2.893	7 75.2 gr. to 100 gr. of water.	29.99	14 to 27	2.931	0.224	3.155
		44 " 95	2.649	—	3.119						
		95 " 44	2.649	—	3.107						
		44 " 0	2.671	—	3.100						
		—	—	—	3.100						
		—	—	—	3.107						
		—	—	—	3.114						
		—	—	—	3.146						
		—	—	—	—						
		—	—	—	—						
8 90.2 gr. to 100 gr. of water.	° C. 29.86	24 to 75	2.755	0.224	2.979	8 90.2 gr. to 100 gr. of water.	29.86	24 to 75	2.755	0.224	2.979
		75 " 95	2.740	—	2.964						
		95 " 119	2.719	—	2.943						
		119 " 95	2.719	—	2.943						
		95 " 75	2.738	—	2.962						
		75 " 24	2.757	—	2.981						
		—	—	—	—						
		—	—	—	—						
		—	—	—	—						
		—	—	—	—						

On looking at the tables it will be seen that the values for piezometers 7 and 8 at 0° C., although agreeing among themselves, are considerably lower than our previous results. We are, however, inclined to attach more weight to these experiments, for as may be seen by comparing the numbers for rising and for falling pressures, they are very concordant. In the experiments at 30° C., the earlier values with the Jena-glass piezometer are again higher. It is evident that the experiment with No. 7 at 30°·19 C. is somewhat faulty; we are unable to give a reason for this.

*The Results for Cane Sugar.*—The experiments at 0° C. are gathered together in Table III. where the columns have the same meaning as for water, except that the concentration of the solution is put under the number of the piezometer in column (1), and when the solution had been made up by weight, its approximate volume concentration (number of grammes per litre) is given in brackets. The numbers in column (4) for the experiments with the Jena-glass piezometers are generally the mean values obtained with a rising and a falling pressure; these, as already mentioned, are by no means concordant. In one or two cases even with No. 7 there were failures due to temperature troubles or to the mercury thread breaking. These remarks apply generally to all our observations.

Again it will be noticed that the No. 7 results are lower on the whole than those for the other piezometers.

The experiments at 30° C. are tabulated in the same way in Table IV., and again the values for piezometer 7 are lower.

*The Results for  $\alpha$ -methyl Glucoside.*—These, both for 0° C. and 30° C., are given in Table V. All the observations are made with either piezometers 7 or 8 and they seem, except in one case, to be good.

*Final Values for the Compressibilities.*—In this communication the compressibilities are only required for the purpose of calculating the  $s$  of PORTER'S equation.\* The solutions themselves are very incompressible, so that even over the range of the highest osmotic pressure the effect on the volume is but small, and therefore the pressure effect on  $s$  will be that of a small correcting term. In these circumstances it will suffice to give the mean coefficients (over the range from one atmosphere to the osmotic pressure of each solution) that we will use later on. In the set of mean values entered in Table VI. greater importance was given to the best experiment with piezometers 7 and 8.

*The Calculation of  $s$ .*—Although it is common knowledge that the quantity  $s$ , for the solutions with which we are concerned, differs but little from unity, yet it seems worth while to give the following analysis (due to Mr. G. W. WALKER), as there are numerous cases in which a detailed statement may be important.

Prof. PORTER† defines  $s_1$  as “the reduction in a practically infinite volume of

\* ‘Roy. Soc. Proc.,’ A, vol. 80, 1908, p. 460.

† *Loc. cit.*

TABLE VI.—Cane Sugar.

Approximate volume concentration.	Weight concentration.	At 0° C.		At 30° C.	
		$k \times 10^{-5}$ .	Pressure range. 1 to osmotic pressure.	$k \times 10^{-5}$ .	Pressure range. 1 to osmotic pressure.
—	34.0	—	—	3.62	1 to 27
420	56.5	3.46	1 to 44	3.31	1 „ 47
540	81.2	—	—	3.00	1 „ 73
660	112.0	2.78	1 to 100	2.73	1 „ 108
750	141.0	2.53	1 „ 135	2.56	1 „ 143
850	183.0	2.33	1 „ 187	2.36	1 „ 199
920	217.5	2.20	1 „ 230	2.28	1 „ 249
960	243.0	—	—	2.15	1 „ 264
$\alpha$ -Methyl Glucoside.					
Approximate volume concentration.	Weight concentration.	At 0° C.		At 30° C.	
		$k \times 10^{-5}$ .	Atmospheres.	$k \times 10^{-5}$ .	Atmospheres.
—	23.0	4.096	1 to 30	3.860	1 to 32
—	54.7	3.327	1 „ 81	3.326	1 „ 82
—	73.3	3.027	1 „ 113	3.104	1 „ 114
—	90.2	2.869	1 „ 141	2.971	1 „ 141

solution when one gramme of solvent escapes”; the pressure being maintained constant. The corresponding quantity for the solute is  $s_2$ .

Hence if  $w$  is the specific volume of the solution at any pressure  $p$ , and  $c_1$  and  $c_2$  are the concentrations (grammes per gramme of solution) of the two constituents, we deduce that

$$s_1 = w - c_2 \partial w / \partial c_2,^*$$

where  $w$  is a function of  $c_2$  and  $p$ , and

$$s_2 = w - c_1 \partial w / \partial c_1,$$

where  $w$  is a function of  $c_1$  and  $p$ .

\* CALLENDAR. ‘Roy. Soc. Proc.’ A, vol. 80, 1908, p. 470, gives this equation without proof. It may be obtained thus: Let  $m_1$  and  $m_2$  be the masses of the two components present in a volume  $V$  of solution, then  $m_1/(m_1 + m_2) = c_1$  and  $m_2/(m_1 + m_2) = c_2$  and  $w = V/(m_1 + m_2)$ . Now add a mass  $\delta m_1$  of solvent, and let the increase in volume be  $\delta V$ , we have  $m_2/(m_1 + m_2 + \delta m_1) = c_2 + \delta c_2$  and  $w + \delta w = (V + \delta V)/(m_1 + m_2 + \delta m_1)$ , from which  $w - c_2 \partial w / \partial c_2 = \delta V / \delta m_1$ , which is  $s_1$ .

From this it follows, since  $c_1 + c_2 = 1$ , that

$$w = s_1 c_1 + s_2 c_2 \quad \dots \quad (1)$$

and

$$c_1 \partial s_1 / \partial c_2 = c_2 \partial s_2 / \partial c_1 \quad \dots \quad (2)$$

The form of (1) at first suggests that  $s_1$  and  $s_2$  are the specific volumes in the solution of the two components. This is not necessarily so. For calling the true specific volumes  $s_1^1$  and  $s_2^1$ , then we have  $w = s_1^1 c_1 + s_2^1 c_2$ , which on differentiating gives

$$s_1^1 = w - c_2 \partial w / \partial c_2 + c_2 (c_1 \partial s_1^1 / \partial c_2 - c_2 \partial s_2^1 / \partial c_1),$$

and

$$s_2^1 = w - c_1 \partial w / \partial c_1 - c_1 (c_1 \partial s_1^1 / \partial c_2 - c_2 \partial s_2^1 / \partial c_1),$$

thus

$$s_1^1 = s_1 \text{ and } s_2^1 = s_2 \text{ only if } c_1 \partial s_1^1 / \partial c_2 = c_2 \partial s_2^1 / \partial c_1.$$

There does not appear to be any adequate ground for supposing this condition is in general satisfied. If it is not, we have  $s_1^1 = s_1 + k c_2$  and  $s_2^1 = s_2 - k c_1$  where  $k = (c_1 \partial s_1^1 / \partial c_2 - c_2 \partial s_2^1 / \partial c_1)$  is in general a function of the pressure and concentration.

Returning now to the calculation of  $s_1$ . Some of the densities given in LANDHOLT and BÖRNSTEIN for cane sugar solutions having been verified experimentally, the remainder of their table was taken as correct; the densities of the  $\alpha$ -methyl glucoside solutions were determined by us and the mean values are tabulated in Table VII.

TABLE VII.—Cane Sugar.

Weight concentration.	$\bar{s}_1$ at			
	0° C.	30° C.		
34.00	0.99768	1.00287		
56.50	0.99515	1.00103		
81.20	0.98157	0.99873		
112.0	0.98690	0.99554		
141.0	0.98321	0.99176		
183.0	0.97842	0.98653		
217.5	0.97399	0.97360		
243.0	0.97117	0.98176		
$\alpha$ -Methyl Glucoside.				
Weight concentration.	Densities at		$\bar{s}_1$ at	
	0° C.	30° C.	0° C.	30° C.
25.0	—	—	—	—
35.0	1.09319	1.08399	0.99810	1.00260
45.0	1.11341	1.10308	0.99709	1.00186
55.0	1.13149	1.12017	0.99597	1.00087
64.0	1.14619	1.13407	0.99491	0.99996
75.0	1.16243	1.14942	0.99354	0.99881
90.0	1.18195	1.16788	0.99166	0.99721
105.0	1.19896	1.18399	0.98974	0.99507

Empirical formulæ were then obtained which represented the experimental values of the densities and the compressibilities (Table VI.) for different concentrations, and from these formulæ the values  $s_1$  were computed as a function of  $c_2$  and  $p_0$ . In PORTER'S equation\*  $s_1$  has to be integrated over a range of pressure from one atmosphere to the osmotic pressure of the particular solution; it was considered sufficiently accurate to regard it as a linear function of the pressure and the mean value,  $\bar{s}_1$  (equals half the sum of the value at the limits) is given in Table VII.

## PART II.

### THE VAPOUR-PRESSURE MEASUREMENTS.

*Description of Apparatus and Method.*—Although the method employed has already been described it may not be out of place to recall it to mind.

Dry air is led through a number of vessels containing the solution, then through a vessel containing the solvent (water), and finally over sulphuric acid in the end vessel of the train. The air is supposed to flow slowly enough to be saturated up to the vapour pressures of the liquids. In these circumstances, if we call the sum of the losses of weight of solution and solvent  $l_0$ , and the loss in the solution alone  $l_1$ , then the observed ratio of the vapour density of the solvent to the vapour density of the solution is  $l_0/l_1$ .

This statement is however subject to various corrections; but, before considering these, it will be convenient to describe the complete installation.

Fig. 3 represents in diagram form the arrangement for passing the air stream over the vessels, as finally modified so as to eliminate the various sources of error, which several years' experience has shown to be possible.

Filtered air, drawn from outside the laboratory, is passed through soda-lime, and then over the surface of sulphuric acid in vessel A, where it is deprived of almost all its moisture. (It may here be mentioned that the chief aim of this final arrangement has been to avoid, as far as possible, any sudden alteration of pressure; the air passages are therefore made as wide as may be and at no point does the air bubble through any liquid.) On leaving A the air passes through another sulphuric acid vessel B which is in, and at the constant temperature of, the bath; it then enters the train of weighed vessels 1, 2, 3, 4, and 5, which contain the various liquids under examination; the last of these, No. 5, is again a sulphuric acid vessel.

From 5 it goes to the regulating valve C. This valve, which was designed by BERKELEY and THOMAS for another research, consists of a biscuit-porcelain filter (*f*) surrounded to a variable height by mercury. It will be seen that the volume of

\* See p. 343.



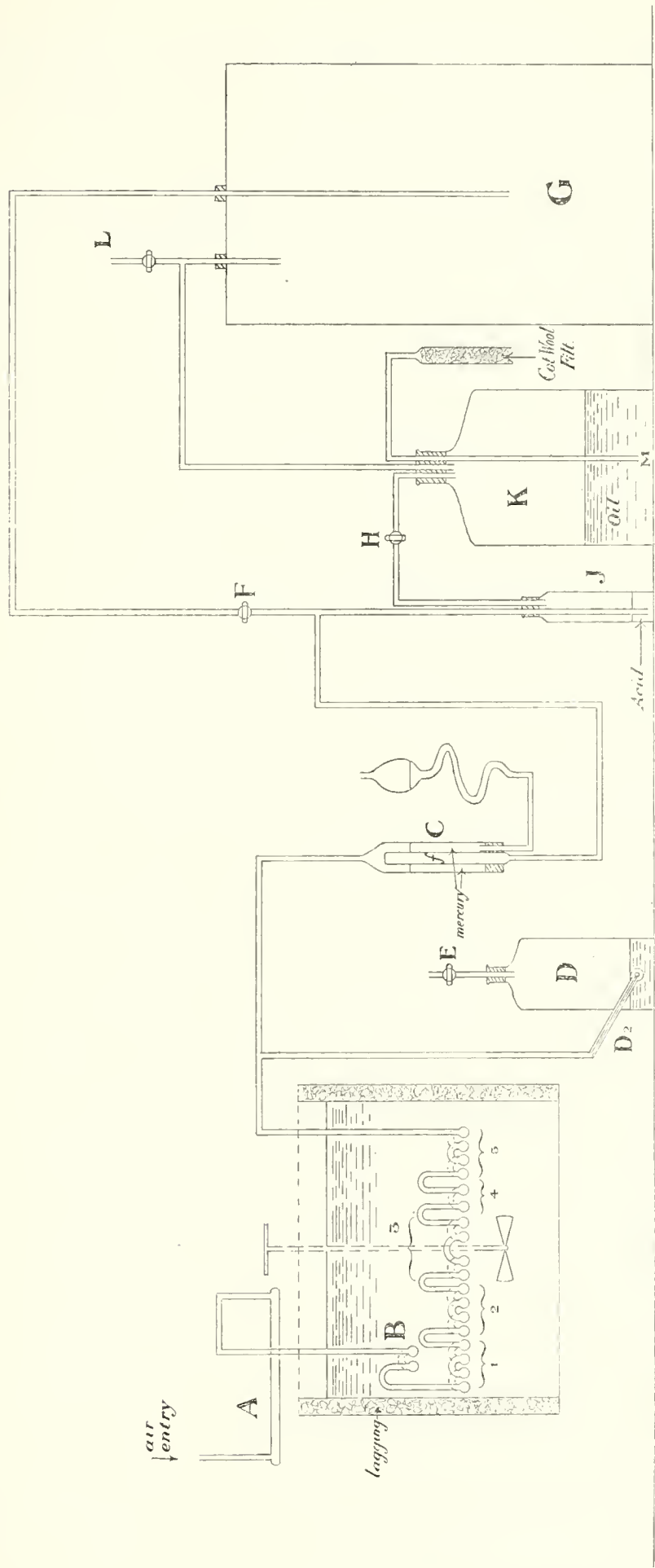


Fig. 3.

air passing through the whole apparatus is approximately proportional to the area of the filter not covered by mercury, and it may be stated that we have found this device most useful, especially when it is provided with a graduated scale to enable one to set the mercury level to a definite height.

Before reaching C, the air has passed a side-tube which connects with the vessel D. This vessel (of 5 litres capacity), containing a small quantity of water, the level of which is observed (telescopically) in the graduated capillary tube  $D_2$ , serves three purposes. With the tap E closed, and the mercury in C adjusted to the proper level, the rise of the water in  $D_2$  is a measure of the rate at which the air is passing; thus any obstruction in the air stream will at once be indicated, while the amplitude of the oscillations (if any) of the water meniscus affords a means of detecting outside atmospheric pulses. Again, with the tap E open (and this is the normal position during an experiment) the outside air pulses are practically eliminated, and any oscillations that may then be apparent are the result of changes in pressure on the exhaust side. It was found that when the iron tank G was added to the apparatus the pulses were so reduced as to be scarcely perceptible.

The air normally passes through tap F into G (200 litres capacity), and tap H is kept closed; this latter tap is only used in conjunction with vessel J when testing the various joints for leaks. A partial vacuum is maintained both in G and in the 15-litre jar K by a Fleuss pump (not shown) which is joined on at L. In the main, the degree of vacuum is determined by the height of oil in K, above the air inlet M.

We will now consider the various corrections that have to be applied to the experimentally determined vapour pressures.

*BURTON'S Correction.*—The most important of these is that which we will call “BURTON'S correction,” for it was he who showed that the effect is not negligible as we had erroneously assumed. The correction is inherent in the method itself, and will be apparent at once when it is realized that the air stream (which has been saturated up to the vapour-pressure of the solution) on entering the water vessel is expanded slightly by the vapour it takes up there; consequently the volume of air when leaving the water vessel is slightly greater than when it left the solution.

This correction, together with the effect due to changes in barometric pressure, was briefly outlined in ‘Nature’ (March 11, 1915, p. 34); there are, however, other factors involved which make a more general discussion desirable.

If we make the assumptions that the temperature of both solution and solvent is the same and remains constant, and that the air space between them is negligibly small, and further, that the air stream flows slowly enough for complete saturation and freedom from turbulent motion, then the following analysis (for which we have to thank Mr. G. W. WALKER) will be applicable.

Let  $p$  be the pressure of the air at any point in the train of vessels and  $v$  its rate of passage in cubic centimetres per second. Let  $\pi_s$  and  $\pi_0$  be the vapour pressures of solution and solvent respectively and  $\rho_1$  and  $\rho_0$  the corresponding vapour densities.

If  $p_1$  and  $r_1$  be the values of  $p$  and  $r$  when the air enters the solution vessel, then the volume of air that passes through this vessel in time  $\delta t$  is

$$\frac{r_1 p_1}{p_1 - \pi_\pi} \delta t,$$

and the mass of vapour carried off is

$$\frac{\rho_1 r_1 p_1}{p_1 - \pi_\pi} \delta t,$$

and the loss of weight will be

$$l_1 = \int_0^t \frac{\rho_1 r_1 p_1}{p_1 - \pi_\pi} dt,$$

where  $t$  is the whole time of the experiment.

In a similar way, if the dry air were passed through the solvent vessel the loss of weight would be

$$l_0 = \int_0^t \frac{\rho_0 r_0 p_0}{p_0 - \pi_0} dt.$$

But in the actual experiment the moist air passes from the solution to the solvent. so that the loss of weight in the solvent vessel is

$$l_0 - l_1 = \int_0^t \left( \frac{\rho_0 r_0 p_0}{p_0 - \pi_0} - \frac{\rho_1 r_1 p_1}{p_1 - \pi_\pi} \right) dt.$$

Since the mass of air passing through is the same at all points,  $r_1 p_1 = r_0 p_0$ . Also as  $r$  is proportional to the effective driving pressure through the whole train of vessels (and to a factor depending on the dimensions of the apparatus), if we assume this pressure and the barometer to be constant, we have

$$\frac{l_0}{l_1} = \frac{\rho_0}{\rho_1} = \frac{p_1 - \pi_\pi}{p_0 - \pi_0}, \quad \dots \dots \dots (3)$$

but  $p_1$  and  $p_0$  are of the order of 0.1 mm. Hg below atmospheric pressure, whilst the difference between them is of order 0.004 mm. Hg; and further, the barometric pressure,  $B$ , is of the order 760 and  $\pi_0$  of 30 mm. mercury; we may, therefore, as a first approximation write

$$\frac{l_0}{l_1} = \frac{\rho_0}{\rho_1} = \frac{B - \pi_\pi}{B - \pi_0},$$

and assuming

$$\frac{\pi_\pi}{\pi_0} = \frac{\rho_1}{\rho_0}$$

we get

$$\frac{\rho_0}{\rho_1} = \frac{l_0}{l_1} \frac{\pi_0}{B} \left( \frac{l_0}{l_1} - 1 \right) \dots \dots \dots (4)$$

If either the barometer or the driving pressure varies, this formula is not strictly correct, and in general we should have to evaluate the integral numerically from a record of the pressures; we may still, however, write

$$l_1 = t \left( \frac{\rho_1 v_1 p_1}{p_1 - \pi_1} \right)_{\text{mean}} \quad \text{and} \quad l_0 = t \left( \frac{\rho_0 v_0 p_0}{p_0 - \pi_0} \right)_{\text{mean}},$$

where the quantities involved must now be given some mean value, which is not necessarily the arithmetic mean.

But in the experiments the magnitude of the quantities makes it clear that the arithmetic mean is a very close approximation to the true value, and hence equation (4) is sufficiently accurate if B is the mean barometer.

To make quite sure that this is correct we have verified it in an extreme case, where during the experiment the barometer varied irregularly by some 30 mm., but no sensible error was introduced. Nevertheless cases may arise in which the error might be important, and attention is therefore drawn to it so that the correction may not be overlooked. For instance, during high winds the barometer fluctuates rapidly, and it is conceivable that equilibrium is not established throughout the apparatus instantaneously. In this case the assumptions made in the formula are not valid, and indeed we have some experimental evidence that the results are affected by rapid air pulses.

As regards a change in the temperature of the bath, obviously the quantities involved in the calculation are also affected, but equation (4), in which the values appropriate to the mean temperature are used, is still a close approximation provided the temperature changes are sufficiently small.

In our experiments  $l_0/l_1$  is always less than 1.22, hence the osmotic pressure, which is proportional to  $\log_e l_0/l_1$ , is approximately proportional to  $(l_0 - l_1)/l_0$ ; thus it is only with the loss of weight of the water vessel that the highest accuracy is required.

We will now endeavour to estimate the errors involved should the assumptions made at the beginning of the preceding analysis not be strictly accurate.

*Solution and Solvent not at same Temperature.*\*—Although the effect of a difference between the temperatures of the solution and solvent could be investigated fully from the equations already established, yet it is thought that the following simple method of considering the matter is sufficient. Take the case of a weight normal solution of cane sugar at 30° C. This solution is the most dilute that we have investigated, and it is here that the error due to a temperature difference has the largest effect. Suppose  $l_0 = 20$  gr. (*i.e.*, 20 gr. of water are evaporated from the whole system during the run) and  $l_0 - l_1 = 0.5$  gr. Now assume a persistent difference in temperature during the whole run of 0°·001 C; this is equivalent to a change of 0.006 per cent. in the vapour density of water; so that the loss in the water vessel will differ from the

\* See note at end of paper.

true value by  $20 \times 0.006/100 = 0.0012$  gr., entailing a per cent. error of 0.2 both in the loss in this vessel and on the calculated osmotic pressure.

Several attempts to explore the distribution of temperature throughout the bath were made with Beckman thermometers and with thermocouples, but, except within about 3 cm. of the surface, no certain indication of a difference approaching to  $0.001$  C. could be detected; further, as a check to this, vapour pressure experiments in which the bath was stirred 50 per cent. faster than the normal rate (in the normal rate, the surface of the water immediately over the stirrer is raised about 1 cm. above the general level) resulted in no change.

Similarly, should the pressure  $p_1$  (see equation (3)) over the solution differ from  $p_0$  over the solvent by as much as 0.015 mm. Hg, an amount which represents a change of 0.02 per cent. on the volume of air passed, we get an error on the loss of weight of the solvent of 0.0004 gr., and this is nearly 0.1 per cent. on the osmotic pressure derived from experiments on a weight normal solution at  $30^\circ$  C. Direct observations (by means of a sensitive oil manometer) of the difference between  $p_1$  and  $p_0$  show that in no case is this quantity greater than  $0.004^*$  mm. Hg, and the consequent correction will be, for the most dilute solutions, about 1 part in 5000. It should be pointed out, however, that the magnitude of the correction is proportional to the vapour pressure of the pure solvent, so that for very volatile liquids or water at a higher temperature the air passages must be wide so as to offer as little resistance to flow as possible.

*Air Space between Solution and Solvent.*—An error, due to the air space between the two vessels, may arise thus. When the barometer is varying no steady state is reached, and it is easy to see that as it takes a finite time for the air to travel from one vessel to the other,  $v_1 p_1$  and  $v_0 p_0$  are no longer equal, and a time lag results.

An estimate of the maximum error due to this cause is the following.

From the dimensions of the apparatus it is computed that, supposing 500 litres of air to pass in 125 hours, it will take 25 seconds to pass from one vessel to the other. If the barometer rises 30 mm. during the run, it is readily found that the solvent vessel will have lost 0.00005 gr. in excess of the amount given by the approximate formula (4).

*Slowness of Air Stream and Turbulent Motion.*—There seems to be no means of subjecting these two factors to mathematical analysis; but in both cases we may safely assume that any effect there may be will be enhanced when we increase the rate at which water vapour is taken from the system. Experiments, the details of which need not be given, were made in this direction, but without any variation in the result; also a further safeguard is provided by the fact that in experiments where there were two or more vessels (containing the solution) in series, the last vessel scarcely changes in weight. It is as well however to point out that owing to the irregular contours of the air passages some turbulent motion must set up,

\* This is for Apparatus A; for Apparatus D the fall of pressure is about 0.001 mm. Hg.

and possibly fluctuations in this may help to cause the slight variations which seem to occur in high winds.

*Weighing Corrections.*—In applying the usual buoyancy corrections there are two special circumstances to be considered. In the earlier part of our research we had been content to regard the loss of weight in the solution as a measure of the change in the volume of displaced air for which the buoyancy correction should be calculated. Having improved the manipulation and consequently the accuracy of the experiments, it was seen that this rough estimate could be bettered if we knew the specific volume of the solution remaining in the vessel at the end of the run. The data required are obtained approximately if we know the initial quantity of solution in each branch and how far crystallization has proceeded.

The magnitude of the correction thus deduced is in no case greater than 0.0015 gr. and may in the calculations of osmotic pressure be neglected; it however is of importance when we balance the losses against the gain by the sulphuric acid in the end vessel.

Similarly, but only since November 5, 1915, have we applied the corresponding correction to the change in the specific volume of the sulphuric acid when it absorbs water. In this case we have succeeded in making the correction more precise, for knowing that practically all the water is absorbed in the first two branches\* of the vessel, it is an easy matter (especially in the new quartz apparatus) to cause their contents to mix, so that having noted the original amount of acid present the specific volume of this new solution can be calculated. The correction obviously depends on the relative quantities of acid and water; it has never risen to a higher figure than 0.0045 gr.

From a series of blank weighings with vessels treated as in an actual experiment it was deduced that the probable weighing error is  $\pm 0.0005$  gr., a quantity which is about the millionth part of the total weight on the pans.

*Other Sources of Error.*—A few other sources of error have been investigated, but as, in the apparatus used, their effect is never large enough to alter the results, they will only be mentioned briefly. There is a small weighing error due to the fact that the air contained in the water vessel† is saturated, and its density is therefore less than that of the air in the balance case. The usual buoyancy correction might have to be modified were it not that the vessels are weighed before and after the experiment under practically the same circumstances. It is found that even two or three degrees difference in the temperature of the balance case, although it causes a change in the vapour pressure, does not affect the weighings.

It was thought that plunging the vessels straight from the laboratory temperature into the bath at 30° C. might bring about some uncertainties; these, if any, are

\* See BERKELEY and HARTLEY, "On a New Form of Sulphuric Acid Drying Vessel," 'Phil. Mag.,' vol. 29, 1915.

† Care is taken that the pressure inside the vessel is the same as that in the balance case.

reduced to small dimensions if care be taken that the full air stream is not turned on before the apparatus has come to the bath temperature; on the other hand, we found that taking the apparatus out of the bath without any preliminary treatment\* caused a large error owing to the fact that the connecting tubes (and other air spaces) cooled more rapidly than the liquids, and so acted as condensers on which moisture was deposited; this trouble was eventually overcome by running cold water into the bottom of the bath (so as to displace the hot water) until it just reached the level of the vessels. In this manner the liquids were caused to cool earlier than the connecting tubes.

*Another Possible Source of Error is that Due to Diffusion.*—A small amount of diffusion of water vapour from the solvent to the sulphuric acid takes place during the time the apparatus is being set up and taken down; the total time taken for these operations is roughly about four hours, and calculation shows that at 12° C. not more than 0·0002 gr. of water would come over.

*The Vessels.*—Four different sets of vessels have been used in this research, and for a proper understanding of the objects for which they were made, a brief description follows.

In the earlier part we used the set of vessels (with their platinum joining tubes, &c.) and the method of oscillating the platform on which they stand in the bath described in 'Phil. Trans.,' A, vol. 209, pp. 177–203. In the same communication it will be noticed that one experiment (p. 188), where there had been no oscillation, gives a result that scarcely differs from the others. This led to a number of test experiments (details need not be given) which satisfied us that oscillation, anyhow under certain circumstances, was not essential.

We will call this set, when oscillated, Apparatus Aa; and without oscillation, Apparatus Ab. It is to be noted that from now onwards oscillation was given up.

In the next set (Apparatus B) which followed the general lines of Apparatus A, but was unfortunately constructed of soft Jena-glass, three changes were made: (1) the capacity of the vessels was largely increased (the diameter of the tubing forming the horizontal branches is now 1·7 cm.) to ensure that, for a dilute solution such as weight-normal sugar, the loss of the water vessels would be large enough to reduce the probable weighing error to 1 part in a 1,000; (2) the dipping tube, that is the tube joining the water and sulphuric acid vessels, was now increased in diameter from 1 mm. to 6 mm; (3) the platinum joining tubes were replaced by glass ones as shown in fig 4, which is a vertical cross-section through the centre of the vessels; A, B, and C are ground and lubricated joints, drowned in mercury; whilst D is a silver sleeve which was added when constructing the quartz-glass apparatus to be described. The object of this new form of joint is to enable the observer to weigh the inverted U-tubes E so as to find out whether water has been deposited in them. We would state here that normally water is only found in the U-tube joining the

\* The precautions to be taken when working at 0° C. will be obvious.

water vessel to the sulphuric acid; when it occurs in the other tubes there has always been some faulty manipulation or a rapid change in the temperature of the bath.

Apparatus C. It was soon noticed that the soft Jena-glass seemed particularly liable to deposition of moisture (possibly this glass is more soluble than others?) and also that cracks were developed in it. Hitherto, it will be recalled, the vessels are constructed so that the air enters at the middle of the first branch and leaves at the middle of the last branch; the stream is thus divided, re-united, divided again and then re-united.

It was thought that possibly better results would be obtained if the air were to enter at one end of the first branch, and, travelling along each branch in succession,

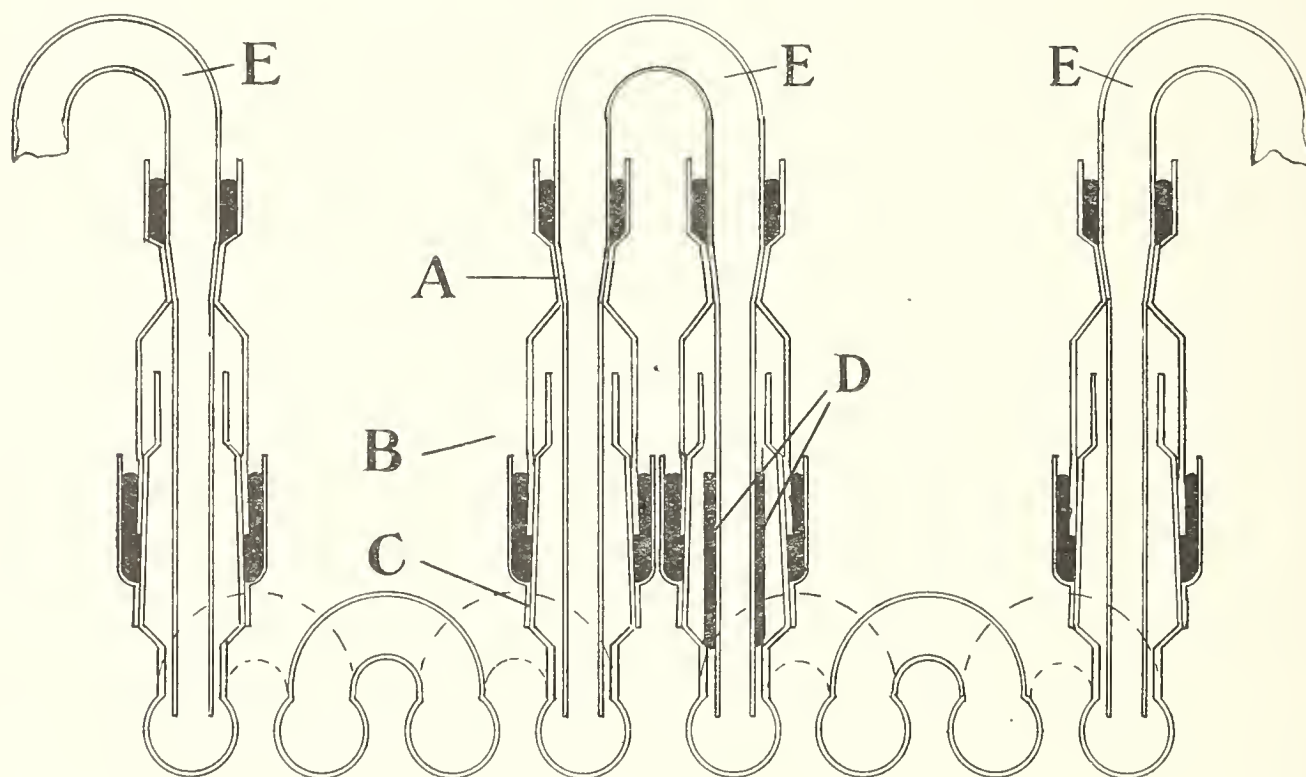


Fig. 4.

were to leave the vessel at the end of the fourth and last branch. Apparatus C was so constructed of ordinary soda-glass, but no apparent gain resulted.

Apparatus D. Meanwhile a number of experiments were made with a view to preventing the deposition of moisture mentioned above. A quartz vessel was substituted for the water vessel in Apparatus B and was found to be an improvement, so it was decided to make all the vessels of silica glass, the joints being similar to fig. 4, with the addition of a silver sleeve D resting on the cone as shown in that figure; this sleeve helps to prevent diffusion into the space surrounding the lower ends of the inverted U-tubes.



Even now water was occasionally deposited where it had no business to be. The cause of this was finally traced to the method we had hitherto employed in cleaning the vessels and their joining tubes. We had made a point of always cleaning out everything with "chromic" acid, and washing this acid out with distilled water (six washings in all) and then drying the parts in a current of air. It was noticed that dew formed at the places where the last drops of water evaporated off. This at once suggested that on evaporation the water left behind it some soluble substance, which, during the subsequent passage of saturated air, formed a solution having a smaller vapour pressure than pure water; hence the deposits. That the water actually did contain soluble matter was easily shown by evaporating off 100 c.c. in a platinum dish.

Efforts to obtain water free from this soluble matter failed completely, even though it was redistilled four times with all the usual precautions for obtaining "conductivity" water. That the deposit shown on the platinum dish did not come from the atmosphere was proved by evaporating off the samples in a desiccator over sulphuric acid. Eventually the vessels were cleaned by giving them a final washing with pure alcohol\* and drying in a current of warm air. Although this procedure was successful in reducing the trouble, yet the platinum tube (bore 6.5 mm.) which joined vessels 4 and 5 (the water to the sulphuric acid) generally contained about 0.0030 gr. of water.

No valid explanation of this phenomenon has yet been found,† and it is the more inexplicable in that three experiments have lately been carried out in which both the third and fourth vessels were reserved for water, with the result that the quartz tube between 3 and 4 contained less than 0.0010 gr., while the platinum tube retained the usual quantity. One of these experiments was arranged so that hydrogen was passed through the train of vessels instead of air.

We would draw particular attention to this question of the deposition of moisture, for there seems to be no doubt that it may have been a source of error in previous determinations of the absolute vapour density of water in air.

*The Experiments at 0° C.*—These experiments were all made with Apparatus Aa. The cane sugar and the  $\alpha$ -methyl together with the method of estimating the water content are described in 'Roy. Soc. Proc.' A, vol. 92, 1916, p. 479. The following is an example experiment.

\* The alcohol used was KAHLBAUM'S purest, re-distilled twice. Samples from the first distillation left deposits on the platinum dish, which were partially soluble in water, but the second distillation was found to be pure.

† If the conclusion come to in the note added at the end of the paper be correct, namely, that the last branch of vessel 4 is at a higher temperature than the remainder of the bath, then condensation in the platinum tube is to be expected.

EXPERIMENT with Cane Sugar at 0° C. Apparatus Aa. (Weight concentration = 182.805.)

Date.	Time.	Temperature.		Barometer.	Weight of vessels.				Remarks.
		Bath.	Balance.		(1.)	(2.)	(3.)	(4.)	
1911. Dec. 12	9.50 a.m.	° C.	° C.	741.5	L. 78.6211				Solution made up on December 11 and vessels filled same evening.  No. (1) contained in first half 20 c.c. and in second half 20 c.c. solution. No. (2) contained in first half 20 c.c. and in second half 15 c.c. solution. No. (3) contained in first half 14 c.c. and in second half 14 c.c. of water. No. (4) contained in first half 10 c.c. and in second half 14 c.c. of H <sub>2</sub> SO <sub>4</sub> .
	10.10 "		9.0		R. 78.6228				
	10.40 "		9.1		<u>78.6219</u> - 0.1098	L. 75.7152			
	11.0 "		9.2		<u>78.5121</u>	R. 75.7167			
	11.30 "		9.4			<u>75.7159</u> - 0.1059	L. 54.3377		
	11.50 "		9.6			<u>75.6100</u>	R. 54.3388		
	12.20 p.m.		9.8			<u>54.3382</u> - 0.0988	L. 81.2685		
	12.40 "		9.8	742.0		<u>54.2394</u>	R. 81.2700		
	1.0 "	(0.55)					<u>81.2692</u> - 0.1095		
	5.0 "	0.35					<u>81.1597</u>		
"	9.0 a.m.	0.39						Started air current.  NOTES. True mean temperature = 0°.51 C. Losses = 3.8872. Gains = 3.8886, including 0.0034 in "dipping" tube. Difference = +0.0014. ("Tot up.") l <sub>0</sub> /l <sub>1</sub> = 1.15901.	
"	5.0 p.m.	0.35							
"	9.0 a.m.	0.40							
"	6.0 p.m.	0.41							
"	9.0 a.m.	0.51							
"	5.0 p.m.	0.45							

EXPERIMENT with Cane Sugar at 0° C. Apparatus Aa. (Weight concentration = 182.805) (continued).

Date.	Time.	Temperature.		Barometer.	Weight of vessels.				Remarks.
		Bath.	Balance.		(1.)	(2.)	(3.)	(4.)	
1911. Dec. 16	9.0 a.m.	°C. 0.42	°C.						
"	5.0 p.m.	0.40							
"	10.0 a.m.	0.51							
"	5.0 p.m.	0.41							
"	9.0 a.m.	0.44							
"	5.0 p.m.	0.51							
"	9.0 a.m.	0.59							
	10.15 a.m.		11.0	744.0	L. 75.2704				
	10.35 "		11.1		R. 75.2724				
	11.5 "		11.2		<u>75.2714</u>				
	11.25 "		11.3		- 0.1130				
	11.55 "		11.4		<u>75.1584</u>				
	12.15 p.m.		11.6		R. 75.7161				
	12.45 "		11.8		<u>75.7152</u>				
	1.5 "		11.9	744.2	- 0.1054				
					<u>75.6098</u>				
					R. 53.8057				
					<u>53.8050</u>				
					- 0.0989				
					<u>53.7061</u>				
								L. 85.1489	
								<u>R. 85.1508</u>	
								<u>85.1498</u>	
								- 0.1049	
								<u>85.0449</u>	

Stopped and took down.

A word of explanation is necessary ; all weighings are made against a sealed counterpoise which is constructed of the same material as the vessels, and has approximately the same area exposed to the air. The counterpoise and vessels are, before weighing, treated with "chromic" acid, washed carefully with distilled water, and finally with pure alcohol. The alcohol is wiped off with linen dusters. It is hoped that this procedure results in leaving the surfaces in the same condition. The letters R and L mean that the counterpoise is on the right or left pan respectively, and the small correcting terms are those due to buoyancy.

The results obtained for these two substances are given in Tables VIII. and IX., and it should be mentioned that in all the tables relating to vapour pressure, columns, which are numbered the same, tabulate corresponding quantities.

Column (1) gives the date of setting the apparatus up in the bath and starting the air current.

Column (2) gives the weight concentration of the solutions, that is the ratio of number of grammes of anhydrous substance to 100 gr. of water.

Column (3) gives the mean temperature\* of the bath during the experiment ; and

Column (4) the mean barometer. It was only after the experiments at 0° C. were finished that the importance of BURTON'S correction was discovered. Although the height of the barometer had not been noted we were able to estimate the mean barometric pressure to an accuracy of 1 mm., from the records of a large-size aneroid barograph which is part of the laboratory equipment. Where by some mischance the barograph has failed, the barometer readings were kindly supplied by the Director of the Radcliffe Observatory at Oxford, to whom our best thanks are due.

Column (5). The numbers in this column are the total loss of weight of solution and solvent vessels ; in the earlier part of the research we filled all solution vessels with the same solution ; later work showed that two different solutions in series might be used, and the numbers marked thus † indicate these experiments. The numbers are the observed values corrected for buoyancy.

Column (6) gives the sum of the observed losses of weight of the solution and water vessels divided by the loss in the solution vessels, *i.e.*, the ratio  $l_0/l_1$ .

Column (7) gives the change in weight in the inverted U-tube ("dipping" tube) connecting the water and sulphuric acid vessels. This tube was always weighed as soon as possible after disconnecting the vessels ; in most experiments with Apparatus Aa a trace of dew, ‡ which quickly disappeared, was noticed on the outer surface of the part of the tube next to the water. A *minus* sign means that the tube lost weight on passing warm air through it ; a positive sign can only be the result of

\* In the cases where this quantity is enclosed in brackets it is to be understood that owing to some slight mishap the experiment is not as trustworthy as others.

‡ Probably the dew (it was seldom observed with the other apparatus) is caused by the cooling of the air stream, when throttled by having to pass through this tube, which is slightly less than 1 mm. in internal diameter.

TABLE VIII.—Cane Sugar at 0° C.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)
Date.	Weight concentration.	Mean value of Temperature of bath.	Barometer during experiment.	Total loss of weight. $l_0$ .	Observed ratio. $l_0/l_1$ .	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	$\rho_0/\rho_1$ .	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 0° C.	"Jump."	Sugar used in experiment.
		° C.	mm.									
Standard Weight Concentration = 56.50 gr. Sugar to 100 gr. Water.												
Mar. 11, 1911	56.631	(0.76)	744	7.2437	1.03612	-0.0004	-0.0004	116	1.03587	0.03516	Not determined.	Pure cane.
Standard Weight Concentration = 81.20 gr. Sugar to 100 gr. Water.												
Feb. 17, 1911	81.269	0.58	748	5.7198	1.05566	+0.0009	+0.0006	116	1.05530	0.05380	Not determined.	Pure cane.
Standard Weight Concentration = 112.00 gr. Sugar to 100 gr. Water.												
Feb. 2, 1911	111.637	0.37	767	5.2181	1.08379	+0.0001	+0.0007	92	1.08328	†0.08034	Not determined.	Pure cane.
" 8, 1912	111.494	0.42	734	4.2419†	1.08264	-0.0003	-0.0007	92	1.08211	†0.07939	"	KAHLBAUM'S 1st sample.
" 20, 1912	112.273	0.61	743	4.2227†	1.08388	-0.0026	+0.0015	92	1.08334	0.07985	"	M.W.C.
Mar. 23, 1912	112.120	0.48	746	3.4719†	1.08321	-0.0010	-0.0015	116	1.08268	†0.07936	"	KAHLBAUM'S 2nd sample.
June 14, 1912	111.906	0.60	749	3.9729†	1.08348	-0.0008	-0.0002	140	1.08295	0.07981	"	M.W.C.
Standard Weight Concentration = 141.00 gr. Sugar to 100 gr. Water.												
Jan. 20, 1911	141.182	0.37	761	3.4378	1.11342	+0.0002	-0.0002	68	1.11272	0.10669	Not determined.	Pure cane.

† In these experiments two different solutions were placed in series.

‡ When taking the mean values (given in Table XIII.) these results have not been used.





faulty manipulation. It must be remembered that the tube has to be weighed as quickly as possible.

Column (8). This column is headed "tot up"; by this we mean that the tabulated numbers are the difference in weight between the gain in the last vessel of the train (which contains sulphuric acid) and the sum of the losses of solution and water; the weight of water found in the "dipping" tube is added to that of the sulphuric acid, and a negative sign means that the losses are the greater, whilst the positive sign means that they are the smaller. It has been pointed out in a previous communication that the closer these numbers approach to zero the greater the probability that the experiment is a good one.

Column (9) gives the number of hours during which the air has passed through the vessels.

Column (10) gives  $\rho_0/\rho_1$  the value of the ratio  $l_0/l_1$  corrected for "BURTON'S" correction (see p. 316) on the assumption that  $p_1$  and  $p_0$  of equation (3) are equal to one another.

Column (11) gives  $\log \rho_0/\rho_1$  corrected to the standard weight concentration\* printed across the page, and also corrected to the standard temperature of 0° C. or 30° C., as the case may be.

*The Experiments at 30° C.*—Before proceeding to enumerate the experiments on sulphuric acid solutions it may be mentioned that since the completion of the work on calcium ferrocyanide we have made over 60 special test experiments (they are in addition to such as are detailed here) which have taken 287 days to complete. For the most part these were directed to testing alterations both in the vessels and in the speed of the air stream; a number were devoted to investigating the influence of ions in the air current (for this purpose a special set of vessels furnished with electrodes was constructed), but with no definite result; others on "tot up," and fall of pressure along the vessels were also made. The changes thus suggested are embodied in Apparatus D, whilst the final method of causing the air to flow is given on p. 316.

We give an example of what we consider to be a satisfactory experiment at this temperature.

The experiments on sulphuric acid solutions we made more for the purpose of testing the experimental conditions than for the determination of vapour pressures. But as they have turned out to be sufficiently concordant we give the details in Table X.

From a study of these figures the following remarks seem justified.

\* This correction is obtained from the equation  $\log_e \rho_0/\rho_1 = bc + dc^2 - ec^3$ , where  $c$  is the weight concentration and  $b$ ,  $d$  and  $e$  are constants. For cane sugar  $b = 4.881 \times 10^{-4}$ ,  $d = 2.4655 \times 10^{-6}$ , and  $e = 4.041 \times 10^{-9}$ ; and for glucoside  $b = 9.54 \times 10^{-4}$ ,  $d = 4.921 \times 10^{-6}$ , and  $e = 1.668 \times 10^{-8}$ . There is a maximum at  $c = 489$  for cane sugar and one at  $c = 204$  for the glucoside.



EXPERIMENT on Dilute Sulphuric Acid. Apparatus B.

Date.	Time.	Temperature of		Barometer.	Weight of vessels.					Remarks.	
		Bath.	Balance.		(1.)	(2.)	(3.)	(4.)	(5.)		
1915 Feb. 13	9.5 a.m.		° C. 9.6	722.2							Filled vessels on Feb. 12. Vessel (1) contained 80 c.c. of the acid. Vessel (2) contained 80 c.c. of the acid. Vessel (3) contained 80 c.c. of the acid. Vessel (4) contained 80 c.c. of water. Vessel (5) contained 20 c.c. H <sub>2</sub> SO <sub>4</sub> in first half and 40 c.c. in second half.
	9.25 "		9.7						L. 58.0795		
	9.55 "		9.8		R. 23.9223				R. 58.0869		
	10.15 "		9.7		L. 23.9152				<u>58.0822</u>		
	10.45 "		9.6		<u>23.9188</u> - 0.0929	L. 25.6163			<u>- 0.1245</u>		
"	11.5 "		9.6		R. 25.6237						
"	11.35 "		9.5		<u>25.6200</u> - 0.0938	R. 27.7765					
"	11.55 "		9.5		<u>25.5262</u>						
"	12.25 "		9.6			L. 27.7703					
"	12.45 "		9.6	718.5		<u>27.7734</u> - 0.0917			L. 14.8985		
"	9.30 a.m.	30.01				<u>27.6817</u>			R. 14.9061	Started air current at 1 p.m.	
"	7.0 p.m.	30.01							<u>14.9023</u> - 0.0955		
"	9.0 a.m.	30.01							<u>14.8068</u>		
"	5.0 p.m.	30.02									
"	9.0 a.m.	30.02									
"	5.0 p.m.	30.02									

NOTES.  
True mean temperature is 29°.90 C.  
Losses = 15.4847.  
Gains = 15.4779 + 0.0038 in "dipping" tube.  
Diff. = -0.0030. ("Tot up.")  
 $l_0/l_1 = 1.02671$ .

## EXPERIMENT on Dilute Sulphuric Acid. Apparatus B (continued).

Date.	Time.	Temperature of		Barometer.	Weight of vessels.					Remarks.	
		Bath.	Balance.		(1.)	(2.)	(3.)	(4.)	(5.)		
1915 Feb. 17	9.0 a.m.	30.02	° C.								
"	5.0 p.m.	30.02									
"	9.0 a.m.	30.02									
"	4.0 p.m.	30.02									
"	8.0 a.m.	30.02									
"	9.55 "			10.4							
"	10.15 "			10.5							
"	10.45 "			10.7	R. 8.8572						
"	11.5 "			10.8	L. 8.8511						
"	11.35 "			10.9	<u>8.8542</u>						
"	11.55 "			10.9	<u>- 0.1092</u>	L. 25.6150					
"	12.25 "			11.0	<u>8.7450</u>						
"	12.45 "			11.1		R. 25.6227					
"	2.5 "		11.3		<u>25.6189</u>						
"	2.25 "		11.3		<u>- 0.0941</u>						
					<u>25.5248</u>						
						R. 27.7766					
						<u>L. 27.7708</u>					
						<u>27.7737</u>					
						<u>- 0.0921</u>					
						<u>27.6816</u>					
							L. 14.4971				
							<u>R. 14.5039</u>				
							<u>14.5005</u>				
							<u>- 0.0965</u>				
							<u>14.4040</u>				

Stopped and took down at  
9 a.m.

Experiments with Sulphuric Acid.—These are given in Table X. The headings of the columns are the same as before. Column (11) gives the  $\log_e \rho_0/\rho_1$  corrected for temperature only, and column (12) headed “jump” is concerned with fluctuations in the flow of air consequent on oscillating the vessels.

TABLE X.—Solutions of Sulphuric Acid at 30° C.

(1.) Date.	(2.) Per cent. H <sub>2</sub> SO <sub>4</sub> .	(3.) Mean value of		(4.) Barometer during experiment.	(5.) Total loss of weight = $l_0$ .	(6.) Observed ratio $l_0/l_1$ .	(7.) Change in weight of “dipping” tube.	(8.) “Tot up.” hours air passed.	(9.) Number of hours air passed.	(10.) $\rho_0/\rho_1$ .	(11.) $\log_e \rho_0/\rho_1$ .	(12.) $\log_e \rho_0/\rho_1$ reduced to 30°·00C. †	(13.) “Jump.”	(14.) Apparatus used.	Remarks.
		Temperature of bath.	° C.												
Mar. 8, '13	24·871	30·13	756	6·0151	1·22084	-0·0011	-0·0019	67	1·21147	0·19183	0·19171	not determined	Aa		
” 14, '13	24·871	30·20	737	6·1286	1·22118	-0·0003	-0·0021	67	1·21151	0·19186	0·19168	”	”		
” 25, '13	24·871	30·06	746	5·9615	1·22087	-0·0003	-0·0015	67	1·21141	0·19178	0·19173	”	”		
Nov. 22, '13	22·446	30·01	752	8·4426	1·17772	-0·0017	-0·0002	91	1·17019	0·15716	0·15716	”	Ab		
Dec. 6, '13	22·446	30·09	747	6·9805	1·17763	-0·0032	+0·0022	68	1·17003	0·15703	0·15695	none	Aa		
” 11, '13	22·446	30·07	755	6·8753	1·17768	-0·0015	+0·0013	91	1·17016	0·15714	0·15708	”	”		
Jan. 8, '14	22·446	30·09	753	5·7385	1·17790	-0·0012	-0·0011	91	1·17034	0·15729	0·15721	”	Ab		
Oct. 26, '14	6·192	30·06	742	17·6036	1·02681	-0·0111	-0·0051*	115	1·02566	0·02534			B	Glass “dipping” tube.	
Nov. 11, '14	6·192	29·94	744	18·3545	1·02699	-0·0119	-0·0102*	115	1·02584	0·02551			”	Glass “dipping” tube.	
” 25, '14	6·192	29·99	745	18·7375	1·02681	-0·0446	-0·0103*	115	1·02567	0·02535			”	Glass “dipping” tube.	
Jan. 8, '15	6·192	30·02	734	7·4370	1·02673	-0·0009	-0·0035	67	1·02557	0·02525			”	Quartz “dipping” tube.	
” 13, '15	6·192	29·98	747	15·4526	1·02674	-0·0061	-0·0020	139	1·02560	0·02528			”	Quartz “dipping” tube.	
Feb. 13, '15	6·192	29·90	730	15·4847	1·02671	-0·0038	-0·0030	139	1·02555	0·02523			”	Platinum “dipping” tube.	

\* In these experiments water was lost to the system by condensing on parts that could not be weighed (actually observed).

† The numbers in column (10) lead to values for the vapour pressures of the solutions which differ as much as 1 per cent. from REGNAULT'S experiments (see LANDHOLT and BORNSTEIN, ‘Tabellen’), but from REGNAULT'S results (which are for different temperatures) a temperature coefficient was calculated by means of which the numbers in column (11) were reduced to 30° C.; unfortunately there seem to be no data for carrying out a similar reduction for the two very dilute solutions.

TABLE X.—Solutions of Sulphuric Acid at 30° C. (continued).

(1.) Date.	(2.) Per cent. H <sub>2</sub> SO <sub>4</sub> .	(3.) Mean value of		(4.) Baro- meter during experi- ment.	(5.) Total loss of weight = $l_0$ .	(6.) Ob- served ratio $l_0/l_1$ .	(7.) Change in weight of "dipping" tube.	(8.) "Tot up." "	(9.) Num- ber of hours air passed.	(10.) $\rho_0/\rho_1$ .	(11.) $\log_e \rho_0/\rho_1$ .	(12.) $\log_e \rho_0/\rho_1$ reduced to 30°.00 C.	(13.) "Jump." "	(14.) Appa- ratus used.	Remarks.
		Tem- pera- ture of bath.	° C.												
Oct. 9, '15†	6.157		747	17.5641	1.02637	-0.0049	-0.0003	115	1.02525	0.02494				D	"Dipping" tube from 0.5 cm. water.
" 20, '15†	6.157	30.01	751	18.2298	1.02627	-0.0054	-0.0065*	115	1.02516	0.02485				"	"Dipping" tube from 0.5 cm. water.
" 28, '15†	6.157	29.96	740	17.9249	1.02627	-0.0031	-0.0024	115	1.02514	0.02483				"	"Dipping" tube from 0.5 cm. water.
Nov. 5, '15†	6.157	29.99	745	18.3081	1.02632	-0.0036	-0.0017	115	1.02520	0.02489				"	"Dipping" tube from 0.3 cm. water.
" 13, '15†	6.157	30.04	749	18.5168	1.02615	-0.0018	+0.0011	115	1.02504	0.02473				"	"Dipping" tube from 0.8 cm. water.
" 24, '15†	6.157	29.95	754	18.7143	1.02632	-0.0034	-0.0005	115	1.02521	0.02490				"	"Dipping" tube from 1.0 cm. water.

\* In these experiments water was lost to the system by condensing on parts that could not be weighed (actually observed).

† These three experiments are the first in which a true buoyancy correction could be made, *i.e.*, it was possible to compute the specific volume of the sulphuric acid in the last vessel after it had absorbed the water.

‡ Approximate buoyancy correction applied for specific volume of sulphuric acid.

If we neglect the experiment of November 22, 1913, where the soda-lime tube was found to be nearly blocked up, the first two sets of experiments, as judged by the figures in column (11), show very good agreement. It is probable that the experiment of January 8, 1914, is slightly too high, on account of air pulses, a gale blowing during the run.

The experiments of October 26, November 11 and 25, in 1914, are only included to show the kind of results obtained when moisture condenses on the connecting tubes and in other parts, the magnitude of this is seen from the numbers in columns (7) and (8); but the last three experiments are in excellent agreement. In the first three of the next set, approximate buoyancy corrections for the specific volume of the sulphuric acid are applied, whilst the last three are properly corrected.

Two important deductions may be drawn:—

(1) The method, even with a liquid having a vapour pressure as high as 31 mm. mercury, is susceptible of considerable accuracy. (2) Confirmation is obtained of the view that the losses on the solution and solvent should be equal to the gain of the sulphuric acid.

*Experiments with Cane Sugar and  $\alpha$ -Methyl Glucoside.*—These are given in Tables (XI.) and (XII.) and the columns have the same signification as before. The numbers in column (12) for both cane sugar and  $\alpha$ -methyl glucoside are derived from the equation  $\log_e \rho_0/\rho_1 = bc + dc^2 - ec^3$  where, for cane sugar,  $b = 5.136 \times 10^{-4}$ ,  $d = 1.866 \times 10^{-6}$ ,  $e = 2.335 \times 10^{-9}$ , with a maximum at  $c = 647$ ; and for  $\alpha$ -methyl glucoside  $b = 9.088 \times 10^{-4}$ ,  $d = 3.891 \times 10^{-6}$ , and  $e = 1.511 \times 10^{-8}$ , with a maximum at  $c = 252$ . The correction for temperature, which in all cases is very small, is assumed to be proportional to the temperature interval.

The numbers in the column headed "jump" (the jump was not determined for the  $\alpha$ -methyl glucoside solution) were obtained as follows:—When the vessels had been weighed at the end of the experiment they were again set up in the bath and a Threlfall oil manometer was connected to the air-stream, so that the fall in the pressure along the vessels could be measured. It was found that at a certain point in the oscillation, there was frequently a distinct and rapid throttling action; the numbers in the column record the change of pressure due to this.\* We would point out that a "jump" taking place at the end of an experiment, when water has already been transferred from one vessel to another, is no proof that the obstruction has been there during the whole run, and conversely, no "jump" does not necessarily mean that there has not been one during part of the run.

The "new sugar" mentioned in the sugar column is some specially pure, which Messrs. Tate, to whom our thanks are due, kindly gave us.

\* The "jump" seems to be connected with the great viscosity of sugar solutions.



TABLE XI.—Cane Sugar at 30° C. (continued).

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)	(14.)
Date.	Weight concentration.	Mean value of Temperature of bath.	Barometer.	Total loss of weight. $l_0$ .	Observed ratio. $l_0/l_1$ .	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	$\rho_0/\rho_1$ .	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	"Jump."	Sugar used.	Apparatus used.
		° C.											
Standard Weight Concentration = 81.20 gr. Sugar to 100 gr. Water.													
June 9, '11	81.262	30.06	747	7.1025	1.05651	-0.0001	+0.0002	68	1.05409	§0.05263	Not de-termined.	Pure cane.	Aa
Sept. 24, '13	81.209	30.11	748	6.6490*	1.05640	-0.0002	-0.0019	67	1.05399	0.05257	0.27 mm.	M.W.C.	"
Oct. 8, '13	81.209	30.01	745	5.9518*	1.05631	-0.0004	-0.0007	67	1.05390	0.05249	0.15 mm.	"	"
Jan. 16, '14	81.262	30.04	748	5.3660*	1.05595	-0.0001	0.0000	67	1.05356	§0.05212	0.5 mm.	"	"
Mar. 19, '14	81.251	(30.11)	729	8.0183	1.05651	-0.0024	+0.0003	91	1.05403	0.05258	oil.	"	Ab
Jan. 25, '16†	81.198	29.95	758	20.7327*	1.05639	-0.0044	-0.0064	139	1.05403	0.05262	oil.	"	D
Standard Weight Concentration = 112.00 gr. Sugar to 100 gr. Water.													
Jan. 17, '13	111.814	30.07	742	8.0082	1.08418	-0.0008	-0.0012	67	1.08058	0.07763	Not de-termined.	M.W.C.	Aa
Feb. 1, '13	111.864	30.04	747	7.8742	1.08427	-0.0006	+0.0013	67	1.08067	0.07764	"	"	"
" 7, '13	111.886	30.00	751	8.1202	1.08415	-0.0009	-0.0009	67	1.08058	0.07760	"	"	"
Standard Weight Concentration = 141.00 gr. Sugar to 100 gr. Water.													
Feb. 14, '13	141.095	30.03	755	6.4649*	1.11335	+0.0007	-0.0006	67	1.10856	0.10297	Not de-termined.	M.W.C.	Aa
Oct. 24, '13	141.096	30.13	743	10.8036*	1.11338	Not de-termined.	Not de-termined.	91	1.10849	§0.10293	0.8 mm.	"	"
July 13, '16	141.257	30.03	751	22.6611*	1.11372	-0.0056	-0.0046	138	1.10889	0.10313	oil.	New sugar.	D

\* In these experiments two different solutions were placed in series.

† Approximate buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

§ Not used in table of mean values.

TABLE XI.—Cane Sugar at 30° C. (continued).

(1.) Date.	(2.) Weight concentration.	(3.) Mean value of		(4.) Barometer.	(5.) Total loss of weight, $l_0$ .	(6.) Observed ratio, $l_0/l_1$ .	(7.) Change in weight of "dipping" tube.	(8.) "Tot up."	(9.) No. of hours air passed.	(10.) $\rho_0/\rho_1$ .	(11.) $\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	(12.) "Jump."	(13.) Sugar used.	(14.) Apparatus used.	Remarks.
		Temperature of bath.	° C.												
May 12, '11	183.213	29.91	741	4.3940	1.16035	-0.0006	+0.0003	67	1.15350	§0.14262	Not de-termined.	Pure cane.	Ab		
Feb. 21, '13	183.560	29.95	755	6.4314	1.16071	-0.0007	-0.0007	67	1.15395	§0.14266	"	"	"		
June 7, '13	182.963	30.01	749	6.0778	1.15969	-0.0006	+0.0005	67	1.15290	0.14232	"	M.W.C.	"		
" 13, '13	182.927	30.10	754	5.9142	1.15958	-0.0009	-0.0005	67	1.15280	§0.14228	Large.	"	"		
" 20, '13	182.944	30.10	751	5.7285	1.15983	-0.0001	-0.0007	67	1.15302	0.14245	Not de-termined.	"	"		
" 27, '13	183.013	30.01	757	5.6330	1.15967	-0.0003	-0.0022	67	1.15295	0.14231	0.15 mm. oil	"	"		
July 8, '13	182.996	30.06	746	5.6438	1.15984	-0.0014	-0.0009	67	1.15300	§0.14238	0.8 mm. oil	"	"		
" 15, '13	182.899	30.03	748	6.2847	1.15984	0.0000	+0.0007	67	1.15303	§0.14250	0.5 mm. oil	"	"		
Sept. 24, '13	182.843	30.11	748	6.6490*	1.15953	-0.0002	-0.0019	67	1.15270	0.14228	0.27 mm. oil	"	"		
Oct. 8, '13	182.683	30.01	745	5.9518*	1.15938	-0.0004	-0.0007	67	1.15255	0.14224	0.15 mm. oil	"	"		
Apr. 21, '14	183.066	30.13	756	7.5503	1.15978	-0.0009	-0.0011	91	1.15300	0.14233		"	Ab	"Dipping" tube 2.4 cm. from water surface.	
May 28, '14	183.079	29.94	754	12.2725	1.15845	-0.0020	-0.0014	91	1.15178	§0.14123		"	C		

Standard Weight Concentration = 183.00 gr. Sugar to 100 gr. Water.

\* In these experiments two different solutions were placed in series.  
§ Not used in table of mean values.



TABLE XI.—Cane Sugar at 30° C. (continued).

(1.) Date.	(2.) Weight concentration.	(3.) Mean value of		(4.) Barometer.	(5.) Total loss of weight, $l_0$ .	(6.) Observed ratio, $l_0/l_1$ .	(7.) Change in weight of "dipping" tube.	(8.) "Tot up."	(9.) No. of hours air passed.	(10.) $\rho_0/\rho_1$ .	(11.) $\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	(12.) "Jump."	(13.) Sugar used.	(14.) Apparatus used.	Remarks.
		Temperature of bath.	° C.												
Standard Weight Concentration = 183.00 gr. Sugar to 100 gr. Water (continued).															
June 6, '14	183.071	30.01	743	11.5499	1.15940	-0.0005	-0.0018	91	1.15257	§0.14192			M.W.C.	C	"Dipping" tube 1.1 cm. from water surface.
" 12, '14	183.071	30.01	752	11.4518	1.15840	+0.0002	-0.0015	91	1.15169	§0.14116			"	"	"Dipping" tube 2.3 cm. from water surface.
" 19, '14	183.071	29.99	748	8.5645	1.15746	0.0000	-0.0015	68	1.15077	§0.14036			"	"	4th branch of water vessel empty.
" 24, '14	183.071	29.99	756	9.2148	1.15958	-0.0004	-0.0042	67	1.15286	§0.14217			"	"	4th branch coated with paraffin wax.
July 10, '14	183.088	29.92	752	8.4568	1.15959	-0.0077	-0.0034	67	1.15287	§0.14216			"	"	4th branch baked.
Oct. 7, '14	182.920	30.01	757	9.1733	1.15962	-0.0046	Lost.	67	1.15290	0.14235			"	B	"Dipping" tube baked.
Jan. 19, '16†	182.737	29.92	750	10.6833	1.15937	-0.0021	-0.0042	67	1.15264	0.14229			New sugar.	D	
June 24, '16‡	183.160	30.02	745	25.3141*	1.15986	-0.0037	-0.0084	138	1.15302	0.14223			"	"	"
Standard Weight Concentration = 217.50 gr. Sugar to 100 gr. Water.															
July 6, '11	218.264	29.95	756	3.9771	1.20150	-0.0003	+0.0017	43	1.19304	§0.17576		Not determined.	Pure cane.	Aa	
Feb. 14, '13	217.632	30.03	755	6.4649*	1.20092	-0.0006	+0.0007	67	1.19243	0.17586		"	M.W.C.	"	
Nov. 1, '13	217.217	30.02	748	9.5373*	1.20029	-0.0006	-0.0007	67	1.19176	§0.17571		Large	"	"	

\* In these experiments two different solutions were placed in series.  
 † Approximate buoyancy correction applied for specific volume of sulphuric acid at end of experiment.  
 ‡ True buoyancy correction applied for specific volume of sulphuric acid at end of experiment.  
 § Not used in table of mean values.

TABLE XII.— $\alpha$ -Methyl Glucoside at 30° C.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)
Date.	Weight concentration.	Mean value of Temperature.	Mean value of Barometer.	Total loss of weight = $l_0$ .	Observed ratio. $l_0/l_1$ .	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	$\rho_0/\rho_1$ .	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	"Jump."	Apparatus used.
Standard Weight Concentration = 35.00 gr. to 100 gr. of Water.												
June 30, 1911	34.779	30.18	746	6.6027	1.03795	+0.0002	+0.0015	67	1.03631	0.03592	Not determined	Aa
Standard Weight Concentration = 45.00 gr. to 100 gr. of Water.												
July 22, 1911	44.938	29.91	753	5.8846	1.05050	-0.0005	+0.0020	67	1.04838	0.04731	Not determined	Aa
Standard Weight Concentration = 55.00 gr. to 100 gr. of Water.												
July 12, 1911	54.869	30.01	760	7.4075	1.06358	0.0000	+0.0007	67	1.06092	0.05930	Not determined	Aa
Standard Weight Concentration = 64.00 gr. to 100 gr. of Water.												
June 16, 1911	63.845	30.04	742	5.8225	1.07573	-0.0010	-0.0003	67	1.07247	0.07016	Not determined	Aa
May 12, 1916†	63.810	30.04	748	17.7474*	1.07555	-0.0028	-0.0025	115	1.07233	0.07007		D
" 19, 1916†	63.810	30.08	754	17.4767*	1.07567	-0.0026	-0.0057	114	1.07246	0.07021		"
June 9, 1916‡	63.818	(30.04)	750	12.1437*	1.07546	-0.0011	+0.0030	90	1.07225	0.06999		"

\* In these experiments two different solutions were placed in series.

† Approximate buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

‡ True buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

TABLE XII.— $\alpha$ -Methyl Glucoside at 30° C. (continued).

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)
Date.	Weight concentration.	Mean value of		Total loss of weight = $l_0$ .	Observed ratio. $l_0/l_1$ .	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	$\rho_0/\rho_1$ .	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	"Jump."	Apparatus used.
		Temperature.	Barometer.									
		° C.										
Standard Weight Concentration = 75.00 gr. to 100 gr. of Water.												
June 3, 1911	75.708	29.98	754	6.3093	1.09208	-0.0004	+0.0002	66	1.08819	0.08363	Not determined	Aa
Oct. 14, 1911	75.904	(30.07)	753	3.0798*	1.09208	-0.0009	+0.0004	67	1.08817	0.08340	"	"
June 5, 1915	75.287	30.01	751	6.2789	1.09137	-0.0006	-0.0024	66	1.08749	0.08352	"	Ab
Standard Weight Concentration = 90.00 gr. to 100 gr. of Water.												
July 10, 1915	90.005	30.16	746	6.9694	1.11277	+0.0001	-0.0014	67	1.10791	0.10253	"	Ab
Dec. 4, 1915†	90.049	29.99	732	14.7591	1.11265	-0.0008	-0.0063	91	1.10777	0.10229	"	D
Standard Weight Concentration = 105.00 gr. to 100 gr. of Water.												
Oct. 9, 1911	105.075	(30.05)	758	2.6210	1.13488	Not determined	+0.0008	45	1.12920	0.12144	Not determined	Aa

\* In these experiments two different solutions were placed in series.

† Approximate buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

We would draw particular attention to the results noted in the long series of experiments with a weight concentration of 183·000 gr. to 100 of water. It would seem, judging from the numbers in column (11) with apparatus Aa (*i.e.*, when oscillating) and apparatus Ab (no oscillation), that the results are more consistent when the "jump" is small.

Coming now to the experiments with apparatus C, it will be noticed at once from the three experiments of May 28, June 6, and June 12, 1914, that the further the bottom of the dipping tube is from the water level (these experiments, unlike a similar set with sulphuric acid, were varied by keeping the water-level constant and altering the length of the dipping tube) the smaller  $\log_e \rho_0/\rho_1$  becomes. In other words, the quantity of water taken away from the water vessel is a function of the vertical distance between the water and the tube.

Obviously one way of explaining this is by supposing that some of the water which was originally in the air-stream condenses on the sides of the vessel before it reaches the dipping tube. That this explanation is probably correct is shown by the next three experiments; in the first of these, the last branch of the water vessels was empty and consequently a large proportion of the water condensed in it; in the next two this branch was coated with either paraffin wax or "bakelite," with the result that the normal values were regained. That these results are normal is shown by the two experiments with apparatus D, where the vessel is of quartz and the dipping tube is some 0·3 cm. away from the surface.

Thus we have conclusively proved that no accurate results can be obtained with these glass vessels, unless the bottom of the exit tube is very close to the surface of the water; incidentally it may be remarked that such is actually the case with apparatus Aa and Ab.

*Air Pulses.*—It will be seen that the deviations in  $\log_e \rho_0/\rho_1$  are larger than can be accounted for by the known probable error of weighing. During the search for an explanation of this, it was noticed that the results, when all other conditions were constant, seemed higher during the prevalence of gales. Unfortunately, this connection (if any) cannot be put on firm ground, because, as already stated, we have made as many alterations in the conditions as possible and consequently there are but few suitable experiments for comparison.

Mr. J. W. WALKER suggested that the anomalies might be due to the greater number and amplitude of the air pulses in high winds.\*

To reduce this source of trouble as much as possible the air current was altered so that there were no pulses of any kind either from the atmosphere or from the Fleuss pump, and the two experiments of June 24 and July 13, 1916, were carried out on the most dilute solution. The results show a satisfactory agreement and differ but little from previous experiments. One interesting fact requires mention. It was noticed

\* We were unable to test this hypothesis as the only suitable records of air pulses, those of Mr. DINES, are kept at the Meteorological Office and Sir N. SHAW would not let us have them for reference.

that in the experiments at 30° C. with dilute sulphuric acid the second vessel scarcely changes in weight, but with both cane sugar and  $\alpha$ -methyl glucoside there is a small but persistent loss; this effect may indicate that the latter two substances suffer a slight decomposition, but experiments designed to elucidate this point are now in progress.

*The Calculation of the Osmotic Pressures.*—The osmotic pressures are connected with the vapour pressures by PORTER'S equation ('Roy. Soc. Proc.' A, vol. 79, p. 521),

$$\int_{\pi_{\pi}}^p s_1 dp = \int_{\pi_{\pi}}^{\pi_0} v dp + \int_{\pi_0}^{p-P} u dp, \dots \dots \dots (5)$$

where P is the osmotic pressure, and p the pressure on the solution;  $\pi_{\pi}$  and  $\pi_0$  are, as before, the vapour pressures of the solution and solvent respectively; v and u are the specific volumes of the solvent vapour and pure liquid solvent respectively.

In our paper on calcium ferrocyanide solutions we give reasons for thinking that equation (5) should be modified so as to be applicable to the vapour densities when measured in air. From the following discussion, which is contributed by Mr. G. W. WALKER, it would seem that we were mistaken, and that the air values may be used without change.

In the experiments the pressure on the pure solvent is one atmosphere. Hence (5) becomes

$$\int_{\pi_{\pi}}^{P+1} s_1 dp = \int_{\pi_{\pi}}^{\pi_0} v dp + \int_{\pi_0}^1 u dp,$$

but  $\partial\pi/\partial p = u/v_{\pi}$  for vapour over the pure solvent. (Cf. PORTER, *loc. cit.*)

Therefore

$$\int_{\pi_0}^1 u dp = \int_{\pi_0}^{\pi_0^1} v dp$$

where  $\pi_0^1$  is the vapour pressure observed. Again,  $\partial\pi/\partial p = s_1 v_{\pi}$  for the vapour over the solution.

Therefore

$$\int_{\pi_{\pi}}^1 s_1 dp = \int_{\pi_{\pi}}^{\pi'_{\pi}} v dp.$$

where  $\pi'_{\pi}$  is the observed vapour pressure of the solution.

Therefore

$$\int_1^{P+1} s_1 dp = \int_{\pi'_{\pi}}^{\pi_0} v dp,*$$

\* This result might have been anticipated had it been noticed that Sir J. J. THOMSON, in articles 90 and 91 of "Applications of Dynamics," shows that the increase in vapour pressure of a pure liquid caused by the pressure of the atmosphere upon it, precisely balances the lowering brought about by the dissolved air in it.

hence

$$\bar{s}P = \int_{\pi'_\pi}^{\pi'_0} v dp,$$

where  $\bar{s}$  is the mean value of  $s$  over the range of 1 to  $1+P$ . If BOYLE'S law is true for the vapour in air we get

$$P = \log_e \pi'_0/\pi'_\pi \times RT/\bar{s}, \dots \dots \dots (6)$$

and modifying this in conformity with (4) we get

$$P = \log_e [l_0/l_1 - (l_0/l_1 - 1) \pi_0/B] \times RT/\bar{s}, \dots \dots \dots (7)$$

where  $[l_0/l_1 - (l_0/l_1 - 1) \pi_0/B] = \rho_0/\rho_1 = \pi'_0/\pi'_\pi$ .

The osmotic pressures calculated by means of (7) are given in Tables XIII. and XIV., in which column (1) gives the weight concentrate. Columns (2) and (5) the values of  $\log_e \rho_0/\rho_1$  obtained as a weighted mean value of the numbers in column (11) of the previous tables. Columns (3) and (6) the values of  $\bar{s}$  used in the calculation, and (4) and (7) the resulting osmotic pressures. Column (8) gives such osmotic pressures as have been observed directly; these are the results tabulated in 'Roy. Soc. Proc.,' A, vol. 92, 1916, pp. 483-484, reduced to the new concentrations. Unfortunately, in that paper, by an oversight, the following two "direct" osmotic pressures were omitted:—A solution of cane sugar of weight concentration 56.631 gave an osmotic pressure of 43.95 atmospheres, another of weight concentration

TABLE XIII.—Cane Sugar.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)
	At 30° C.			At 0° C.			
Weight concentration.	$\log_e \rho_0/\rho_1$ .	$\bar{s}$	Calculated osmotic pressure.	$\log_e \rho_0/\rho_1$ .	$\bar{s}$ .	Calculated osmotic pressure.	Direct osmotic pressure.
			atmospheres.				
34.00	0.01950	1.00287	26.82	—	—	—	—
56.50	0.03429	1.00103	47.25	0.03516	0.99515	43.91	43.84
81.20	0.05256	0.99873	72.59	0.05380	0.99157	67.43	67.68
112.00	0.07762	0.99554	107.55	0.07983	0.98690	100.53	100.43
141.00	0.10305	0.99176	143.33	0.10669	0.98321	134.86	134.71
183.00	0.14231	0.98653	198.98	0.14711	0.97842	186.86	—
217.50	0.17586	0.97360	249.16	0.18080	0.97399	230.70	—
243.00	—	—	—	0.20666	0.97117	264.46	—

TABLE XIV.— $\alpha$ -Methyl Glucoside.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)
	At 30° C.			At 0° C.			
Weight concentration.	$\log_e \rho_0/\rho_1$ .	$\bar{s}$ .	Calculated osmotic pressure.	$\log_e \rho_0/\rho_1$ .	$\bar{s}$ .	Calculated osmotic pressure.	Direct osmotic pressure.
			atmospheres.				
35·00	0·03592	1·00260	49·42	0·03878	0·99810	48·29	48·11
45·00	0·04731	1·00186	65·14	0·05153	0·99709	64·22	63·96
55·00	0·05930	1·00087	81·73	0·06451	0·99597	80·50	81·00
64·00	0·07011	0·99956	96·75	0·07699	0·99491	96·17	96·24
75·00	0·08352	0·99881	115·34	0·09253	0·99354	115·74	115·92
90·00	0·10241	0·99721	141·66	0·11368	0·99166	142·46	—
105·00	0·12144	0·99507	168·34	0·13553	0·98974	170·18	—

56·713 gave an osmotic pressure of 44·05 atmospheres; in neither case was there any "solution leak." Table XV. gives our calcium ferrocyanide results after applying BURTON'S correction.

TABLE XV.—Calcium Ferrocyanide at 0° C.

Weight concentration.	Calculated osmotic pressure.	Direct osmotic pressure.
31·389	41·10	41·22
39·504	70·59	70·84
42·889	86·62	87·09
47·219	112·97	112·84
49·857	131·33	131·00

The results for cane sugar and  $\alpha$ -methyl glucoside are plotted against weight concentration in Diagrams I. and II. It is interesting to observe that the curves at 0° C. and 30° C. for  $\alpha$ -methyl glucoside intersect.

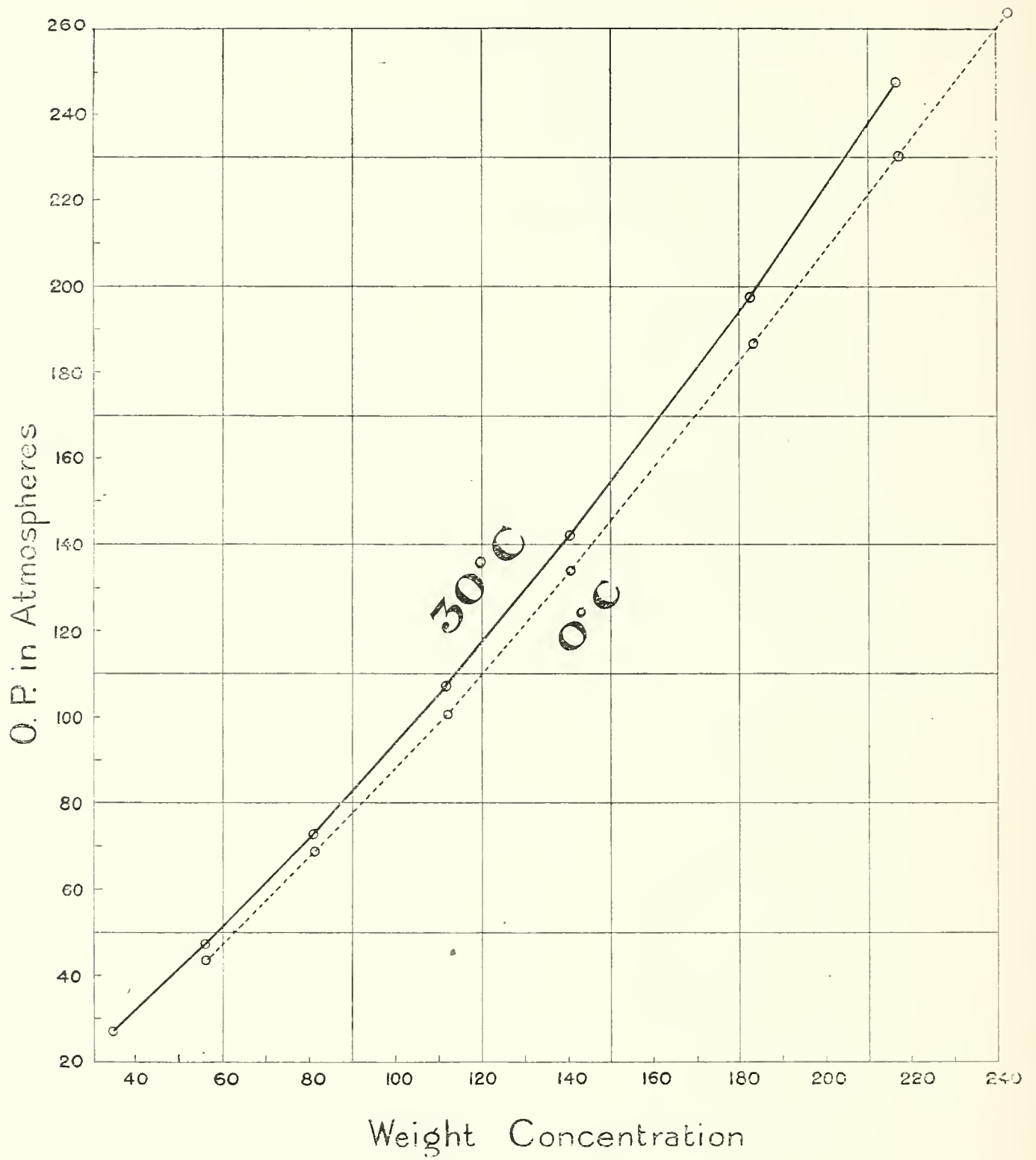
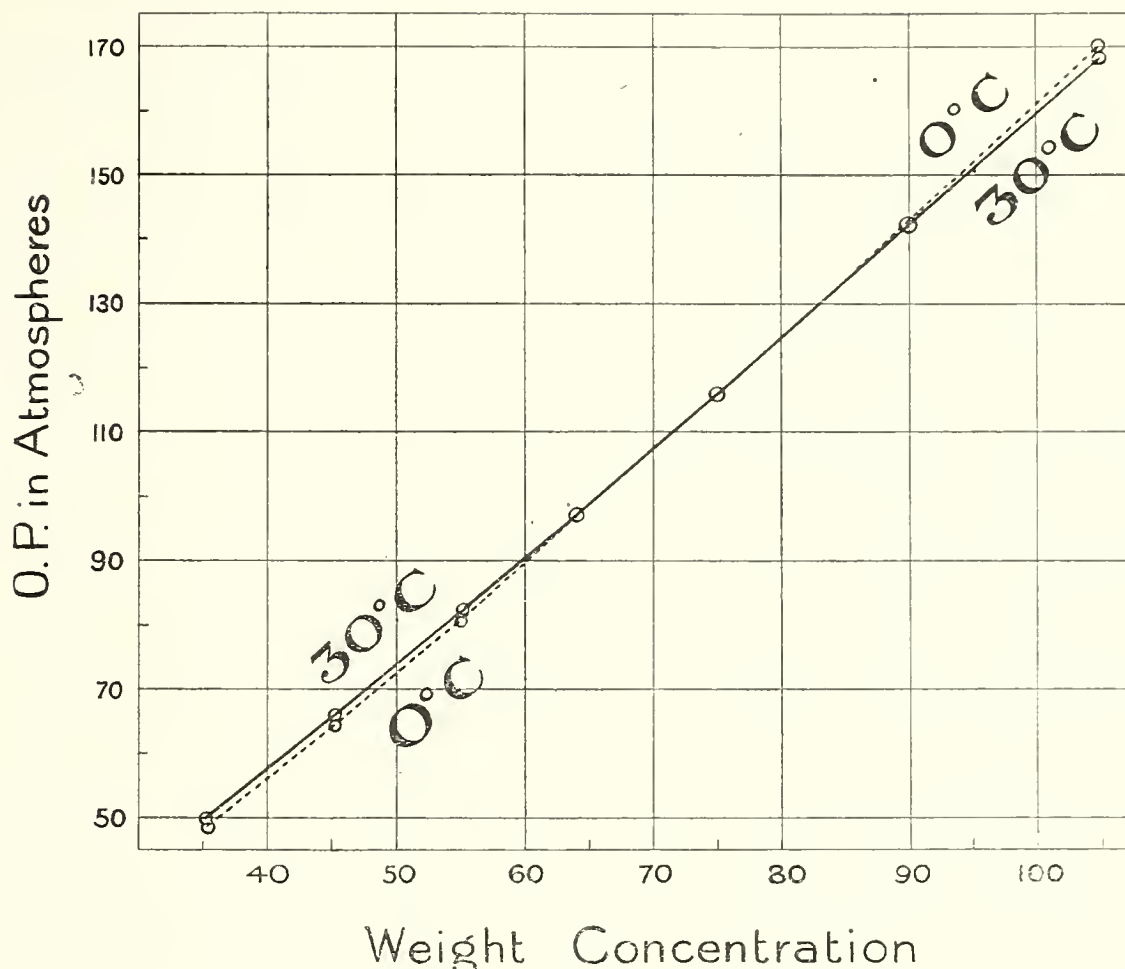


Diagram I. Cane sugar.



Diagram II.  $\alpha$ -methyl glucoside.

*Note added by Lord BERKELEY, April 5, 1919.*

[During the course of further work on vapour pressures at 30° C., Mr. E. STENHOUSE and I have found that with apparatus D when the 3rd and 4th vessels each contain water,\* the latter always gives up a measurable quantity of vapour to the air stream. A number of experiments, which need not be detailed, have proved that the air on leaving 3 is saturated; yet 4 loses, on the average 0·000235 gr. of water per gramme of total vapour carried to, and absorbed by, the sulphuric acid in vessel 5.

Three explanations seem to me to be possible:

(1) The current of air may not be fast enough to prevent an extra loss caused by diffusion to the sulphuric acid. (It is to be noted that when no air passes, about 0·03 gr. of water diffuses in the time usually taken for an experiment.) This hypothesis is ruled out by the fact that in an experiment with water in 3, 4 and the first two branches at 5 (the other two containing sulphuric acid), 4 still showed the usual loss in weight.

(2) Remembering that the vapour is practically all absorbed in the first branch of 5, it seemed possible that the sudden drop in pressure caused by this absorption

\* It is only with apparatus D, where the deposition of water in the quartz joining tubes is very small, that we have been able to put two water vessels in series.

might disturb the air stream over the adjacent water sufficiently to upset the steady conditions of flow demanded by theory. Testing this hypothesis by an experiment in which the sulphuric acid was absent, there was the usual loss in 4. Incidentally this experiment strengthens the conclusion come to under (1), and it also shows that the heat generated in 5 by the absorption of the water is not the cause of the trouble.

(3) Nevertheless I am driven to the assumption that a permanent inequality of temperature between vessels 3 and 4 is maintained. Unfortunately, when exploring the bath by means of thermocouples, as mentioned on p. 318, it was not realized that the presence of the train of vessels might make a difference to the free circulation of the bath water. A further examination with a Beckman thermometer (reading to  $0^{\circ}02$  C. and estimating to  $0^{\circ}002$  C.), placed alternately over the last branches of 3 and 4 respectively (it is only the exit branches that matter), seems to show that the latter is  $0^{\circ}002$  C. higher than the former. No stress should be laid on this result, for its magnitude only became apparent when the readings had been averaged and disentangled from the oscillations in the temperature of the bath as a whole. It is noteworthy, however, that a difference of  $0^{\circ}003$  C. between the two vessels is sufficient to account for the observed loss.

Whatever be the cause of the loss of water in vessel 4 of apparatus D, it is obvious that a correction should be applied to the experiments with that set of vessels. It seems probable that a correction should also be applied to the experiments with the other apparatus, but as the method of heating the bath, and the original position of the heaters cannot be recovered exactly, I am unable to determine what the correction should be.

The accompanying table gives, for the experiments with D, the corrected values together with the osmotic pressure calculated from the mean  $\log_e \rho_0/\rho_1$ .

It will be seen that the percentage difference between the new and old values of  $\log_e \rho_0/\rho_1$  diminishes as the concentration increases. Taking the values for cane sugar, the difference for the weight concentration of 34 gr. per 100 water is about 1 per cent., while at 183 it is only 0.14 per cent.; we may therefore feel confident that for higher concentrations the values given in the body of this communication would not be modified appreciably even if we were in a position to apply the correction under discussion.]

SULPHURIC Acid at  $30^{\circ}$  C.

Date.	$\rho_0/\rho_1$ .	$\log_e \rho_0/\rho_1$ .
Oct. 9, 1915 . . . . .	1.02502	0.02472
„ 20, 1915 . . . . .	1.02493	0.02462
„ 28, 1915 . . . . .	1.02491	0.02460
Nov. 5, 1915 . . . . .	1.02497	0.02466
„ 13, 1915 . . . . .	1.02482	0.02451
„ 24, 1915 . . . . .	1.02498	0.02467

## CANE Sugar at 30° C.

Date.	Weight concentration.	$\rho_0/\rho_1$ .	$\log_e \rho_0/\rho_1$ corrected to standard weight concentration and 30° C.	Osmotic pressure. Atmospheres.	Mean osmotic pressure. Atmospheres.
Standard weight concentration = 34.00 gr. sugar to 100 gr. of water.					
Jan. 25, 1916 . . . . .	33.941	1.01947	0.01931	26.56	26.52
June 24, 1916 . . . . .	33.965	1.01942	0.01926	26.49	
July 13, 1916 . . . . .	33.980	1.01945	0.01927	26.50	
Standard weight concentration = 81.20 gr. sugar to 100 gr. water.					
Jan. 25, 1916 . . . . .	81.198	1.05379	0.05239	72.36	
Standard weight concentration = 141.00 gr. sugar to 100 gr. water.					
July 13, 1916 . . . . .	141.257	1.10865	0.10289	143.11	
Standard weight concentration = 183.0 gr. sugar to 100 gr. water.					
Jan. 19, 1916 . . . . .	182.737	1.15240	0.14211	198.70	198.63
June 24, 1916 . . . . .	183.160	1.15277	0.14201	198.56	

 $\alpha$ -METHYL Glucoside at 30° C.

Date.	Weight concentration.	$\rho_0/\rho_1$ .	$\log_e \rho_0/\rho_1$ corrected to standard weight concentration and 30° C.	Osmotic pressure. Atmospheres.	Mean osmotic pressure. Atmospheres.
Standard weight concentration = 64.00 gr. $\alpha$ -methyl glucoside to 100 gr. water.					
May 12, 1916 . . . . .	63.810	1.07210	0.06986	96.37	96.38
„ 19, 1916 . . . . .	63.810	1.07222	0.06997	96.53	
June 9, 1916 . . . . .	63.818	1.07203	0.06977	96.24	
Standard weight concentration = 90.00 gr. to 100 gr. water.					
Dec. 4, 1915 . . . . .	90.049	1.10748	0.10203	141.13	

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VI. *The Ultra-Violet Band of Ammonia, and its Occurrence in the Solar Spectrum.*

By A. FOWLER, *F.R.S., Professor of Astrophysics, and C. C. L. GREGORY, B.A.,  
Research Student, Imperial College, South Kensington.*

Received December 15, 1917,—Read January 24, 1918.

[PLATE 2.]

*Introductory.*

A QUESTION of great interest in connection with the solar spectrum is that of the origin of the thousands of unidentified faint lines which were catalogued by ROWLAND in his "Preliminary Table of Solar Spectrum Wave-lengths." Some of these lines may possibly be identical with faint lines in metallic spectra which have not yet been completely tabulated, but in view of the presence of bands of cyanogen, carbon and hydrocarbon, the possibility of the correspondence of most of them with band spectra of other substances should not be overlooked.

As a contribution to this inquiry, the present investigation was undertaken primarily in order to determine whether Group P in the ultra-violet region of the solar spectrum might not be mainly due to the presence of ammonia in the absorbing atmosphere of the sun. Ammonia was already known to give a remarkable band in this region, having its position of maximum intensity near  $\lambda$  3360, but it had not been investigated in sufficient detail to permit of an adequate comparison with the solar tables. Photographs have accordingly been taken with spectrographs of high resolving power for the purpose of this comparison, and, as will appear from the details which follow, it has been established that the ammonia band is certainly represented in the solar spectrum, and accounts for a considerable number of faint lines for which no other origins have been suggested.

In view of the unusual appearance of the band, an attempt has also been made to elucidate the chief features of its structure.

*Previous Observations.*

The characteristic ultra-violet band of ammonia, about  $\lambda$  3360, appears to have been first described by EDER, who observed it in the flame of ammonia burning in

oxygen.\* Other bands in the ultra-violet which were attributed to ammonia by EDER were afterwards found to be identical with DESLANDRES' third positive group of bands of nitrogen. New determinations of the positions of the ammonia bands in the visible spectrum were also made by EDER, but it is not necessary to consider these for the present investigation. In the case of the ultra-violet band, the thirty-four wave-lengths tabulated by EDER evidently refer to unresolved groups of band lines, and only serve for identification when instruments of small resolving power are employed.

More recently, the band has been described and illustrated by LEWIS, as it appears in the spectra of vacuum tubes containing mixtures of nitrogen and hydrogen.† Its occurrence was observed with these gases in any proportion, but not in the case of either gas alone. As obtained in this way, the band was complicated by superposed bands of nitrogen, and higher resolution than that employed was considered necessary to effect the separation satisfactorily.

The band in question has been noted occasionally in various experiments carried on at the Imperial College during several years. It has been observed in the flame of imperfectly dried cyanogen, in the spectra of vacuum tubes, and with enclosed arcs under reduced pressure, as well as in the ammonia flame itself. In all cases the band appeared under circumstances in which its presence could be attributed to combined nitrogen and hydrogen, but the spectroscopic evidence does not exclude the possibility of some combination other than ammonia. In the course of the present investigation it has further been found that the brighter parts of the band sometimes occur feebly in the spectrum of the copper arc, and even in that of the ordinary carbon arc in air.

#### *Experimental Procedure.*

A preliminary investigation was undertaken to find a source that would give the band sufficiently isolated, and at the same time bright enough to be photographed with high dispersion. Vacuum tube methods proved unsatisfactory on account of the superposition of bands of nitrogen. The purest band was obtained from an ammonia flame fed with oxygen. An ordinary blowpipe was found to be a convenient arrangement, ammonia being passed through the outer tube, and a stream of oxygen through the inner one. The apparatus employed is illustrated in fig. 1. Ammonia of specific gravity 0.880 contained in the flask A was heated by a Bunsen flame, but not sufficiently to cause the liquid to boil. The vessel B was introduced as a means of condensing most of the water vapour, which otherwise condensed in the tubes of the blowpipe and extinguished the flame. The mercury gauge at C provided a convenient means of measuring the pressure, which was maintained at about 10 cm. of mercury. Oxygen was supplied from a cylinder of the compressed gas. The

\* 'Denkschr. Wien Akad.,' vol. 60, p. 1 (1893).

† 'Astrophys. Jour.,' vol. 40, p. 154 (1914).

flame produced in this way could be kept fairly steady, and had a small, but intensely bright, central core of a yellow colour, which was surrounded by a paler envelope. The flame was pointed in the direction of the collimator of the spectrograph, and an image of the bright central core was focussed on the slit by a quartz lens. Photographs were first taken with a small quartz spectrograph giving a dispersion of about  $60\text{\AA}$  per millimetre at  $\lambda$  3360, and with a quartz Littrow instrument giving a dispersion in the same region of  $7\text{\AA}$  per millimetre.

In view of the need for the highest attainable resolution of the central parts of the band, an attempt was made to photograph the spectrum of the flame in the 3rd order of a 10-foot concave grating, in which the dispersion is  $1.85\text{\AA}$  per millimetre. An exposure of 12 hours, however, yielded only a feeble trace of the band, and it was

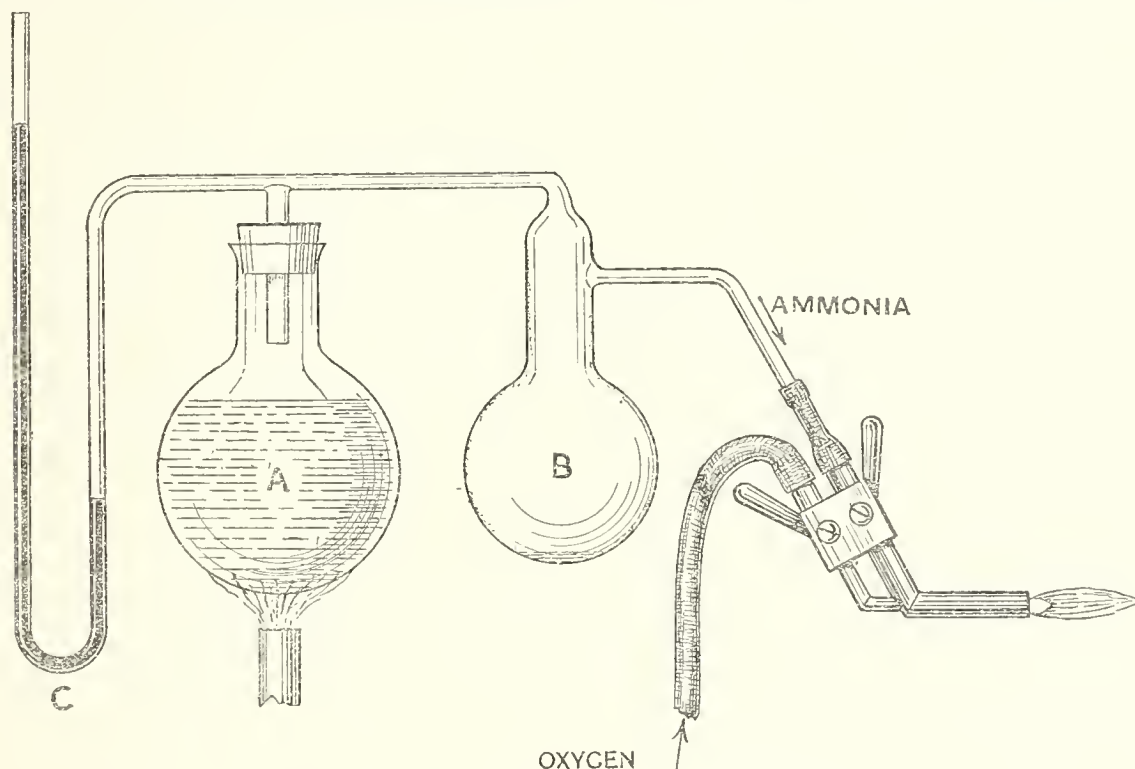


Fig. 1. Apparatus employed for ammonia flame.

evident that very much longer exposures would be necessary to give satisfactory photographs for measurement. Difficulties were anticipated in maintaining steady instrumental conditions, as the regular mounting is still detained in Russia, and only a temporary arrangement of the grating was available.

Advantage was therefore taken of the possibility of producing the band in the electric arc, which had previously been noted in the course of experiments made for other purposes. In the first arrangement tried the arc was enclosed in a glass globe provided with side tubes for the admission of the electrodes, and with a quartz window through which the arc could be observed, as in a previous investigation on the spectrum of magnesium.\* It was found, however, that the quartz window became obscured by the condensation of water-vapour, and it was therefore replaced

\* 'Phil. Trans.,' A, vol. 209, p. 449 (1909).

by a metal disc having a small aperture through which the light of the arc could pass to the spectrograph. A constant stream of ammonia, which was drawn off by a water pump, was caused to flow through the apparatus. The arc was on a 200-volt circuit, and the current used was 1.8 amperes. The electrodes were of copper.

The grating was mounted so as to give a normal spectrum, and precautions were taken to avoid mechanical displacements. The temperature of the laboratory was also kept as constant as possible during the exposures, which were of about 60 minutes' duration. An internal shutter, detached from the other parts of the spectrograph, was arranged next the plate to allow of two comparison spectra being photographed, one before and one after the ammonia spectrum.

A photograph of the copper arc in air, which was taken to facilitate the elimination of lines introduced by the electrodes, showed that the copper employed contained impurities of nickel and silver. In the case of very strong lines, "ghosts" were also present, and there were a few lines belonging to the second and fourth order spectra; these are marked by double dots in fig. V., Plate 2.

The ammonia band occurs incidentally in an excellent photograph of the magnesium arc under reduced pressure, taken in 1913 by Mr. W. JEVONS, in the 4th order of the 10-foot grating; the band is here somewhat confused by nitrogen, but many of the ammonia lines can be quite certainly identified, and the high resolution has been of special value in connection with very close groups near the extreme ends of the band.

#### *General Description of the Band.*

The general features of the ammonia band will be best gathered from the photographs reproduced in Plate 2. With low dispersion, as will be seen from fig. I., the band resembles a double line having components of unequal intensity, but there are indications of banded structure on both sides in photographs which have received sufficient exposure. With somewhat higher dispersion, as in fig. II., the real structure of the band becomes more evident; it shows a closer resemblance to the ordinary type of band, such as those found in nitrogen, with the exception that the component lines fade off in both directions from the apparent head.

In fig. III., taken with the still higher dispersion of the quartz Littrow spectrograph, many of the band lines are resolved into groups of three, which cannot properly be called triplets on account of the variable spacing. The central maximum about 3360, however, remains imperfectly resolved. With the highest resolution employed—that of the 3rd order grating—additional groups of three are separated, and the central maximum is seen to consist of a great number of closely crowded lines (figs. IV. and V.). The secondary central maximum about 3371, which corresponds to the weaker component of the doublet which represents the band with low dispersion, is also resolved into a large number of component lines. It will be observed that while the central maximum degrades in both directions, the secondary maximum degrades only towards the red.

In the arc, the central and secondary maxima are more fully developed than in the flame, in the sense that the band lines extend to greater distances from the two heads. That the majority of the additional lines are really due to ammonia, and have not been introduced from other possible sources in the arc, is sufficiently proved by the series investigation, which shows that many of them are associated with the lines which appear in the flame. This greater development of the central parts of the band in the arc is accompanied by a weakening of the groups of three in the vicinity of the maxima, and a relative intensification of those further away.

Similar modifications have also been noted in the case of vacuum tube spectra when discharges of different intensity have been employed. No special experiments have been made in this connection, but in some photographs of the spectrum of nitrogen where ammonia appears as an impurity, it has been observed that the groups of three near the central maxima are developed relatively strongly by feeble discharges, while strong discharges enhance the groups away from the maxima. Increased intensity of discharge thus appears to produce the same change of spectrum as the increase of temperature in passing from the flame to the arc.

Estimates of the intensities of the lines in both flame and arc have accordingly been included in the general list (Table V.), but the comparison of the two sources in the region of the central maximum is incomplete on account of the smaller resolution in the photographs of the flame spectrum.

The wave-lengths of the lines were determined in the usual manner by interpolation with respect to lines of iron, as given by BURNS. Lines of nickel originating in the poles employed for the arc spectrum, for which wave-lengths are also given by BURNS, served for the detection of small displacements of the reference spectra, and to indicate the corrections to be applied. Most of the lines could be measured on the grating plates of the arc spectrum, but some were obscured by lines due to the poles, and their positions were necessarily determined from the quartz Littrow photographs of the flame spectrum. It is hoped that in most cases the wave-lengths are accurate to within 0.01A.

Details of the wave-lengths and intensities are included in Table V.

#### *Structure of the Band.*

*The Groups of Three.*—A considerable amount of regularity in the structure of the ammonia band is obvious by mere inspection of the photographs. This is especially the case with regard to the groups of three, which extend for more than 70A on each side of the central maximum. There are three series on the less refrangible side which coalesce towards the red, and three on the more refrangible side which coalesce towards the violet. To facilitate discussion, those on the less refrangible side have been designated  $\alpha$ ,  $\beta$ ,  $\gamma$ , and those on the more refrangible side  $\delta$ ,  $\epsilon$ ,  $\zeta$ , in order of increasing refrangibility in the groups of three in each case.

Data for the consideration of the regularity in these series are collected in Tables I. and II., the first referring to  $\alpha$ ,  $\beta$ ,  $\gamma$ , and the second to  $\delta$ ,  $\epsilon$ ,  $\zeta$ . The wave-

TABLE I.—The Series  $\alpha$ ,  $\beta$ ,  $\gamma$ .

$\alpha$ series.				$\beta$ series.				$\gamma$ series.			
$\lambda$ , I.A.	$\nu$ , vac.	$d_1$ .	$d_2$ .	$\lambda$ , I.A.	$\nu$ , vac.	$d_1$ .	$d_2$ .	$\lambda$ , I.A.	$\nu$ , vac.	$d_1$ .	$d_2$ .
3450·36	28,974·34	28·33		3450·36	28,974·34	28·33					
46·99	29,002·67	28·05	- 3	46·99	29,002·67	28·13	- 2				
43·66*	030·72	27·77	- 3	43·65*	030·80	27·85	- 3				
40·37*	058·49	27·81	0	40·35*	058·65	27·91	1	3440·33	29,058·82		
37·08*	086·30	27·95	1	37·05*	086·56	28·03	1	36·99	087·05	28·23	1
33·78	114·25	28·00	1	33·74	114·59	28·25	2	33·65	115·35	28·30	1
30·48	142·25	28·32	3	30·41	142·84	28·40	2	30·30	143·78	28·43	2
27·15	170·57	28·45	1	27·07	171·24	28·80	4	26·93	172·44	28·66	3
23·81	199·02	28·86	4	23·69	200·04	29·12	3	23·53	201·41	28·97	2
20·43	227·88	29·00	1	20·28	229·16	29·17	1	20·11	230·61	29·20	3
17·04	256·88	29·13	1	16·87	258·33	29·49	3	16·66	260·13	29·52	3
13·64	286·01	29·37	2	13·43	287·82	29·89	4	13·18	289·97	29·84	4
10·22	315·38	29·60	2	09·95	317·71	30·28	4	09·66	320·19	30·22	3
06·78	344·98	29·92	3	06·43	347·99	30·44	2	06·12	350·66	30·47	4
3403·31	374·90	30·24	3	3402·90	378·43	30·78	3	3402·54	381·54	30·88	3
3399·81	405·14	30·39	2	3399·34	409·21	31·09	3	3398·93	412·74	31·20	5
96·30	435·53	30·54	2	95·75	440·30	31·50	4	95·27	444·46	31·72	2
92·78	466·07	30·85	3	92·12	471·80	31·83	3	91·58	476·39	31·93	7
89·23	496·92	30·76	- 1	88·46	503·63	32·25	4	87·84	509·03	32·64	2
85·70	527·68	30·64	- 1	84·76	535·88	32·50	3	84·07	541·90	32·87	8
82·19	558·32	30·44	- 2	81·04	568·38	33·09	6	80·22	575·55	33·65	8
78·71	588·76	29·63	- 8	77·26	601·47	34·40	13	76·29	609·98	34·43	8
75·33	618·39	27·58	- 21	73·34?	635·87			72·19?	645·97	35·99	16
72·19?	645·97										

\* Unresolved; separations assumed.

TABLE II.—The Series  $\delta$ ,  $\epsilon$ ,  $\zeta$ .

$\delta$ series.				$\epsilon$ series.				$\zeta$ series.			
$\lambda$ , I.A.	$\nu$ , vac.	$d_1$ .	$d_2$ .	$\lambda$ , I.A.	$\nu$ , vac.	$d_1$ .	$d_2$ .	$\lambda$ , I.A.	$\nu$ , vac.	$d_1$ .	$d_2$ .
3358.04?	29,970.85	39.19									
53.63	810.04	36.31	29	3350.85	29,834.77	28.79					
49.55	846.35	35.06	13	47.62	863.56	30.80	- 20	3346.42	29,874.26	28.68	
45.62	881.41	33.99	11	44.17	894.36	31.23	- 4	43.21	902.94	30.00	- 13
41.82	915.40	33.33	7	40.68	925.59	31.30	- 1	39.86	932.94	30.23	- 2
38.10	948.73	32.59	7	37.19	956.89	31.18	1	36.49	963.17	30.39	- 2
34.47	29,981.32	32.14	5	33.72	29,988.07	31.06	1	33.11	29,993.56	30.26	1
30.90	30,013.46	31.57	6	30.27	30,019.13	30.68	4	29.75	30,023.82	30.15	1
27.40	045.03	30.91	7	26.87	049.81	30.20	5	26.41	053.97	29.77	4
23.98	075.94	30.34	6	23.53	080.01	29.72	5	23.12	083.74	29.26	5
20.63	106.28	29.58	8	20.25	109.73	29.13	6	19.89	113.00	28.67	6
17.37	135.86	29.00	6	17.04	138.86	28.55	6	16.73	141.67	28.20	5
14.18	164.86	28.16	8	13.90	167.41	27.79	8	13.63	169.87	27.43	8
11.09	193.02	27.29	9	10.85	195.20	26.93	9	10.62	197.30	26.65	8
08.10	220.31	26.42	9	07.90	222.13	26.07	9	07.70	223.95	25.89	8
05.21	246.73	25.55	9	05.05	248.20	25.18	9	04.87	249.84	24.91	10
3302.42	272.28	24.40	12	3302.30	273.38	24.13	11	3302.15	274.75	23.96	10
3299.76	296.68	23.26	11	3299.67	297.51	23.07	11	3299.54	298.71	22.88	11
97.23	319.94	22.17	11	97.16	320.58	21.81	13	97.05	321.59	21.62	13
94.82	342.11	20.67	15	94.79	342.39	20.46	14	94.70	343.21	20.19	14
92.58*	362.78	19.17	15	92.57*	362.85	19.19	13	92.51	363.40	19.01	12
90.50*	381.95	17.83	13	90.49*	382.04	17.74	15	90.45	382.41		
88.57	399.78	16.00	18	88.57	399.78	16.00	17				
86.84	415.78			86.84	415.78						

\* Unresolved; separations assumed.

length on the international scale ( $\lambda$ , I.A.), the wave number *in vacuo* ( $\nu$ ), and the first and second differences ( $d_1$  and  $d_2$ ) are shown for each series. The figures in the

second decimal place in  $\nu$  and  $d_1$  are entitled to but little weight, but they have been included for the more consistent determination of  $d_2$ , which is given in tenths. The observed positions of some of the unresolved  $\alpha\beta$  and  $\delta\epsilon$  pairs are replaced by estimated positions of the components, in order that the course of the series may be more completely traced.

When due allowance is made for irregularities in the second differences, which are very sensitive to small errors in the wave-lengths, it is clear that the series as a whole cannot be satisfactorily represented by the usual approximate formula  $\nu = a + b(m + \mu)^2$ . Such a formula represents a series in which the distances between successive lines ( $d_1$ ) are in arithmetical progression, so that the second differences ( $d_2$ ) would be constant, and not one of the series approximates closely to this condition.

The actual wave-numbers of the members of the different series could only be effectively plotted on a very large scale, but the peculiarities of the series can be shown better in some respects by curves which have  $d_1$  for ordinates, and successive integral values of  $m$  for abscissæ, the initial value of  $m$  being chosen arbitrarily. Such curves are shown in fig. 2, and it will be seen that they depart widely from the linear form implied by the above-mentioned formula. The curves also fail to show any symmetry in the arrangement of the groups of series on the two sides of the central maximum, such as might have been expected from the general appearance of the spectrum.

Considering the series  $\alpha, \beta, \gamma$ , it will be seen that they begin with coincident, or nearly coincident, faint lines on the red side, and that the distance from line to line at first diminishes slightly and then increases. In  $\beta$  and  $\gamma$  the subsequent increase is continuous, so far as the series can be identified, and if the later lines have been correctly assigned, no other members in the immediate neighbourhood are to be expected. In the  $\alpha$  series, the distance  $d_1$  passes through a maximum value, as in the case of the main series of  $\lambda$  3883 cyanogen which has recently been further discussed by BIRGE.\* The  $\alpha$  curve, however, differs from the cyanogen curves in having a double curvature, and while the greatest value of  $d_1$  occurs among the weaker lines near the end of the series in cyanogen, it occurs among the brighter members in ammonia  $\alpha$ . The later portion of the  $\alpha$  curve is rather steep, and the identification of the next member of the series, which is involved in the secondary central maximum, is consequently difficult; the line  $\lambda$  3372.19 ( $\nu$  29645.97), however, fits fairly well on the continued curve, and if this really belongs to the series it would probably be the last member.

The series  $\delta, \epsilon, \zeta$ , resemble the first three in commencing with faint unresolved lines, which are far removed from the central maximum, but the  $d_1-m$  curves show no change of curvature near the beginning of the series. In the  $\delta$  series the distance between successive lines increases continuously as the central maximum is approached, but in  $\epsilon$  and  $\zeta$  it passes through a maximum as in  $\alpha$ .

\* 'Astrophys. Jour.,' vol. 46, p. 85 (September, 1917).



BIRGE has found a hyperbolic relation between  $d_1$  and  $m$  in the case of cyanogen, but it does not seem that this is applicable to the series under consideration, with the possible exception of  $\epsilon$  and  $\zeta$ . While it is possible to give approximate formulæ of the usual type for these series over a large part of their ranges, there seems little hope at present of finding any accurate formula which can be adapted to all of them. One can hardly resist the conclusion that there is some connection between the groups of three and the central maxima, but no numerical relation has yet been established.

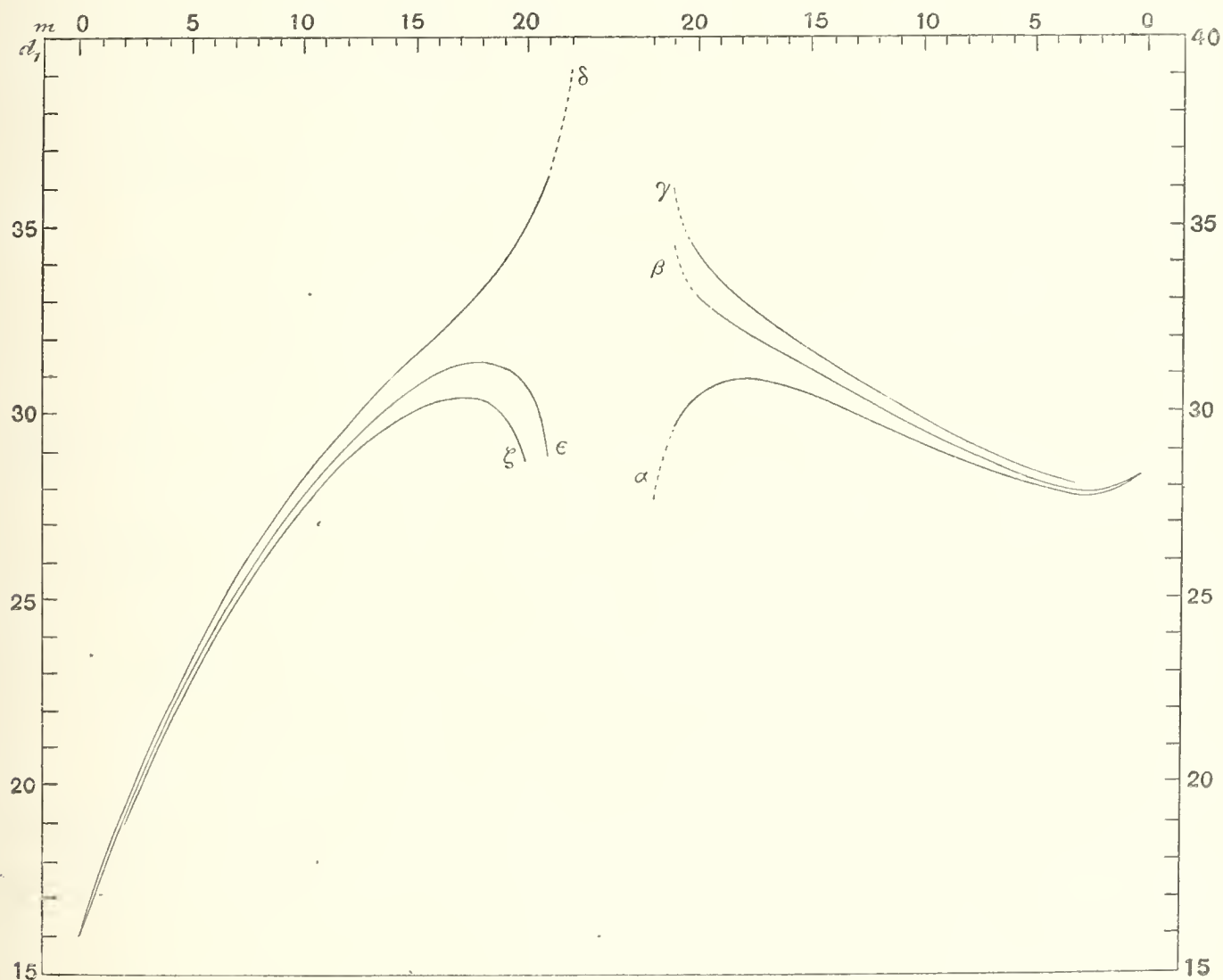


Fig. 2. Curves representing the varying distances between successive lines in the series  $\alpha$  to  $\gamma$ .  
(The dotted portions of the curves are somewhat doubtful.)

It should be noted that in addition to the main series formed from the groups of three, there are other fragmentary series of fainter lines having intervals between successive lines of the same order of magnitude as those of the main series. These are indicated in the general table by  $\alpha'$ ,  $\alpha''$ , and  $\delta'$ .

*The Central Maxima.*—The series which constitute the central and secondary maxima, so far as they have been identified, do not appear to present any unusual

features. In each case there are several superposed series, and some of the lines, which are probably unresolved composites, have to be assigned to two or more series. The probable series belonging to the secondary maximum have been designated  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ , and  $\alpha_4$ ; those on the red side of the chief maximum  $b_1$  and  $b_2$ ; and those on the more refrangible side of the chief maximum  $c_1$ ,  $c_2$ , and  $c_3$ . There is some uncertainty as to the  $c$  series, as alternative arrangements of the lines appear to be consistent with series relationships.

The lines belonging to the various series are indicated in the general table, but a clearer idea of their character may be obtained from fig. 3, where the series are plotted to scale. The complete spectrum is first shown, with lines of lengths proportional to the intensities, and below these are drawn the separate series. It will be seen that a large proportion of the band lines fall into the nine series, and it is quite probable that all of them could be assigned to series if it were possible to employ still greater

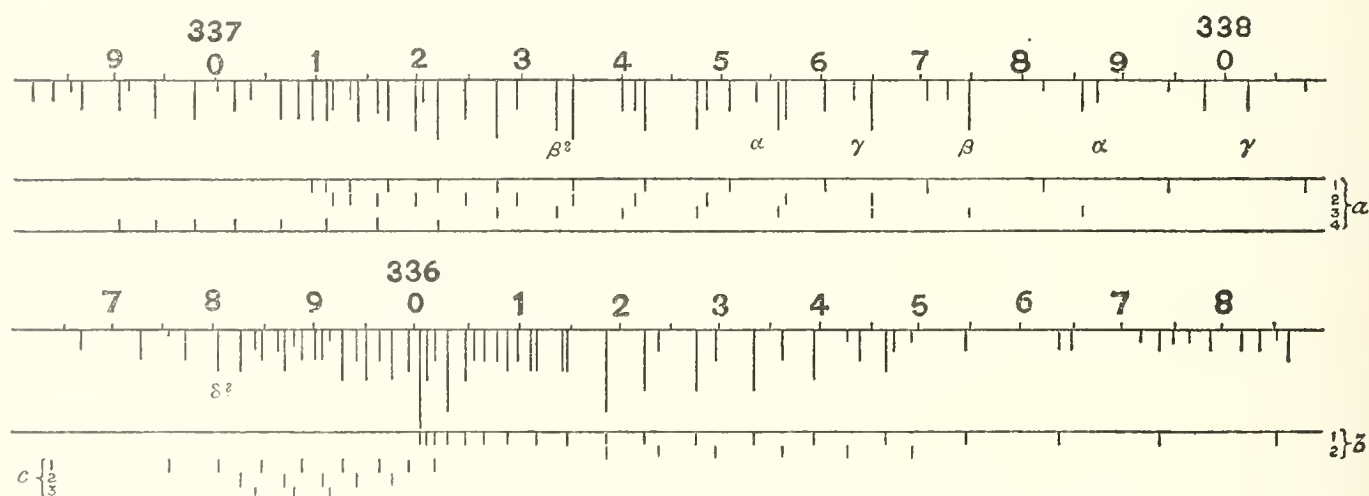


Fig. 3. Resolution of the central and secondary maxima into series.

resolving power. It will suffice to give numerical data for  $b_1$  as a further indication of the characteristics of the series involved in the central maximum. These are shown in Table III.

The series is closely represented by the formula—

$$\nu = 29755.176 - 0.6935m + 0.03327m^2 - 0.008326m^3.$$

where  $m$  has values ranging from 3 to 21. The greatest deviation in wave-number is 0.41, corresponding to a difference of 0.045Å between the observed and calculated values. The differences between the observed and calculated wave-numbers are shown in the last column of the table, and it will be seen that they are sufficiently systematic to indicate the imperfection of the formula. There would be no difficulty in calculating such formulæ for the other series, but it is not clear that they would serve any immediately useful purpose.

TABLE III.—Series  $b_1$  of the Central Maximum.

$\lambda$ , I.A.	$\nu$ , vac.	$d_1$ .	$d_2$ .	O - C. †
3368.53	29678.18			0.00*
67.38	88.32	10.14		
66.36	97.31	8.99	1.2	+0.31
65.46	29705.26	7.95	1.0	+0.41
64.66	12.32	7.06	0.9	+0.35
63.95	18.60	6.28	0.8	+0.22
63.32	24.16	5.56	0.7	+0.11
62.76	29.11	4.95	0.6	0.00*
62.26	33.53	4.42	0.5	-0.03
61.84	37.25	3.72	0.7	+0.04
61.47	40.52	3.27	0.5	-0.01
61.16	43.27	2.75	0.5	+0.03
60.90	45.56	2.29	0.5	+0.03
60.68	47.51	1.95	0.3	0.00*
60.48	49.28	1.77	0.2	+0.02
60.31	50.78	1.50	0.3	+0.18
60.19	51.84	1.06	0.4	+0.37
60.10	52.64	0.80	0.3	+0.34
60.04	53.17	0.53	0.3	+0.24
				0.00*

\* Used in calculation of constants.

† O - C is expressed in wave-number.

#### *Comparison with the Solar Spectrum.*

Details of the comparison with the solar spectrum are included in the general catalogue of ammonia band lines given in Table V. To facilitate the comparison, the wave-lengths of the ammonia lines have been corrected to the scale of ROWLAND by the addition of 0.14A, as shown in the fifth column. The entries under "sun" are taken directly from ROWLAND'S table, and in the densest region of the central maximum, extending from 3363.5 to 3358.0, the solar lines have been tabulated in

full. A direct comparison of the two spectra in the neighbourhood of the central maximum is given in fig. 5, Plate 1, where the ammonia spectrum is reproduced as a negative in order to represent its appearance in absorption.

The comparison is complicated by the approximate coincidences of many of the ammonia lines with lines of metallic origin in the solar spectrum, or with unidentified lines which have intensities too great to allow of their being assigned to ammonia alone. As ROWLAND'S limit of resolution appears to be about  $0.04\text{\AA}$ , ammonia lines may evidently be masked in this way by solar lines showing considerable differences in wave-length. Direct evidence of the presence of all the ammonia lines in the sun, such as would be afforded by identity of wave-lengths throughout, is therefore not to be expected.

There is also some uncertainty as to the completeness of ROWLAND'S list of wave-lengths, and as to the uniformity of his estimates of intensity. In this connection, a photograph of the solar spectrum in the HIGGS' collection of the Royal Astronomical Society has been to some extent utilised as a general check on ROWLAND in the region of the ammonia band. While the tabulated intensities on the whole were closely confirmed, there are several lines for which ROWLAND'S estimates appear to need revision. Attention is drawn to some of these in the column of remarks in Table V. As regards the wave-lengths, the relation between the international scale and the scale of ROWLAND is by no means simple. Comparison of the solar lines with the positions on the international scale given for the iron and nickel lines by BURNS shows that whilst the average difference in the region of the ammonia band is about  $0.14\text{\AA}$ , there is no consistent agreement among the different lines. Deviations from the mean in a selected region frequently amount to nearly  $0.01\text{\AA}$ , and there are occasional variations of  $0.02\text{\AA}$  and upwards. These irregularities are not necessarily due wholly to errors of measurement, but may also be caused by differences in the effective level at which the various lines are produced in the solar atmosphere. It would seem, however, that if due regard be paid to intensities, coincidences within  $0.02\text{\AA}$  may not be without significance.

Notwithstanding the difficulties affecting the comparison, there is abundant evidence that the ammonia band is present in the solar spectrum. The most convincing proof is perhaps afforded by the strongest part of the central maximum, extending from  $3360.45$  to  $3360.08$  (ROWLAND'S scale). As will be seen from fig. V., Plate 2, and from Table V., there is a complete correspondence of the solar and laboratory spectra as regards this group, except that the line  $3360.45$  may be slightly reinforced in the sun by a line of nickel.\* This agreement is emphasised by the presence of a background of dark continuous spectrum which is sharply bounded in each of the two spectra by the outer two of the five lines involved. There is a similar dark ground covering the adjacent group  $3360.82$  to  $3360.63$ , which is also clearly common to the two spectra.

\* A nickel line in this position is given by ROWLAND, but not by EXNER and HASCHEK.

The coincidences in the case of the central maximum as a whole are scarcely less striking. The majority of the solar lines in this region in fact appear to be due to ammonia, as will be seen from the table, where the solar lines from 3363·4 to 3358·0 are tabulated in full in order to bring out this feature. In this small region there are 47 solar lines, at an average distance apart of 0·117A, and 37 ammonia band lines, at an average distance of 0·149A. Thirty-four of the ammonia lines are either represented directly by reasonably appropriate lines in ROWLAND'S table, or fall upon solar lines of recognised or probable metallic origins. The absence of one of the remaining three lines is satisfactorily accounted for by its low intensity. In the case of the outstanding lines 3361·61 and 3359·89, the solar line corresponding to the first appears to be masked by dark ground extending between the adjacent solar lines, while the second is probably included in the nebulous line 3359·936. The coincidences are clearly too numerous and too systematic to be considered accidental.\* Confirmative evidence of their reality is afforded by the identity of narrow bright interspaces in the two spectra, especially those at 3361·0, 3360·9, 3360·5, 3360·0, 3359·7, and 3359·5, which will be clearly seen on reference to the photographs, these appear to be produced by patches of continuous background which are common to the two spectra. The discussion of the central maximum may thus be considered to establish the presence of ammonia in the sun beyond all doubt.

Analysis of the secondary maximum, occupying the region 3371 to 3378, leads to a similar conclusion, and there can be no doubt that the majority of the coincidences of lines of ammonia with faint solar lines in this part of the spectrum also have a real significance.

As regards the groups of three, forming the series  $\alpha$  to  $\zeta$ , there is also a close general agreement, and the few irregularities may well be caused by imperfect estimates of the wave-lengths and intensities in the two spectra, or by the approximate superposition of lines of other substances. If it were not for interference by metallic lines in the case of the sun, a good test would be provided by the series investigations. Supposing the coincidences to be genuine, the wave-lengths of the solar lines should show the series relations with the same order of accuracy as those of the ammonia lines themselves, and the intensities of the lines should be consistent with the series relationship. This test cannot be completely applied to any one of the six series, on account of near coincidences with metallic lines, but it may be worth while to take the chief lines of the  $\delta$  series as an illustration. The facts with regard to these are collected in Table IV.

It will be observed that while three of the metallic lines (3341·967, 3320·783,

\* In order to get a rough idea of the proportion of coincidences which might be merely accidental, the 37 ammonia wave-lengths in the region 3363·5 to 3358·0 were compared with the 47 solar lines from 3563·5 to 3558·0. The total number of approximate coincidences was 14, as compared with 34 in the true region, and of these, 5 were with lines assigned to metals. There was no systematic agreement of intensities in this case.

TABLE IV.—Evidence for  $\delta$  Series in the Solar Spectrum.

Ammonia.				Sun.				
Intensity in arc.	$\lambda$ (ROWLAND).	$d_1$ .	$d_2$ .	Origin.	Intensity.	$\lambda$ .	$d_1$ .	$d_2$ .
4	3349.69	3.93			00	3349.695		
4	45.76	3.80	13		00	45.761	3.934	140
4	41.96	3.72	08	Ti	4	41.967	3.794	074
4	38.24	3.63	09		0	38.247	3.720	086
4	34.61	3.57	06		0	34.613	3.634	077
5	31.04	3.50	07		1N	31.056	3.557	034
5	27.54	3.42	08	Ni	2	27.533	3.523	119
5	24.12	3.35	07		0	24.129	3.404	058
4	20.77	3.26	09	Mn, Fe	2	20.783	3.346	077
3	17.51	3.19	07		0	17.514	3.269	089
3	14.32	3.09	10	Mn	0	14.334	3.180	084
3	11.23	2.99	10		0	11.238	3.096	097
3	08.24	2.89	10		0N	08.239	2.999	114
2	05.35				000	05.354	2.885	

3314.334) produce no appreciable disturbance of the first and second differences, some disturbance is caused by the unidentified line 3331.056, and by the nickel line 3327.533. If, however, the former be assumed to include a line shorter in wave-length by only 0.016A, and the latter to include a line of wave-length greater by 0.010A, the series connection would be shown as accurately by the solar lines as by those of ammonia.\* The probable composite character of 3331.056 is in fact suggested by its nebulous appearance, and by its intensity being too great to allow of its being assigned wholly to ammonia. The agreement in the intensities is also satisfactory on the whole. The series investigation, so far as it goes, thus confirms the identification of some of the solar lines with band lines of ammonia. A general consideration of the intensities of the representatives of the  $\alpha$  to  $\zeta$  series in the solar spectrum appears to indicate a closer agreement with the arc than with the flame spectrum, the lines in the neighbourhood of the central maximum being relatively

\* The second differences 077, 034, 119, 058 would then become 061, 076, 083, 068.

enfeebled in each case. This is in accordance with the fact that all the brighter lines composing the central and secondary maxima as seen in the arc, some of which do not occur in the flame, are represented in the solar spectrum.

The outcome of the comparison is to show that of the 260 band lines of ammonia in the region  $\lambda$  3450 to  $\lambda$  3286, there are about 140 which correspond with previously unidentified faint lines in the solar spectrum. About 100 of the remaining lines are obscured by lines for which metallic origins have been found, or fall upon lines which are too strong in the sun to be attributed entirely to ammonia, and the few which fail to appear in the sun are all of low intensity.

It may be that additional solar lines are identical with lines composing the bands of ammonia which appear in the visible spectrum, but there are at present no experimental data for effective comparison.

#### *Description of Table V.*

The first five columns of the table give details of the ammonia band lines, showing the series to which they have been assigned, the intensities in the flame and arc, and the wave-lengths on the international and ROWLAND scales. The following three columns show the wave-lengths, intensities, and origins of solar lines occupying about the same positions as the ammonia lines, as given by ROWLAND. Between  $\lambda$  3363.5 and  $\lambda$  3358.0 all the solar lines are tabulated, in order to show the large proportion due to ammonia in the region of the central maximum of the ammonia band. In the column of remarks, the following references have been adopted to avoid repetition.

- (1) Solar line probably not wholly due to ammonia, as indicated by excessive intensity.
- (2) Intensity of solar line probably over-estimated by ROWLAND, as inferred from a HIGGS' photograph.
- (3) Very close ammonia lines, which are only vaguely resolved in the 3rd order of the 10-foot grating.

It should be noted that the resolving power in the case of the flame was less than that in the case of the arc spectrum.

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons.

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		$\lambda$ ROWLAND.	Inten- sity.	Origin.	
	Flame.	Arc.	I.A.	ROWLAND.				
$\alpha, \beta$		0	3450.36	3450.50	3450.469	5	Fe	
$\alpha, \beta$		1	46.99	47.13	47.154	00N		
$\alpha, \beta$		1	43.65	43.79	43.791	5d?	Co	
$\alpha, \beta$	0	2	40.36	40.50	40.505	0N	Fe	
$\gamma$		0	40.33	40.47				
$\alpha, \beta$	1	3	37.06	37.20	37.190	3		
$\gamma$		0	36.99	37.13	37.116	000N		
$\alpha$	1	2	33.78	33.92	33.905	0N		
$\beta$		2	33.74	33.88				
$\gamma$	1	1	33.65	33.79				
$\alpha$		2	30.48	30.62				
$\beta$	2	2	30.41	30.55	30.545	00N		Probable faint solar line on edge of Zr 30.671.
$\gamma$		1	30.30	30.44	30.428	00		
$\alpha$	2	2	27.15	27.29	27.263	3	Fe	Solar line from HIGGS.
$\beta$		2	27.07	27.21	[27.220]	00		
$\gamma$	2	1	26.93	27.07	27.046	0000		(2).
$\alpha$		2	23.81	23.95	23.972	0N		
$\beta$	3	2	23.69	23.83	23.848	7	Ni	(2).
$\gamma$		2	23.53	23.67	23.667	00N		
$\alpha$	3	3	20.43	20.57	20.575	0		(2).
$\beta$		3	20.28	20.42	20.417	00		
$\gamma$	2	3	20.11	20.25	20.240	00		
$\alpha$		3	17.04	17.18	17.198	00		
$\beta$	4	3	16.87	17.01	17.001	00		
$\gamma$		3	16.66	16.80	16.808	0		
$\alpha$	4	4	13.64	13.78	13.782	0		
$\beta$		4	13.43	13.57	13.597	2	Ni	
$\gamma$	3	3	13.18	13.32	13.275	5d?	Fe	} Ammonia may be in- cluded in solar lines.
$\alpha$		4	10.22	10.36	10.386	1	Zr	
$\beta$	3	4	09.95	10.09	10.080	00		(2).
$\gamma$		3	09.66	09.80	09.803	0		
$\alpha'$	00		09.20	09.34	09.346	2	Fe	
$\alpha$		3	06.78	06.92	06.943	5d?	Fe	
$\beta$	3	4	06.43	06.57	06.572	3	Fe	
$\gamma$		3	06.12	06.26	06.254	00		
$\alpha'$	00		05.43	05.57				
$\alpha$		4	03.31	03.45	03.478	2	Fe, Ti	
$\beta$	4	4	02.90	03.04	03.033	0		
$\gamma$		4	02.54	02.68	02.685	0		
$\alpha''$	00		02.21	02.35	02.352	000		
$\alpha'$		00	01.66	01.80	01.778	0000N		
$\alpha$	5	4	3399.81	3399.95	3399.942	0N		
$\beta$		4	99.34	99.48	99.489	3	Fe	
$\gamma$	4	4	98.93	99.07	99.059	0		
$\alpha''$		00	98.43	98.57	98.551	0000N		
$\alpha'$	00		97.86	98.00				
$\alpha$		6	96.30	96.44	96.437	0		
$\beta$	6	4	95.75	95.89	95.882	0		



TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.		Origin.	Remarks.
Series.	Intensity.		Wave-length.		$\lambda$ ROWLAND.	Inten- sity.		
	Flame.	Arc.	I.A.	ROWLAND.				
$\gamma$	4	4	3395.27	3395.41	3395.408	00N	Fe	
$\alpha''$	00		94.64	94.78	94.746	3		
$\alpha'$	00		93.99	94.13			Ti	Not given as Ti by KILBY.
$\alpha$	6	4	92.78	92.92	92.926	0		
$\beta$	6	4	92.12	92.26	92.259	0	Ti, Zr.	
$\gamma$	5	4	91.58	91.72	91.726	0		
$\alpha'$	0	0	90.07	90.21				
$\alpha$	6	5	89.23	89.37	89.387	00		
$\beta$	6	5	88.46	88.60	88.604	0N		
$\gamma$	5	5	87.84	87.98	87.988	5d?		
	0N		87.27	87.41				
	00	2	86.55	86.69	86.691	00N		
$\alpha'$	0	1	86.13	86.27				
		1	85.87	86.01	86.005	0000N		
$\alpha$	6	5	85.70	85.84	85.861	00	Fe?	
	0	1	85.24	85.38	85.361	3	Co	
$\beta$	5	5	84.76	84.90	84.908	1		(1).
$\gamma$	4	5	84.07	84.21	84.225	00		
$\alpha, \alpha_1$	7	4	82.19	82.33	82.340	0		Corrected solar $\lambda = 81.170$ .
$\beta$	5	3	81.04	81.18	81.202	0000		
$a_1$		1	80.78	80.92	80.889	1	Sr?	
$\gamma$	4	3	80.22	80.36	80.397	3	Ti	
$a_3$		3	79.80	79.94	79.961	3	Cr	
$a_1$		1	79.43	79.57	79.577	000		
	0		79.25	79.39				
$\alpha$	6	2	78.71	78.85	78.824	2	Fe	
$a_3$		3	78.58	78.72	78.723	00		
$a_1$		1	78.18	78.32	78.320	00		
$a_3$		5	77.48	77.62	77.622	3	Ti	
$\beta$	5	2	77.26	77.40	77.408	00		
$a_1$		2	77.04	77.18	77.202	0N	Co	
$a_2, a_3$		5d?	76.48	76.62	76.630	2	Fe	
$\gamma$	4	2	76.29	76.43	76.414	0		(1).
$a_1$		3	76.01	76.15	76.164	00		Arc includes faint Cu } " " " Ni } <sup>(3)</sup> .
$a_2$		4	75.62	75.76	75.768	000	Ni	
$a_3$		5	75.57	75.71	75.698	1		
$\alpha$	6	2	75.33	75.47	75.478	0N		
$a_1$		3	75.08	75.22	75.231	00		
$a_2$		3	74.84	74.98	74.981	000		
$a_3$	0	5	74.75	74.89	74.872	1	Zr	Arc includes faint Ni.
$a_1$		5	74.23	74.37	74.358	4	Ni	
$a_2$		3	74.14	74.28	74.271	000		(1).
$a_3$		3	74.00	74.14	74.119	2		
$a_1, a_2$		6	73.50	73.64	73.642	0		
$a_3, \beta?$	5	5	73.34	73.48	73.452	0		Solar line probably double.
		0	73.12	73.26				
$a_2$		3	72.95	73.09	73.105	0N		(1).

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		$\lambda$ ROWLAND.	Inten- sity.	Origin.	
	Flame.	Arc.	I.A.	ROWLAND.				
$a_1, a_3$	2	6d ?	3372.77	3372.91	3372.901	5	Ti, Pd	
$a_2$		4	72.46	72.60	72.609	00N	Fe	
$a_1, a_4$	6	6d ?	72.19	72.33	72.314	0		Also series $\alpha ?$ , $\gamma ?$
		2	72.06	72.20	72.225	1	Fe	
$a_2$		5	71.99	72.13	72.124	4	Ni, —	Arc includes faint Ni.
$a_1$	1	4	71.71	71.85	71.852	00		
$a_2, a_4$		3	71.61	71.75	71.745	000		
		4	71.39	71.53	71.535	00		} Difficult group in arc, which includes a faint metallic line.
$a_1, a_2$	1	?	71.34	71.48				
$a_2$		3	71.15	71.29	71.296	00		
$a_1, a_4$		4	71.10	71.24	71.246	00		
$a_1$	6 {	4	70.97	71.10	71.110	0		
		4	70.81	70.95	70.933	4	Fe	
$a_4$	1	4	70.62	70.76	70.770	1Nd ?	Zr, Mn	
		0	70.44	70.58	70.584	2	Ti	
	2 {	2	70.31	70.45	70.468	2	Co	
$a_4$		3	70.18	70.32	70.330	0N		(2).
		1	70.02	70.16	70.173	00		(1).
$a_4$	2	4	69.78	69.92	69.932	0		
$a_4$	4	3	69.38	69.52	69.506	0N		
		1	69.17	69.31				
$a_4$	4	3	69.03	69.17	69.190	0		
	2	3	68.65	68.79	68.793	00		
$b_1$		1	68.53	68.67	68.680	00		(1).
	0 {	2	68.36	68.50	68.496	000		
		2	68.18	68.32	68.319	1	Mn	
	2	2d ?	67.87	68.01	68.029	2	Ti, Ni, Fe	(1).
		1	67.67	67.81	67.812	0		
$b_1$		1	67.49	67.63				
		2	67.38	67.52	67.527	0000		
		1	67.18	67.32	67.297	1	Fe ?	
		2	66.47	66.61	66.594	000		
$b_1$		2	66.36	66.50	66.494	000		
		0	65.96	66.10				
$b_1$	00	2	65.46	65.60	65.581	0		(1).
$b_2$	1	1	64.93	65.07	65.081	0000		
		2	64.73	64.87	64.832	00		Corrected solar $\lambda = 64.870$ .
$b_1$	00	4	64.66	64.80	[64.786]	00		Solar line added from HIGGS.
	1	3	64.38	64.52	64.535	0Nd ?		
$b_2$		1	64.26	64.40	64.408	1	Co	
$b_1$	1	5d ?	63.95	64.09	64.055	0		Solar line wide enough to include ammonia.
$b_2$	0	3	63.61	63.75	63.750	1	Ni	
$b_1$	1	6	63.32	63.46	63.442*	0d ?	Co	*
					63.298	0000N		

\* From 3363.4 to 3358.0 the solar lines are tabulated in full.

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		$\lambda$ ROWLAND.	Inten- sity.	Origin.	
	Flame.	Arc.	I.A.	ROWLAND.				
$b_2$	00	3	3362.97	3363.11	3363.107	0		
$b_1$	2	6	62.76	62.90	62.936	4Nd?	Co	
					62.782	1		
					62.727	0000		
$b_2$		2	62.38	62.52	62.528	0		
$b_1$	3	6	62.26	62.40	62.402	2d?		(1).
					62.275	1		
					62.087	2	Ti	
$b_1, b_2$	6	8	61.84	61.98	61.988	0		
					61.906	1		
					61.704	3Nd?	Co	
$b_1$	1	4	61.47	61.61				Solar line merged in dark ground.
		4	61.42	61.56	61.568	0N		
					61.421	2		
$b_1$	4	4	61.16	61.30	61.327	8	Ti	
		4	61.10	61.24	61.241	1		(2).
		3	60.98	61.12	61.141	0		
$b_1$	4	4	60.90	61.04	61.055	1	Ti	
		3	60.80	60.94	60.988	0		Corrected solar $\lambda = 60.942$ .
$b_1$	3	3	60.68	60.82	60.828	0		Dark ground, both in sun and ammonia.
		3	60.58	60.72	60.741	0		
$b_1$		5	60.48	60.62	60.631	0		
					60.485	1	Cr	
$b_1$		8	60.31	60.45	60.444	2	Ni	Ni not given by EXNER and HASCHEK.
$b_1, c_1$	10	3	60.19	60.33	60.345	0		Dark ground, both in sun and ammonia.
$b_1$		5	60.10	60.24	60.258	0		
$b_1$		10d?	60.04	60.18	60.181	2		
$c_1$		4	59.94	60.08	60.066	0		
$c_2?$		5	59.75	59.89	59.936	1N		Solar line wide enough to include ammonia.
					59.823	2		
$c_1$		3	59.63	59.77	59.769	1		(1).
		5	59.50	59.64	59.636	2	Fe?	
$c_2$		3	59.41	59.55	59.542	1		(2).
$c_1$	4	5	59.28	59.42	59.420	1	Co	
$c_3$		1	59.15	59.29				
$c_2$		3	59.08	59.22	59.248	3N	Ni	Not Ni in ammonia arc.
		3	59.02	59.16	59.144	00		
$c_1$	3	3	58.89	59.03	59.035	2N		(1).
$c_3$		1	58.80	58.94	58.929	00		(2).
$c_2$		4	58.70	58.84	58.832	0		
		2	58.65	58.79	58.771	00		(2).
$c_1$	4	3	58.48	58.62	58.649	4	Ti, Cr	
$c_3$		2	58.42	58.56	58.542	00		(2).
$c_2$		4	58.28	58.42	58.416	3	Ti	
					58.276	0000		

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		$\lambda$ ROWLAND.	Inten- sity.	Origin.	
	Flame.	Arc.	I.A.	ROWLAND.				
$c_1, \delta?$	5	4	3358.04	3358.18	3358.182 58.076*	IN 0000		*
$c_1$	5	3	57.72	57.86	57.874	0		(1).
		0	57.56	57.70	57.703	0		
	5	3	57.28	57.42	57.412	2	Zr	
	4	2	56.66	56.80	56.821	2	Fe	
	2	1	55.18	55.32	55.363	4	Fe	
$\delta$	1		53.91	54.05	54.057	000N		(1).
	6	2	53.63	53.77	53.768	00N	Zr	
	0	1	53.10	53.24	53.262	2		
$\epsilon$	1		51.77	51.91				(1).
	3	1	50.85	50.99	50.985	000		
$\delta$		0	49.85	49.99				(1).
	10	4	49.55	49.69	49.695	00		
$\delta'$	0	0	48.68	48.82	48.820	000		(1).
	0	0	47.94	48.08	48.072	3	Fe	
$\epsilon$	4	2	47.62	47.76	47.760	00N		(1).
	$\zeta$	3	0	46.42	46.56	46.557	0	
			2	46.28	46.42	46.414	00	
$\delta$	8	4	45.62	45.76	45.761	00		
$\delta'$	0	1	44.86	45.00	45.015	000		
$\epsilon$	5	2	44.17	44.31	44.315	00		(1).
	$\zeta$	4	1	43.21	43.35	43.366	0	
		1	43.01	43.15	43.156	00		
$\delta$	0	1	42.33	42.47	42.442	3	Fe	(1).
	8	4	41.82	41.96	41.967	4	Ti	
$\delta'$	00		41.15	41.29	41.300	0000N		
$\epsilon$	6	2	40.68	40.82	40.823	00N		(1).
	$\zeta$	6	3	39.86	40.00	40.011	1	
		0	?	39.30	39.44	39.438	000N	
$\delta$	0	0	38.80	38.94	38.944	0000		(1).
	8	4	38.10	38.24	38.247	0		
		1	37.67	37.81	37.803	3	Fe	
$\epsilon$	6	4	37.19	37.33	37.319	1N	Co	Possibly obscured in sun by Mg 36.820 (8N).
		1	36.75	36.89				
$\zeta$	6	2	36.49	36.63	36.635	00N		
$\delta$	7	4	34.47	34.61	34.613	0		
$\epsilon$	7	4	33.72	33.86	33.854	0		Co
		2	33.40	33.54	33.526	2		
$\zeta$	7	3	33.11	33.25	33.250	0		Co
		1	33.05	33.19				
$\delta$	7	5	30.90	31.04	31.056	1N		Sn?
		1	30.59	30.73	30.745	000		
$\epsilon$	7	5	30.27	30.41	30.438	1		Co
		$\zeta$	6	4	29.75	29.89	29.902	
			1	28.19	28.33	28.341	00	

\* From 3363.4 to 3358.0 the solar lines are tabulated in full.

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		$\lambda$ ROWLAND.	Inten- sity.	Origin.	
	Flame.	Arc.	I.A.	ROWLAND.				
$\delta$	6	5	3327.40	3327.54	3327.533	2	Ni	
$\epsilon$	5	4	26.87	27.01	26.998	3	Ti	
$\zeta$	5	4	26.41	26.55	26.553	0		
$\eta$	5	5	23.98	24.12	24.129	0		
$\theta$	5	4	23.53	23.67	23.669	0		
$\iota$	5	4	23.12	23.26	23.256	00		
$\kappa$	4	4	20.63	20.77	20.783	2	Mn, Fe	
$\lambda$	4	3?	20.25	20.39	20.391	7	Ni	Obscured in arc by Ni.
$\mu$	4	3	19.89	20.03	20.032	0		
$\nu$	3	3	17.37	17.51	17.514	0		
$\xi$	3	3	17.04	17.18	17.174	00		
$\omicron$	3	3	16.73	16.87	16.871	00		
$\pi$	3	3	14.18	14.32	14.334	0	Mn	
$\rho$	3	3	13.90	14.04	14.042	00N		
$\sigma$	3	3	13.63	13.77	13.774	1		(1).
$\tau$	3	3	11.09	11.23	11.238	0		
$\upsilon$	3	3	10.85	10.99	10.996	0		
$\phi$	3	3	10.62	10.76	10.777	1N		(1).
$\chi$	3	3	08.10	08.24	08.239	0N		
$\psi$	3	3?	07.90	08.04	08.035	00N		Obscured in arc by Cu.
$\omega$	2	2	07.70	07.84	07.845	4	Fe	
$\omicron$	2	2	05.21	05.35	05.354	000		
$\kappa$	2	2	05.05	05.19	05.194	000		
$\lambda$	2	2	04.87	05.01	05.001	00	Mn	
$\mu$	2	2	02.42	02.56				Obscured in sun by Na 02.510 (6).
$\nu$	2	2	02.30	02.44	02.443	0000N		
$\xi$	1	1	02.15	02.29	02.289	0000N		
$\zeta$	2	2	3299.76	3299.90	3299.905	0		(1).
$\eta$	2	2	99.67	99.81	99.804	0		(1).
$\theta$	1	1	99.54	99.68	99.652	0N?	Mn	
$\iota$	1	1	97.23	97.37	97.381	0		(1).
$\kappa$	2	1	97.16	97.30	97.301	0	Co	
$\lambda$	0	0	97.05	97.19	97.194	0N		(1).
$\mu$	1	1	94.82	94.96	94.949	00N		{ Just resolvable in 4th order plate.
$\nu$	1	1	94.79	94.93				
$\xi$	0	0	94.70	94.84	94.849	000		
$\zeta$	1	1	92.58	92.72	92.728	4	Fe	
$\eta$	0	0	92.51	92.65	92.636	0		(1).
$\theta$	0	1	90.50	90.64	90.642	0N		(1).
$\iota$	0	0	90.45	90.59	90.602	00		
$\kappa$	0	1	88.57	88.71	88.705	2	Ti	
$\lambda$	0	0	86.84	86.98	86.980	0N		(1).

*Description of Plate.*

Fig. I. is enlarged from a photograph of the spectrum of the flame of ammonia fed with oxygen; taken with a small quartz spectrograph. The bright band on the left is due to water vapour.

Fig. II. is from a photograph taken with a quartz spectrograph of moderate dispersion, the source being a flame of imperfectly dried cyanogen burning in an atmosphere of oxygen. The bright band on the left is due to water vapour.

Fig. III. shows the band of the ammonia flame as photographed with the large quartz spectrograph.

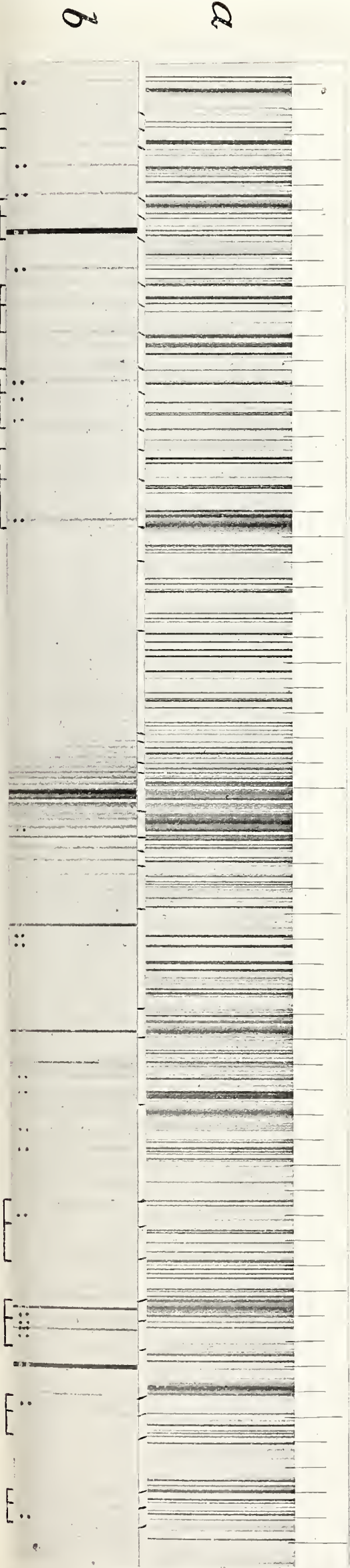
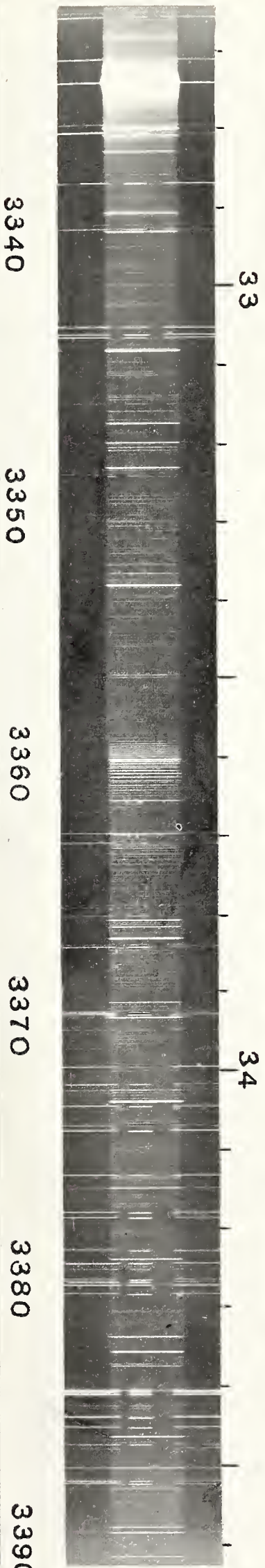
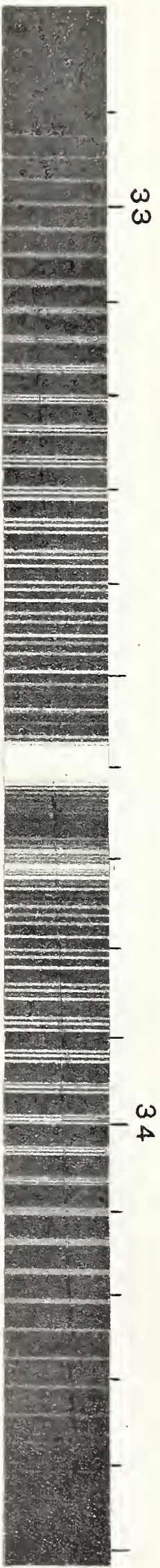
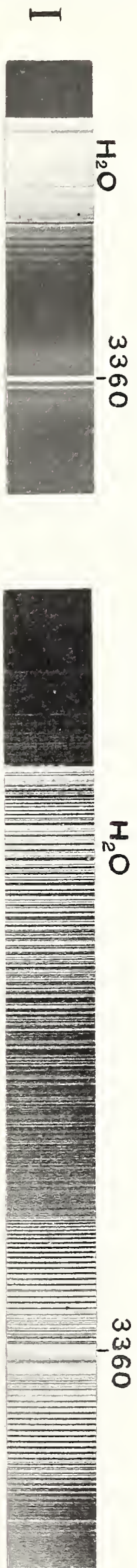
Fig. IV. is from a photograph taken in the 3rd order of a 10-foot concave grating. The short lines at the edges are those of the iron comparisons. The middle spectrum is that of the copper arc in ammonia.

Fig. V. (*a*) is the solar spectrum, from a photograph by HIGGS; (*b*) is the copper arc in ammonia, as fig. IV. It is shown as a negative to facilitate comparison with the solar absorption lines. Metallic lines are marked by double dots, except in the case of iron comparison lines, which are short lines along the middle of the spectrum. The scale is that of ROWLAND. (There is a slight difference of scale of the two enlargements, but several lines common to the two spectra are indicated.)

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[PLATES 3 AND 4.]

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FORMERLY FELLOW OF TRINITY COLLEGE, CAMBRIDGE.

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VII. *Surface Reflexion of Earthquake Waves.*

By GEORGE W. WALKER, *A.R.C.Sc., M.A., F.R.S., formerly Fellow of Trinity College, Cambridge.*

Received June 28,—Read November 1, 1917.

[PLATES 3 AND 4.]

A SEISMOGRAM, or instrumental time record of the earth movement produced by an earthquake at some distance, may be divided into three main parts, known as the first phase, the second phase, and the long-wave phase respectively. As a rule, the experienced observer has little difficulty in distinguishing these phases, and although difficult cases do arise, there is general agreement that the three divisions are characteristic and correspond to definite properties of the earth.

The beginning of the first phase is denoted by P and the beginning of the second phase by S, and these are interpreted as representing the arrival of longitudinal and transversal waves which start simultaneously at the focus of the earthquake and reach the observing station at different times. By general convention P and S are also used to represent the time interval between the occurrence of the earthquake and the arrival of the corresponding waves at the observing station.

Time curves giving the values of P and S as functions of the epicentral distance were obtained by ZÖPPRITZ in 1907 ('Göttinger Nachrichten'). The tables of values are in general use at seismological observatories. They have proved remarkably successful in determining epicentres of earthquakes, and the theoretical analysis by WIECHERT has led to inferences about the interior of the earth which are of the greatest interest. Doubtless as observational data improve these time curves may have to be modified, but only by way of correction and not as regards the main broad features.

In addition to the primary features called P and S, a seismogram may show well-marked sharp impulses, and in WIECHERT'S opinion these represent the arrival of waves that have undergone one or more reflexions at the earth's surface. On this view  $PR_n$  would denote a longitudinal wave that has been reflected  $n$  times at the surface, thus dividing the epicentral distance into  $(n+1)$  equal parts, and a similar notation  $SR_n$  would apply to transversal waves. We may also contemplate waves  $P_nS_m$  that have undergone change from longitudinal to transversal (or *vice versa*) on reflexion.

There is no doubt that observation supports the view that these effects actually occur. But there are difficulties. The times of arrival are not always in agreement with theoretical calculation from the curves for P and S, and the relative magnitudes of the reflected waves to P and S undergo changes at different distances that are difficult to understand. Thus it is doubtful if the reflexions are shown at all at less than 3000 km.; at 8000 km.  $PR_1$  is about as large as P, while at 12,000 km.  $PR_1$  is substantially larger than P.

The present investigation was undertaken with a view to throwing some light on these peculiar phenomena. Owing largely, no doubt, to the circumstance that most observatories possess instruments for recording only the horizontal components (some have only one), discussion has in many cases been confined to the phenomena shown in that component. The introduction of a really reliable apparatus for the vertical component by Prince GALITZIN, about seven years ago, has led to results of great value, and has shown how important it is to study the vertical and horizontal components in conjunction.

Analysis of the time curves for P and S led WIECHERT and ZÖPPRITZ to the conclusion that the corresponding seismic rays do not travel in straight lines from the focus, but that they dip down into the earth as if the speed of propagation increased with the depth. The results of their investigation will be found in GALITZIN'S 'Lectures on Seismometry,' or my own monograph on 'Modern Seismology.'

The surface values are 7.17 km. per second for P and 4.01 km. per second for S. These are substantially higher than the values found for surface rocks, and emphasize the fact that in using the term surface we do, on this view, imagine the heterogeneous crust of the earth replaced by a purely ideal surface at which the speeds acquire the values stated. The justification of this assumption and the determination of the true effect of the crust will have to be undertaken before long.

We have now to consider the magnitude of the ground movement experienced when a wave is incident on the surface. This problem has been dealt with by KNOTT ('Phil. Mag.,' 1899) and WIECHERT ('Gött. Nach.,' 1907), but only partially. We shall assume that at reflexion the waves may be treated as plane and the surface as plane.

In the figure (1) let OX represent the intersection of the earth's surface supposed plane with the plane of the paper and let OZ be drawn vertically downwards. The lower side

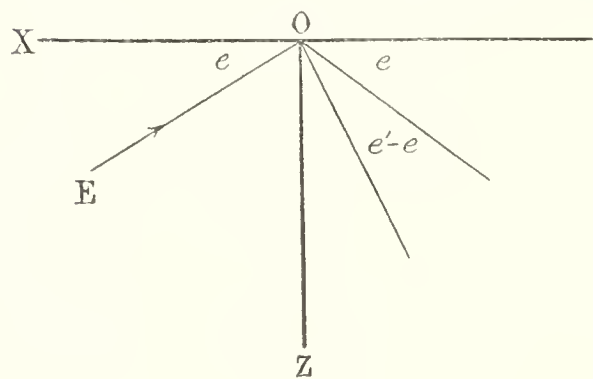


Fig. 1.

of OX represents the earth, in which the speeds of propagation of longitudinal and transversal waves are  $V_1$  and  $V_2$  at the surface. The upper side of OX is a vacuum in which no waves are propagated.

Let a ray EO be incident at the point O, making an angle  $e$  with OX. This angle is usually called the angle of emergence. The term is misleading. It is really the co-angle of incidence in the optical analogy, and when occasion arises I propose to call it the angle of impingence.

(1) Let the incident wave be longitudinal. The component displacements  $\xi_1$  and  $\zeta_1$  are

$$(\xi_1, \zeta_1) = -A (\cos e, \sin e) f \{t + (x \cos e + z \sin e)/V_1\},$$

where  $f$  is any arbitrary function.

This wave gives rise to a reflected longitudinal disturbance making an equal angle  $e$  on the other side of OZ, expressed by

$$(\xi_2, \zeta_2) = -A_2 (\cos e, -\sin e) f \{t + (x \cos e - z \sin e)/V_1\},$$

and a reflected transversal disturbance making an angle  $e'$  on the other side of OZ, expressed by

$$(\xi_3, \zeta_3) = A_3 (\sin e', \cos e') f \{t + (x \cos e' - z \sin e')/V_2\}.$$

At the surface of separation OX the stresses must vanish, and this requires that

$$\frac{\partial \xi}{\partial z} + \frac{\partial \zeta}{\partial x} = 0$$

and

$$(V_1^2 - 2V_2^2) \left( \frac{\partial \xi}{\partial x} + \frac{\partial \zeta}{\partial z} \right) + 2V_2^2 \frac{\partial \zeta}{\partial z} = 0,$$

when  $z = 0$ .

Thus we get the relations

$$A - A_2 = \mu A_3 \cos 2e' / \sin 2e,$$

$$A + A_2 = \mu^{-1} A_3 \sin 2e' / \cos 2e',$$

where

$$\mu = V_1/V_2 \quad \text{and} \quad \mu \cos e' = \cos e.$$

It may be noted that

$$\sin 2e (A^2 - A_2^2) = \sin 2e' A_3^2,$$

which satisfies the energy condition that the rate of arrival of energy by the incident waves is equal to the rate at which energy passes away by the reflected waves.

Solving the above equations, we get

$$A_2/A = \frac{\{\sin 2e \sin 2e' - \mu^2 \cos^2 2e'\}}{\{\sin 2e \sin 2e' + \mu^2 \cos^2 2e'\}},$$

$$A_3/A = \frac{2\mu \sin 2e \cos 2e'}{\{\sin 2e \sin 2e' + \mu^2 \cos^2 2e'\}}.$$

The resultant horizontal movement along OX is H, where

$$H = -(A + A_2) \cos e + A_3 \sin e',$$

thus

$$H/A = -\frac{2\mu^2 \sin e \sin 2e'}{\{\sin 2e \sin 2e' + \mu^2 \cos^2 2e'\}}.$$

The resultant vertical movement along OZ is V, where

$$V = -(A - A_2) \sin e + A_3 \cos e'$$

thus

$$V/A = \frac{2\mu^2 \sin e \cos 2e'}{\{\sin 2e \sin 2e' + \mu^2 \cos^2 2e'\}}.$$

The apparent angle of emergence  $\bar{e}$  is given by

$$\tan \bar{e} = V/H = -\cot 2e',$$

and hence

$$\sin \bar{e} = 1 - 2\mu^{-2} \cos^2 e,$$

a relation obtained by WIECHERT.

TABLE I.—Longitudinal Disturbance Incident.

$$\mu = 1.788, \quad \mu \cos e' = \cos e.$$

$e.$	$e'.$	$A_2/A.$	$A_3/A.$	$H/A.$	$V/A.$
0	56 0	-1.0000	-0.0000	-0.0000	-0.0000
5	56 8	0.4814	0.3797	0.8322	0.3407
10	56 35	0.2229	0.5946	1.2592	0.5398
15	57 18	0.0985	0.7380	1.4918	0.6830
20	58 18	0.0544	0.8466	1.6084	0.8054
25	59 33	0.0609	0.9346	1.6563	0.9219
30	61 2	0.1023	1.0039	1.6570	1.0381
35	62 44	0.1689	1.0587	1.6219	1.1555
40	64 38	0.2537	1.0909	1.5574	1.2732
45	66 42	0.3501	1.0989	1.4692	1.3894
50	68 56	0.4537	1.0797	1.3585	1.5016
55	71 17	0.5584	1.0315	1.2307	1.6077
60	73 46	0.6607	0.9534	1.0846	1.7047
65	76 20	0.7553	0.8465	0.9256	1.7908
70	78 58	0.8383	0.7131	0.7556	1.8640
75	81 41	0.9070	0.5566	0.5743	1.9225
80	84 26	0.9580	0.3817	0.3867	1.9651
85	87 12	0.9894	0.1941	0.1952	1.9913
90	90 0	1.0000	0.0000	0.0000	2.0000

In general  $A_2$  vanishes for two values of  $e$ , and in the particular case  $\mu^2 = 3$ , which holds for an ideal material with POISSON'S ratio =  $\frac{1}{4}$ , the values at which  $A_2$  vanishes are  $e = 12^\circ 47'$  and  $e = 30^\circ$ .



If, however, we take the surface values given by ZÖPPRITZ, viz.,  $V_1 = 7.17$  km. per second,  $V_2 = 4.01$  km. per second, we have  $\mu = 1.788$ , and  $A_2$  does not vanish for any real value of  $e$ , but falls to a very small minimum about  $e = 20^\circ$ .

The numerical values of  $A_2$ ,  $A_3$ ,  $H$ , and  $V$  for different angles of impingence are given in Table I., and the results are also shown graphically in fig. 2, wherein  $A$  is taken as numerically  $-1$ .

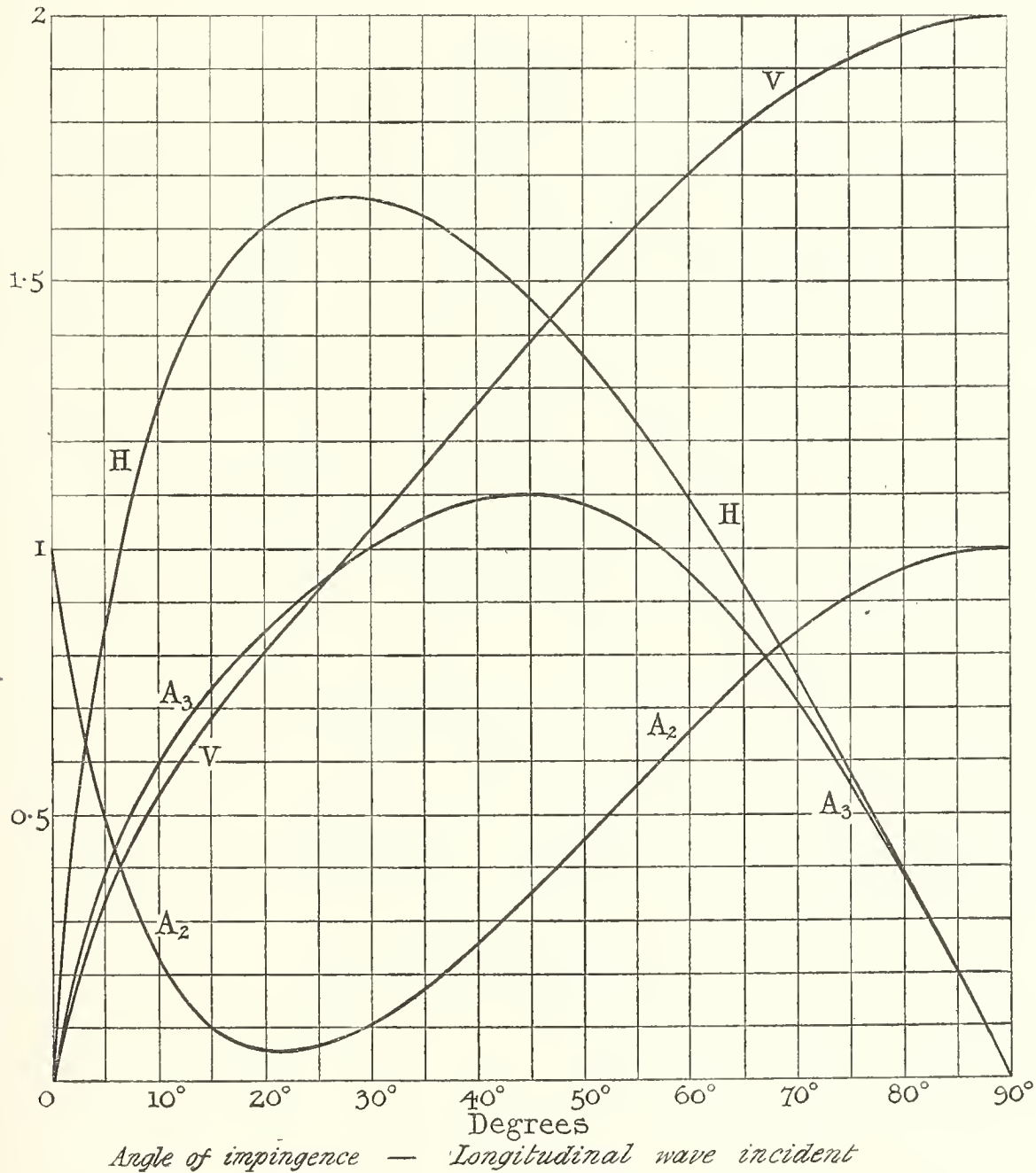


Fig. 2.

(2) If the incident wave is transversal and the vibration at right angles to the plane of the paper there is no reflected longitudinal wave for any angle of incidence, and the reflected transversal wave at an angle  $e$  is equal in magnitude to the incident wave. The resultant motion of the ground is entirely horizontal at right angles to

OX and precisely twice the magnitude of the incident disturbance for all angles of incidence.

(3) If the incident wave is transversal and the vibration in the plane of the paper we may assume that the incident disturbance is represented by

$$(\xi_1, \zeta_1) = A (-\sin e, \cos e) f \{t + (x \cos e + z \sin e)/V_2\}.$$

This will give rise to a reflected transversal disturbance at an angle  $e$  on the other side of OZ, expressed by

$$(\xi_2, \zeta_2) = A_2 (\sin e, \cos e) f \{t + (x \cos e - z \sin e)/V_2\},$$

and a reflected longitudinal disturbance at an angle  $e'$  on the other side of OZ, expressed by

$$(\xi_3, \zeta_3) = A_3 (-\cos e', \sin e') f \{t + (x \cos e' - z \sin e')/V_1\}.$$

The vanishing of the stresses at the surface of separation leads to the relations

$$A - A_2 = -\mu A_3 \cos 2e / \sin 2e,$$

$$A + A_2 = -\mu^{-1} A_3 \sin 2e' / \cos 2e,$$

where

$$\mu = V_1/V_2 \quad \text{and} \quad \mu \cos e = \cos e'.$$

We note that the energy condition is satisfied by these equations.

Solving the equations, we get

$$A_2/A = \frac{\{\sin 2e \sin 2e' - \mu^2 \cos^2 2e\}}{\{\sin 2e \sin 2e' + \mu^2 \cos^2 2e\}},$$

$$A_3/A = -\frac{2\mu \sin 2e \cos 2e}{\{\sin 2e \sin 2e' + \mu^2 \cos^2 2e\}}.$$

The resulting horizontal motion of the ground is H, where

$$H/A = \frac{2\mu^2 \sin e \cos 2e}{\{\sin 2e \sin 2e' + \mu^2 \cos^2 2e\}},$$

and the resulting vertical motion is V, where

$$V/A = \frac{2\mu \sin e' \sin 2e}{\{\sin 2e \sin 2e' + \mu^2 \cos^2 2e\}}.$$

For the ideal case  $\mu^2 = 3$ ,  $A_2$  would vanish for  $e = 55^\circ 44'$  and  $e = 60^\circ$ ; but in our actual case  $\mu = 1.788$ ,  $A_2$  does not vanish but falls to a small minimum near  $e = 58^\circ$ . In the present case there is no real value of  $e'$  until  $e$  attains the value  $56^\circ$ . Thus in the range from  $e = 0^\circ$  to  $e = 56^\circ$  there is no reflected longitudinal disturbance, but there is a type of disturbance practically confined to the surface of separation and

a reflected transversal wave differing in phase from the incident wave. Within this range the values of  $A_2$ ,  $A_3$ ,  $H$  and  $V$  are complex, except at the special point  $e = 45^\circ$ ,

TABLE II.—Transversal Wave Incident.

$$\mu = 1.788, \quad \mu \cos e = \cos e'.$$

Angles Less than the Critical Angle  $56^\circ$ .

$e$ .	Mod $A_2/A$ .	Mod $A_3/A$ .	Mod $H/A$ .	Mod $V/A$ .
0	1.0000	0.0000	0.0000	0.0000
5	1.0000	0.3084	0.2768	0.4587
10	1.0000	0.4744	0.4306	0.7316
15	1.0000	0.5371	0.4971	0.8733
20	1.0000	0.5465	0.5199	0.9632
25	1.0000	0.5228	0.5157	1.0371
30	1.0000	0.4700	0.4852	1.1114
35	1.0000	0.3820	0.4169	1.1953
40	1.0000	0.2401	0.2802	1.2942
45	1.0000	0.0000	0.0000	1.4142
50	1.0000	0.4635	0.6446	1.5120
55	1.0000	1.5389	2.3986	0.3726

Angles  $e$  from  $56^\circ$  to  $90^\circ$ .

$e$ .	$e'$ .	$A_2/A$ .	$A_3/A$ .	$H/A$ .	$V/A$ .
56 0	0	-1.0000	+2.7685	-4.4261	+0.0000
56 8	5	0.4814	2.0235	3.2462	0.4654
56 35	10	0.2229	1.5983	2.5946	0.7043
57 18	15	0.0985	1.3419	2.2206	0.8343
58 18	20	0.0544	1.1776	2.0035	0.8996
59 33	25	0.0609	1.0660	1.8806	0.9263
61 2	30	0.1023	0.9841	1.8165	0.9267
62 44	35	0.1689	0.9176	1.7907	0.9071
64 38	40	0.2537	0.8577	1.7898	0.8710
66 42	45	0.3501	0.7985	1.8047	0.8217
68 56	50	0.4537	0.7355	1.8292	0.7598
71 17	55	0.5584	0.6672	1.8588	0.6883
73 46	60	0.6607	0.5910	1.8899	0.6066
76 20	65	0.7553	0.5074	1.9200	0.5177
78 58	70	0.8383	0.4168	1.9469	0.4226
81 41	75	0.9070	0.3186	1.9694	0.3212
84 26	80	0.9580	0.2155	1.9861	0.2163
87 12	85	0.9894	0.1091	1.9966	0.1092
90 0	90	1.0000	0.0000	2.0000	0.0000

for which they become real. For  $e$ , between  $56^\circ$  and  $90^\circ$ , the values are all real. We thus divide Table II. giving numerical values into the range  $e = 0^\circ$  to  $56^\circ$ , for

which the "modulus" is given, and the range  $e = 56^\circ$  to  $90^\circ$ , for which the values are real and for which there is a real reflected longitudinal wave as well as a real reflected transversal wave.

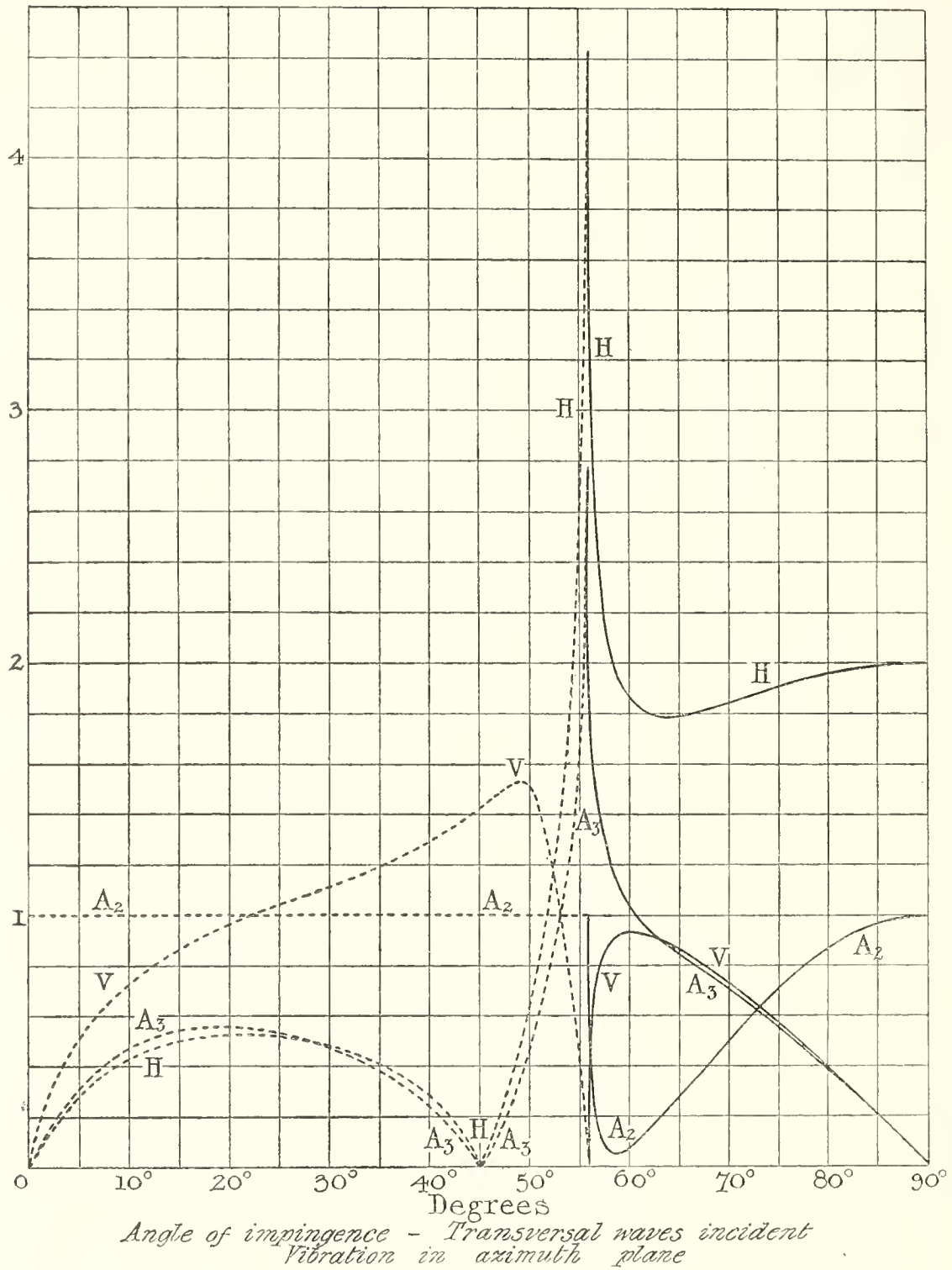


Fig. 3.

These results are exhibited graphically in fig. 3, wherein A has been taken as numerically 1, and for convenience, the - sign has been disregarded.

It is important to remember that the results we have obtained for reflexion of elastic disturbance are not confined to periodic waves (*cf.* Lord KELVIN, 'Phil. Mag.,'

1899). The function we have denoted by  $f$  may be any arbitrary function provided it represents a disturbance that can be propagated into an undisturbed region (see LOVE, 'Theory of Elasticity,' p. 283). Thus as long as  $A_2$  and  $A_3$  remain real precisely the same functional form represents the incident and reflected disturbances. This is the case for longitudinal disturbance impingent at all angles  $e$  from  $0^\circ$  to  $90^\circ$ , for transversal disturbance (vibration horizontal) at all angles  $e$  from  $0^\circ$  to  $90^\circ$ , and for transversal disturbance (vibration vertical) at the particular angle  $e = 45^\circ$  and from  $e = \sec^{-1} \mu$  (about  $56^\circ$ ) to  $90^\circ$ . But when  $A_2$  and  $A_3$  becomes complex, as in the case of transversal waves (vibration vertical) for angles  $e$  between  $0^\circ$  and  $\sec^{-1} \mu$ , we must start by taking a complex form for  $f$  and finally select the real parts from the various expressions in the manner familiar in optical theory.

Let  $f(\theta)$  be the incident transversal disturbance where

$$\theta = t + (x \cos e + z \sin e)/V_2,$$

then the Fourier resolution of  $f(\theta)$  gives

$$f(\theta) = \pi^{-1} \int_{-\infty}^{+\infty} f(\lambda) d\lambda \int_0^\infty \cos \alpha (\theta - \lambda) d\alpha.$$

Since in the reflected transversal disturbance

$$A_2/A = e^{i\phi_2},$$

the real part of the corresponding disturbance is

$$\pi^{-1} \int_{-\infty}^{+\infty} f(\lambda) d\lambda \int_0^\infty \cos \{ \alpha (\theta_2 - \lambda) + \phi_2 \} d\alpha,$$

where

$$\theta_2 = t + (x \cos e - z \sin e)/V_2.$$

We also have

$$A_3/A = M_3 e^{i\phi_3}.$$

There is no real angle of reflexion of the longitudinal disturbance, but if we write

$$\theta_3 = t + x \cos e / V_1 \quad \text{and} \quad \cosh \psi = \mu \cos e,$$

the longitudinal disturbance is expressed by

$$\xi_3 = \pi^{-1} \int_{-\infty}^{+\infty} f(\lambda) d\lambda \int_0^\infty M_3 \cosh \psi e^{-V_1^{-1} \alpha z \sinh \psi} \cos \{ \alpha (\theta_3 - \lambda) + \phi_3 \} d\alpha,$$

$$\zeta_3 = \pi^{-1} \int_{-\infty}^{+\infty} f(\lambda) d\lambda \int_0^\infty M_3 \sinh \psi e^{-V_1^{-1} \alpha z \sinh \psi} \sin \{ \alpha (\theta_3 - \lambda) + \phi_3 \} d\alpha.$$

The character of the reflected transversal disturbance will depend on the precise form of  $f(\lambda)$ , and, in general, the reflected disturbance will differ from the incident disturbance. There will be a "trail."

We have not introduced dispersion, but if this exists (as most probably it does) it will give rise to a "trail" with all classes of disturbance, not confined to the special range we have just considered, in a manner analogous to a pressure disturbance travelling over deep water (see LAMB, 'Hydrodynamics').

The angle of impingence may be calculated from the time curve by means of the formula due to WIECHERT,

$$\cos e = V_0 dT/d\Delta,$$

where  $dT/d\Delta$  is the slope of the time curve at epicentral distance  $\Delta$  and  $V_0$  is the surface value of the speed of the corresponding wave whether longitudinal or transversal. The results are given in Table III. along with the computed value of  $\bar{e}$  for longitudinal waves and the value as directly observed at Pulkovo by measurement of the horizontal and vertical disturbance.

We now consider the magnitude of the first impulse P. Fig. 2 shows that for a given value of the incident longitudinal disturbance the horizontal motion of the ground exceeds the vertical until the angle of impingence is about  $47^\circ$ , where the two become equal. For greater values of  $e$  the vertical motion exceeds the horizontal. Further, H attains its maximum for  $e = 27^\circ$  and thereafter diminishes, which V continues to increase right up to  $90^\circ$ .

Thus quite apart from the falling off of amplitude with distance on account of spherical divergence, we should expect H to diminish in importance as we pass to great distances, while V, being relatively small for small distances, becomes equal to H for  $\Delta$  about 2800 km., and for greater distances V exceeds H, the ratio being about 2 at 7000 km. and still greater as the distance increases.

This is in general agreement with observation both at Pulkovo and Eskdalemuir, where it has been observed that at about 2500 km. V is about the same magnitude as H, while at 8000 km. or more V is much greater than H.

Actual numbers were published by GALITZIN ('Lectures on Seismometry') and are included in Table III., wherein  $\bar{e}$  observed is given by  $\tan \bar{e} = V/H$ , V and H being directly observed.

The agreement of theory and experiment is good at about 3000 km. and again at 8500 km., and beyond, but a discordant feature is shown in the intermediate range.  $\bar{e}$  as calculated continues to increase, but  $\bar{e}$  as actually observed falls to a minimum at 4000 km. substantially less than the calculated value.

Now the general effect of the crust might be expected to make  $\bar{e}$  greater than the value calculated from the time curves. It is extremely difficult to account for the discrepancy actually observed. In view of the exhaustive tests applied by GALITZIN to his instruments, I do not think the discrepancy can be attributed to instrumental error. Many more observations have since been made at Pulkovo, and the results will be awaited with interest. We shall also require observations at other stations before we can decide whether the effect is peculiar to Pulkovo or characteristic of

TABLE III.

Epicentral distance. $\Delta$ in kilometres.	For P.			For S. $e$ from time curve.
	$e$ from time curve.	$\bar{e}$ computed.	$\bar{e}$ observed at Pulkovo.	
0	0	22	—	0
500	11	23	—	12
1,000	21	27	—	22
1,500	30	32	—	30
2,000	37	37	—	37
2,500	44	42	48	43
3,000	49	47	44	49
3,500	53	52	43	54
4,000	57	54	42	57
4,500	60	58	43	60
5,000	63	60	44	62
5,500	65	62	46	63
6,000	65	62	48	63
6,500	65	63	51	63
7,000	65	63	54	64
7,500	66	63	58	64
8,000	66	64	62	65
8,500	67	64	65	65
9,000	67	65	67	66
9,500	68	66	68	67
10,000	69	67	70	67
10,500	70	67	71	68
11,000	70	68	72	69
11,500	71	69	72	70
12,000	72	70	73	71
12,500	73	71	73	72
13,000	74	72	74	73

the earth as a whole. The explanation will then have to be sought either in some structural peculiarity of the rocks composing the crust at Pulkovo or else in a modification of the general time curves. But until the required data are available we must be content with recording a discrepancy that requires further examination in the future.

The first impulse P which arrives by a path of minimum time must be regarded as the only part of a seismogram that arises from one definite cause. Immediately after P the seismogram is due to a variety of causes. Thus in discussing any subsequent pronounced effects that occur it is important to keep in view that they are superimposed on general disturbance which we do not for the moment seek to disentangle.

The relative magnitude of a reflected longitudinal disturbance  $PR_n$  that has been reflected  $n$  times at the surface to that of the first impulse P may be regarded as determined by two main circumstances: (1) As a disturbance proceeds outwards

from the focus it undergoes reduction of amplitude by spherical divergence and general scattering as the wave proceeds through the earth; (2) at each reflexion a sudden change of amplitude takes place.\* The first factor appears to be much too difficult to deal with at present. A tentative law of diminution of amplitude suggests itself, viz.,  $S^{-1}e^{-kS}$ , where  $S$  is the length of the path. The factor would then be  $\frac{S}{S_n}e^{-k(S_n-S)}$ . The numerical labour of testing this is rather serious, and from some rough trials I do not think it contains much promise of explaining the observations.

Accordingly, I pass to the second factor, which is within our powers and which goes a considerable way to explaining the facts. In so far as it fails it may give a clue to the proper form of the first factor.

Starting with epicentral distance  $\Delta$ , Table III. give the corresponding angle  $e$  and fig. 2 the values of  $H$  and  $V$  for the first impulse  $P$ . For  $PR_n$  we divide  $\Delta$  into  $(n+1)$  parts and obtain the value of  $e$  corresponding to  $\Delta/(n+1)$ . Fig. 2 then gives the corresponding values of  ${}_nA_2$ ,  $H_n$  and  $V_n$ . Thus the horizontal and vertical components of motion where  $PR_n$  meets the surface are  $({}_nA_2)^n H_n$  and  $({}_nA_2)^n V_n$ .

Table IV. shows the results obtained in this way for different distance  $\Delta$ , and between each column of magnitudes the time interval between the disturbances has

TABLE IV.

Epicentral distance $\Delta$ in kilometres.	P.	Time difference.	$PR_1$ .	Time difference.	$PR_2$ .	Time difference.	$PR_3$ .	Time difference.	$PR_4$ .
		seconds.		seconds.		seconds.		seconds.	
1,000	H	1.62	0.25	1	0.12	0	0.076	0	0.045
	V	0.83	0.086		0.047		0.031		0.021
2,000	H	1.60	0.084	3	0.018	1	0.0091	1	0.011
	V	1.20	0.043		0.0080		0.0039		0.0049
3,000	H	1.38	0.17	10	0.0044	4	0.00078	1	0.00040
	V	1.48	0.094		0.0022		0.00036		0.00018
6,000	H	0.93	0.59	55	0.067	25	0.0018	9	0.000023
	V	1.79	0.64		0.050		0.0011		0.000013
9,000	H	0.86	0.71	118	0.26	62	0.032	24	0.00094
	V	1.82	1.12		0.27		0.027		0.00065
12,000	H	0.68	0.70	182	0.42	106	0.11	68	0.014
	V	1.89	1.35		0.59		0.12		0.012

been inserted. It should be understood that for each distance the primary incident disturbance is taken as unity.

\* It may even be the case that disturbances travelling in different directions from the focus have different magnitudes.



Only the first four reflexions are computed, and even this is rather far for the short distances. The time curve is not sufficiently known for short distances and, moreover, the effect of finite depth of focus would come in.

We first note that successive reflexions differ in sign. The table shows that for distances up to 3000 km. the reflected effects are small in comparison with  $P$ , but as we pass to 6000 km.  $PR_1$  becomes about two-thirds of  $P$  in the horizontal component and about one-third in the vertical component. As we pass to 12,000 km.  $PR_1$  actually exceeds  $P$  in the horizontal component and is only somewhat less in the vertical component. Moreover, the second reflection, and even the third, are not insignificant.

The table also shows that when the reflected wave has angle  $e$  about  $20^\circ$  there is a large drop in the magnitude. As in the case of 2000 km., the successive reflexions show a tendency to increase for a certain range, although they must finally vanish. In this connexion I may refer to a point which I have elsewhere proved, viz., that longitudinal disturbance cannot be propagated along a plane surface. Prof. TURNER, 'B.A. Report,' 1915, remarks that this is in apparent conflict with KNOTT's result, that there is complete reflexion when  $e = 0$ . There is, however, no conflict, for although the reflected amplitude is then exactly equal to the incident amplitude, there is a change of sign, so that the two disturbances exactly annul and there is no resultant motion at all.

We turn now to the experimental evidence. Reflected waves have never been recognised as distinct features for  $\Delta$  less than 3000 km. I may, however, draw attention to two records ('Modern Seismology') of Turkish earthquakes  $\Delta$  about 2500 km. and a Pulkovo record of an Icelandic earthquake  $\Delta$  about 2500 km. (July 26, 1913). These all show somewhat similar disturbance within the 40 seconds succeeding  $P$ , and raise the question whether the whole series of reflexions which must occur within this time could have combined to affect the seismogram measurably.

When we reach  $\Delta$  from 6000 km. to 9000 km.,  $PR_1$  becomes a marked feature comparable with  $P$  itself, and  $PR_2$  only slightly less so, but  $PR_3$  and the succeeding reflexions are not clearly made out. Specimen records, figs. 4 and 5 (Plates 3 and 4), to which we shall return, exhibit this. Passing to  $\Delta$  from 10,000 km. to 12,000 km. we can usually trace the reflexions a little further, and  $PR_1$  may be two or even three times the magnitude of  $P$ .

Thus the numbers in Table IV. are in remarkably good general agreement with observation, showing how  $PR_1$  acquires increasing importance as  $\Delta$  increases. But although the table goes in the right direction it does not go far enough. It removes, however, the main difficulty in understanding the variations, and suggests the necessity of investigating reflexion from a variable layer instead of an ideal surface, and also of considering the effect of spherical divergence. The traces, figs. 4 and 5, are photographically reproduced from those issued by GALITZIN in 1914, but are

reduced to  $\frac{5}{8}$  original size. The lettering of the reflexion is the Pulkovo judgment, and I have added arrows to show the theoretical times.

We note how sharp P is in fig. 4 as compared with fig. 5.  $PR_1$  is a quite clear feature in both, although it arrives earlier than the theoretical time by 30 to 40 seconds. In fig. 4  $PR_1$  is still sharp in the horizontal components but smoother in the vertical. It is distinctly smaller than P and clearly of opposite sign. In fig. 5  $PR_1$  is smooth in all components, and only slightly less than P. In this case, also, it is of opposite sign to P. In fig. 4  $PR_2$  arrives about the theoretical time. It is smoother than P in all components, about the same magnitude as  $PR_1$ , and of the same sign as P. In fig. 5  $PR_2$  is apparently early, is about the same magnitude as  $PR_1$ , and I think of the same sign as  $PR_1$ . In fig. 4  $PR_3$  is about right as regards time, but is a somewhat vague movement, and  $PR_4$  is absent. In fig. 5  $PR_3$  and  $PR_4$  marked as earlier than the theoretical time are, in my opinion, too insignificant to merit consideration. Thus theory agrees in some respects and differs in others.

The appearance of P and its reflexions in fig. 5 is strongly suggestive of a limited train following an impulse, and the same may be said of  $PR_2$  and  $PR_3$  in fig. 4.

As we have shown, such an effect (established by LAMB for water waves) might be produced by dispersion or reflexion from a variable layer, my own view being that dispersion is not of much importance in seismology. On either hypothesis, however, a sharp impulse may on reflexion give rise to a limited train of periodic waves of distinctly larger amplitude than the primary impulse without violating the principle of energy. Everything depends on the sharpness with which the impulse rises to its maximum (*e.g.*, 1 second) and the number and period of the waves set up. Such an effect may be a contributing factor in the apparent magnitude of the reflexions as compared with P.

The discrepancy in time between  $PR_1$  and the theoretical value obtained from the time curve for P is not a mere accident in the two cases shown. A large number of others will be found in the Pulkovo 'Bulletins.' From an inspection of these it appears on average that at 6000 km.  $PR_1$  is some 10 seconds early, at 8000 km. about 30 seconds, at 10,000 km. it is correct, while at 12,000 km. it is about 10 seconds late.

In conjunction with GALITZIN'S observed values of the emergence angle  $\bar{e}$ , we get confirmation that the primary curve for P, as given by ZÖPPRITZ, requires revision. The change required is a depression of the ordinates of the time curve extending from 2000 km. to 6000 km. I mention this because, when the time curves are revised, I think it would be extremely unwise to make any alteration without considering the valuable information revealed by the times for the reflected waves and the apparent angle of emergence  $\bar{e}$  by direct measurement. The last members of the P reflexions, although I do not think they can really acquire any importance,

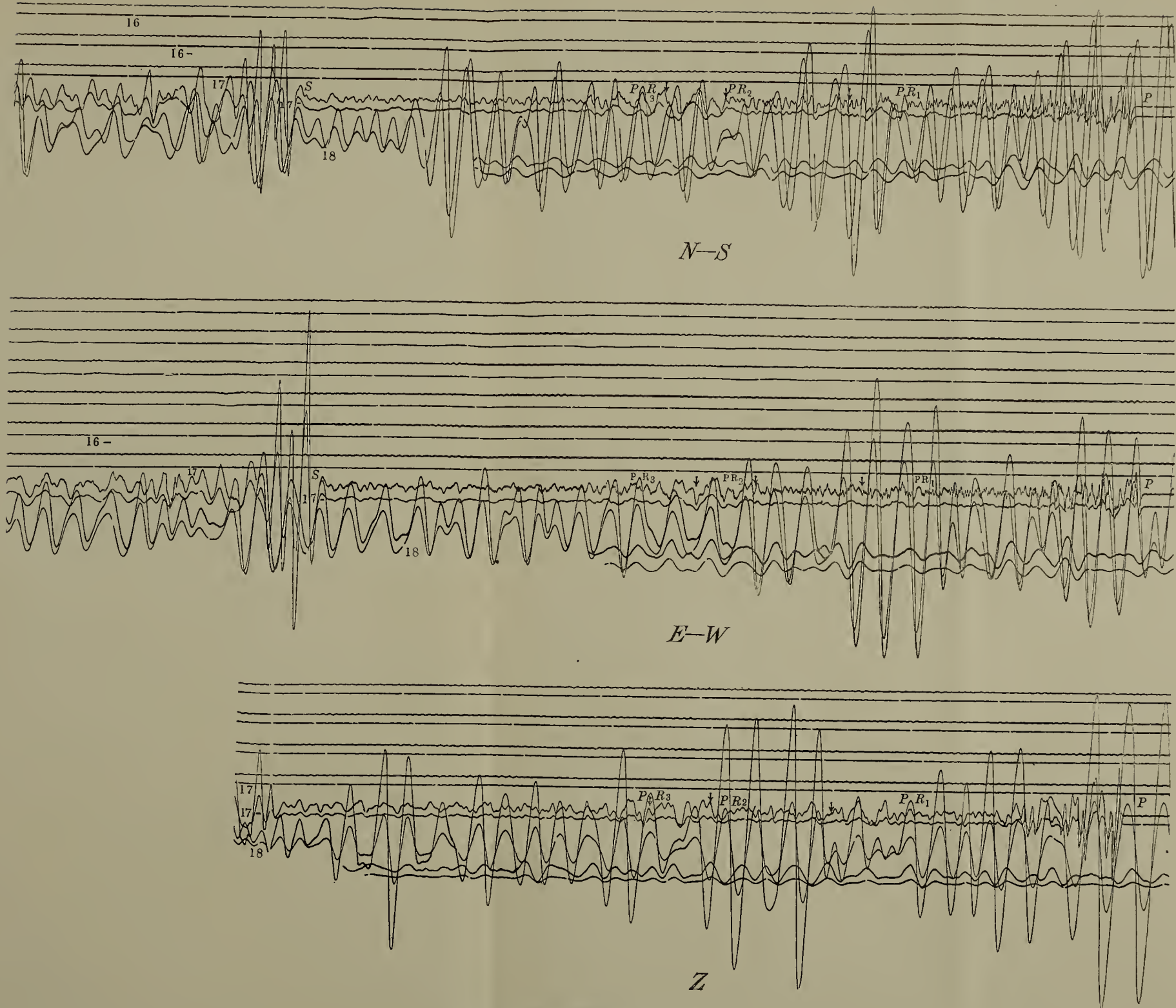


Fig. 4. Pulkovo seismogram, August 1, 1913.

Deduced epicentre— $\Delta = 7100$  km.,  $\phi = 47^\circ$  N.,  $\lambda = 155^\circ$  E.

NOTE.—Pulkovo recorded each component on two scales of magnification. Time breaks at one minute intervals.



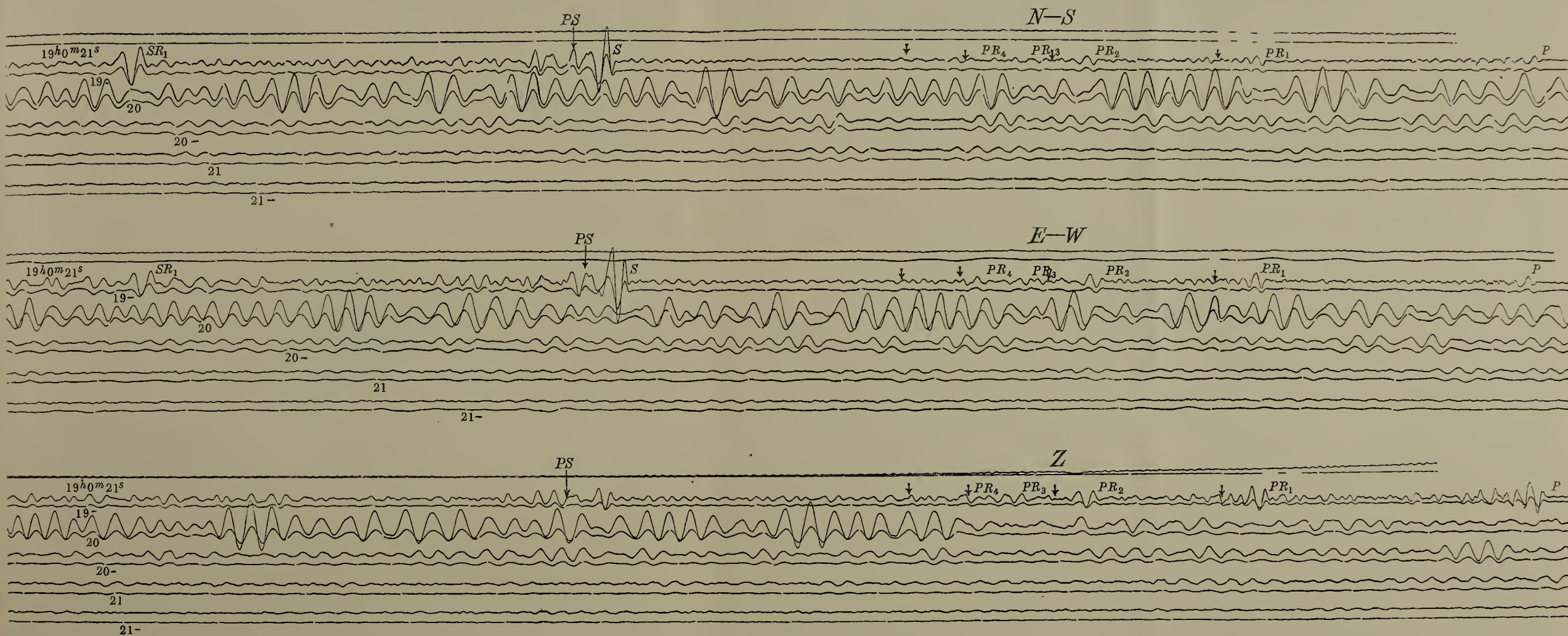


Fig. 5. Pulkovo seismogram, August 15, 1913.  
 Deduced epicentre— $\Delta = 8540$  km.,  $\phi = 27^\circ$  N.,  $\lambda = 142^\circ$  E.



arrive before S until  $\Delta$  is 11,000 km., but for  $\Delta$  11,500 km. and more they arrive after S (according to ZÖPPRITZ'S curve).

We now pass to consideration of the second phase. If we regard the start of the second phase S as representing the arrival of transversal waves we must resolve the disturbance into two: (1) transversal waves with direction of vibration at right angles to the plane containing the station, epicentre and earth's centre, which I will call the azimuth plane; (2) transversal waves with vibration in the azimuth plane.

For the waves vibrating at right angles to the azimuth plane, the vibration is entirely horizontal, there is no vertical component and the waves are reflected without change.

For the waves vibrating in the azimuth plane the matter is more complicated and depends on the angle of impingence. For angles up to  $56^\circ$ , *i.e.*, for  $\Delta$  about 4000 km., the reflexion is complex. There will be a reflected transversal wave, but it may differ in type from the incident disturbance. There is no true reflected longitudinal wave, but a disturbance confined to the surface exists. I think there is little doubt that this latter disturbance is an important factor in the generation of "Rayleigh" waves. Fig. 3 shows the "modulus" of the disturbance in dotted lines. We cannot speak of an angle of emergence for this region, but we note that the modulus of the reflected transversal wave remains constant and = 1 from  $e = 0^\circ$  up to  $e = 56^\circ$ . The horizontal motion modulus is 0 at  $e = 0^\circ$ , rises to a maximum at  $e = 22^\circ$ , and falls again to zero at  $e = 45^\circ$ , thereafter it rises rapidly to a value of 4.42 at  $e = 56^\circ$ . The vertical motion modulus, always greater in this range than that of H, reaches a maximum of 1.52 at  $e = 48^\circ$  and then falls to 0 at  $56^\circ$ .

As soon as we pass  $e = 56^\circ$  there is a longitudinal as well as a transversal reflected disturbance without change of type.  $A_2$  falls rapidly to 0.05 as  $e$  increases to  $58^\circ$ , and thereafter increases to 1 as  $e$  passes to  $90^\circ$ .  $A_3$  falls from 2.77 at  $e = 56^\circ$  to 0 at  $90^\circ$ . The horizontal movement falls from 4.42 at  $e = 56^\circ$  to about 1.8 at  $e = 63^\circ$  and recovers to 2 at  $e = 90^\circ$ . The vertical component rises to 0.92 at  $e = 60^\circ$  and then falls to 0 at  $e = 90^\circ$ . We may note that V is always less than H in this range, the least value of H/V being just under 2 at  $e = 63^\circ$ .

The very rapid change in value of V and H from  $e = 45^\circ$  to  $e = 65^\circ$ , or  $\Delta$  from 2500 km. to 5500 km., is most remarkable, and suggests the necessity for a very thorough examination of records for such distances.

S is often very far from sharp, and even in the cases where there is a sharp S, it rapidly develops into a highly periodic disturbance. A well-known feature is the comparatively small amount of vertical disturbance in S. We now find good reason for this.

Little has been done in analysing S from actual records, and our results show how difficult the matter is without the guiding information provided by the phenomena of reflexion. GALITZIN made some analyses of S in his book, but he assumed that the transversal wave arrived at the same angle as P. We have, however, a direct

means of examining this point by means of the vertical component. The following examples, taken from specimens published by GALITZIN, illustrate the matter:—

(1) Fig. 5. August 15, 1913.  $\alpha =$  azimuth  $= 58^{\circ} 37'$  N.E.  $\Delta = 8540$  km. Epicentre  $27^{\circ}$  N.,  $142^{\circ}$  E.

Second phase sharp in E.

Movement South  $= 0$ . East  $= 7.1$  mm. Vertical  $= 2.0$  mm.

Thus along  $\alpha$  we get  $6.1$  mm.  $\perp$  to  $\alpha$   $3.7$  mm. So that  $H/V = 3.0$ , and from the curve, fig. 3,  $e =$  about  $57^{\circ}$  (or  $73^{\circ}$ ).

(2) Fig. 4. August 1, 1913.  $\alpha = 38^{\circ} 24'$  N.E.  $\Delta = 7100$  km. Epicentre  $47^{\circ}$  N.,  $155^{\circ}$  E. Second phase sharp in E.

North  $= 3.0$  mm. West  $= 23.0$  mm. Vertical  $= 6.0$  mm.

Therefore along  $\alpha$  we get  $11.9$  mm.  $\perp$  to  $\alpha$   $19.9$  mm. Hence  $H/V = 2$ , or  $e$  about  $60^{\circ}$ .

(3) July 26, 1913.  $\alpha = 49^{\circ} 26'$  N.W.  $\Delta = 2490$  km. Epicentre  $67^{\circ}.5$  N.,  $18.6$  W.

Second phase sharp in E.

South  $= 9.5$  mm. West  $= 11.0$  mm. Vertical  $= 2.0$  mm.

Therefore along  $\alpha$   $2.2$  mm.  $\perp$  to  $\alpha$   $14.4$  mm. Therefore  $H/V = 1.1$ , or  $e$  is  $< 56^{\circ}$ , and, perhaps, about  $53^{\circ}$ .

(4) January 13, 1915.  $\alpha = 37^{\circ} 21'$  S.W.  $\Delta = 2280$  km. Epicentre  $42^{\circ} 0'$  N.,  $13^{\circ} 42'$  E.

Second phase sharp in E.

South  $= 15$  mm. West  $= 30$  mm. Vertical  $= 66$  mm.

Therefore along  $\alpha$   $30.1$  mm.  $\perp$  to  $\alpha$   $14.8$  mm.  $H/V$  about  $0.5$ . Therefore  $e$  is  $< 56^{\circ}$ , about  $50^{\circ}$ .

These cases are in general agreement with the results of reflexion theory and encourage further examination. Great care has to be exercised in getting precisely corresponding pure movements in all three components, as within even a few seconds the resultant vibration changes rapidly and the peaks do not precisely correspond in all components.

Case (1), fig. 5, illustrates this point very well. The first movement in S to East (which agrees precisely in time with the vertical motion up) reaches its maximum just as the North-south component begins to move. This second movement is first a little to South, then to North, the maximum throw to North coinciding in time with the maximum throw to West and the maximum throw down. Only a very open time scale shows this, and with a contracted scale we should probably have associated the first movements to East and to South together.

In case (1) the second movement of S, which follows the first movement immediately, is South  $= 3.5$  mm., West  $= 8.4$  mm., Vertical  $= 3.0$  mm. This gives



9.0 mm. along  $\alpha$  and 1.4 mm. at right angles to  $\alpha$  and  $H/V = 3$ , the same as in the first movement. The angle of impingence deduced is  $57^\circ$  or  $73^\circ$ , the ambiguity arising from the fact that in this region of reflexion  $H/V$  has the same value for two different angles. We cannot settle the ambiguity except by observations for different distances, and the fact that case (2) gives  $e$  close to  $60^\circ$  (the minimum value of  $H/V$  being about 2 at this point), suggests that the larger angle  $73^\circ$  is probably the right one. The value from the time curve is  $65^\circ$ , and the discrepancy is of importance. I consider the test by direct observation of the angle a very searching one, and likely to throw considerable light on the question of the accuracy of the time curves.

Passing to the reflexion of transversal waves  $SR_n$ , we have to observe that when the vibration is perpendicular to the azimuth plane no change is introduced by reflexion, so that such waves proceed as before. The vibration in the azimuth plane undergoes change in type for  $\Delta$  less than 4000 km., and at greater distances change of magnitude and change of sign. This introduces very profound changes in the character of the effects to be expected.

In Table V. I have calculated the relative magnitudes of S and  $SR_1$  to be expected on account of reflexion alone and for the waves vibrating in the azimuth plane.

TABLE V.

$\Delta$ in kilometres.	Vibration in azimuth plane. S.	Time interval in seconds.	$SR_1$ .
1,000 { H	0.52	4	0.46
{ V	1.0		0.79
2,000 { H	0.36	28	0.52
{ V	1.22		1.0
3,000 { H	0.50	71	0.48
{ V	1.52		1.1
4,000 { H	2.3	131	0.36
{ V	0.82		1.22
5,000 { H	1.8	197	0.16
{ V	0.92		1.36
6,000 { H	1.78	254	0.50
{ V	0.90		1.52
7,000 { H	1.78	298	1.62
{ V	0.88		0.76
8,000 { H	1.78	329	0.28
{ V	0.86		0.10
9,000 { H	1.80	354	0.13
{ V	0.84		0.06
10,000 { H	1.80	373	0.25
{ V	0.82		0.13
11,000 { H	1.83	397	0.32
{ V	0.76		0.16
12,000 { H	1.85	427	0.32
{ V	0.72		0.16

I have enclosed in thick lines the region within which the reflexion is complex and the result probably untrustworthy. I have used the values of  $e$  obtained from the time curve, so that the table is only of value in showing the large changes that may be expected. My hope is that the apparent complexity of the observed results will no longer discourage the investigator, but, on the contrary, will yield to careful treatment and lead to results of great value in seismological theory.

Case (1), fig. 5, is such a remarkably clear record and so free from ambiguity that I venture to add a discussion of the  $SR_1$  shown in it.  $SR_1$  is quite clear in the horizontal component, but practically negligible in the vertical component. We find, however, that  $SR_1$  is about 40 seconds earlier than the theoretical time calculated from the time curves. This is also what we found for  $PR_1$ . Thus while the time

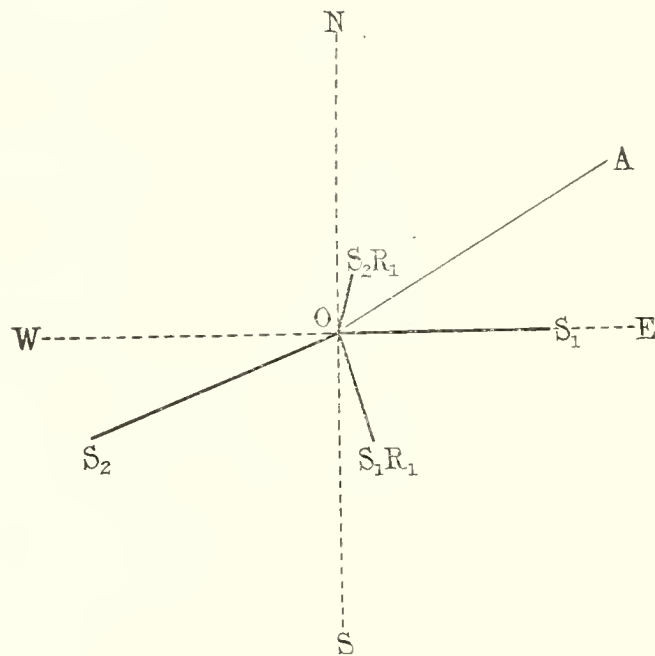


Fig. 6.

interval  $S-P$  is not sensibly in error, in my opinion at least, up to 10,000 km., I think that several independent lines of reasoning suggest that the time curves for  $P$  and  $S$  should be sensibly depressed from about 2500 km. up to 6000 km.

The first sharp movement is entirely to North, and this movement attains its maximum before the East-west component begins to move. We thus enquire whether this movement in  $SR_1$  is related quantitatively to any movement in  $S$ . Proceeding as formerly to ascertain the effects due to reflexion of waves which would otherwise produce the same results at the observation station, I have drawn in fig. 6 the conclusions at which we should arrive.

$OS_1$  and  $OS_2$  represent the first two movements in  $S$ , and  $OS_1R_1$ ,  $OS_2R_1$  are the corresponding effects to be expected in  $SR$ . They are obtained as follows: Resolve  $OS_1$  or  $OS_2$  into its components in and at right angles to the azimuth plane  $OA$ .

The former component suffers no reduction by reflexion, but the latter is altered. The amount depends on what are the correct impingence angles for S and SR. There is room for considerable latitude in this, but I have taken provisionally  $73^\circ$  for S and  $57^\circ$  for SR. With these values the component in the azimuth plane suffers reduction in the proportion 6.7 in H and 6.6 in V, and the sign is reversed. We thus get  $OS_1R_1$ ,  $OS_2R_1$  for the expected horizontal movement, while the vertical movement is very small indeed.

While the results are thus horizontal movements in the North-south component, they do not agree with the observed movement in SR.  $S_1R_1$  is of the opposite sign and  $S_2R_1$  is too small. While the result is perhaps disappointing, I am still convinced that, reasoning conversely, the systematic analysis of the observed movement of the SR for a number of cases is certain to lead to valuable information as to the circumstances of reflexion, even if it involves a change of our ideas as to the full meaning of these reflexions.

At considerable epicentral distances theory indicates that the general effect of reflexion is to suppress rapidly the component in the azimuth plane and make the  $SR_n$ 's more truly at right angles to the azimuth plane. But there is an important difference between these successive reflexions and the  $PR_n$ 's. These tail off to nothing, while the transversal waves, as soon as the reflexion takes place at angles less than  $56^\circ$ , may be expected to undergo a change of type rather than of magnitude. Thus the tail of the transversal waves merges into the start of the long wave phase as observation undoubtedly shows to be the case.

In my opinion the marked periodicity of the transverse reflexions indicates more clearly than do the longitudinal reflexions the necessity for examining the effects of reflexion from a variable layer of thickness comparable with the geological crust.

The present discussion would be incomplete without some reference to waves that have been changed from transversal to longitudinal, or *vice versa*, on reflexion. These waves were called *Wechselwellen* by WIECHERT. The vibration must be in the azimuth plane, and they cannot show as a distinct phenomenon until the distance exceeds that for which the angle of impingence for transversal waves in the azimuth plane exceeds  $56^\circ$ . From the time curves this would be about 4000 km., but GALITZIN'S direct observations of  $\bar{e}$  would make the distance over 7000 km.

These *Wechselwellen* must be made up of two parts: (1) transversal waves starting from the origin and reaching the station as longitudinal; (2) longitudinal waves starting from the origin and reaching the station as transversal. We should naturally seek to compare the first with the S waves and the second with the P waves, while there is no necessary connexion between the two except that they arrive together, and the vibration should be in the azimuth plane. It must, of course, be understood that in making any such comparisons we assume what is not at all likely to be the case, viz., that waves starting from the origin are symmetrical about the origin. We are, in fact, simply estimating the changes due to reflexion

without considering the other circumstances that may lead to differences in the relative magnitude of P and S and their reflexions.

We may best illustrate the possibilities by taking the theoretical case 8500 km., which corresponds closely to fig. 5. The theoretical angle of impingence is  $67^\circ$ , and we find that the PS or SP wave divides the arc so that the longitudinal waves correspond to 2000 km. angle  $e = 37^\circ$  and the transversal to 6500 km. angle  $e = 64^\circ$ , while PS arrives 40 seconds after S.

Taking unit amplitude in each case, we have the following relative values for H and V:—

	H.	V.
P . . . . .	-0.86	-1.82
PS . . . . .	+1.9	-0.94
S . . . . .	-1.8	+0.82
SP . . . . .	-1.4	-1.06

The signs are important. The absolute sign of V is determined by the actual record and may be + or - for either P or S. PS and SP theoretically arrive together and interfere, but it is likely that they may not coincide in time exactly in practice. However that may be, we see that large relative changes may be expected.

If V is of the same sign for P and S we might have a small V in the Wechselwellen and a large H, while if V is of opposite signs for P and S, the reverse holds. Theoretically, we have the means of separating the two constituents of this phenomenon by means of the vertical component record if the angles of impingence are known.

Thus if A and B are the proportions of PS and SP present at the station, we have

$$K_1A + K_2B = H, \quad K_3A - K_4B = V,$$

where H and V are observed at the station, and  $K_1 \dots K_4$  are known numerical factors depending only on the angles of impingence and independent of any other circumstance.

We may have a wave twice reflected, viz., PPS. In the present case it would divide the arc into two of 1500 km., corresponding to longitudinal waves  $e = 30^\circ$ , and one of 5500 km., corresponding to transversal waves  $e = 63^\circ$ . It should arrive 28 seconds after PS.

We might carry the argument to multiple reflexions until the arc corresponding to transversal waves is that for which  $e$  reaches the critical value  $56^\circ$ . Beyond this the argument must cease. Turning to the case fig. 5, we recognise disturbances following after S, but find it difficult to regard these as Wechselwellen because the

vibration is not in the azimuth plane. The clearest movement which satisfies this condition I have marked provisionally as PS. It is South 4.5 mm., West 7.0 mm., vertical 2.5 down. This gives azimuth  $57\frac{1}{2}^\circ$  N.E. instead of  $58\frac{1}{2}^\circ$  N.E. derived from P, which is really quite good agreement. Taking the theoretical angles of impingence, we get

$$-1.79A - 1.60B = -8.3 = -\sqrt{4^2 \cdot 5 + 7^2 \cdot 0},$$

$$+0.88A - 1.20B = 2.5,$$

whence  $A = 3.9$  mm.,  $B = 0.8$  mm., as the amplitudes of PS and SP at incidence at Pulkovo.

I am, however, doubtful about the movement, for while E and V are clear enough the N movement is conspicuously like the return of the seismograph to rest after an earlier excursion, and if so the assumption that this is PS is false.

From examination of a number of records for different distances, both from Pulkovo and Eskdalemuir, I am very much disposed to think that the Wechselwellen are not clearly separated from S until the distance exceeds 9000 km., and that at greater distances one is very apt to mistake them for S itself. Indeed I am convinced that I made the mistake myself. If this view is correct, it raises the question whether the marked periodicity which one associates with S at shorter distances is not really due to the Wechselwellen coming earlier than the present time curves would suggest.

In conclusion, it appears that quantitative analysis of reflexion theory on simple lines removes a number of difficulties that have hitherto attended interpretation of seismograms, and suggests that a systematic examination of both times and magnitudes of P, S, and at least PR, SR, and PS or SP, is likely to afford important information about the primary time curves. It is manifest that horizontal component seismographs alone are quite inadequate.

So far as the present investigation fails to resolve all the difficulties, it suggests the proper lines of further investigation.

These are (1) investigation of the reflexion of waves from a variable layer of thickness comparable with that of the earth's crust; (2) investigation of the propagation of an impulse from a disturbed centre into the earth, in order to gain some idea of the relative magnitude of disturbance in different directions and at different distances. The results even for a uniform earth would be a valuable guide towards the law of absorption of waves, for the determination of which material undoubtedly exists in the observed magnitude of reflected waves.

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Received February 2,—Read February 21, 1918.

THE investigation of the crystals of the four salts of the series  $R_2M(SeO_4)_2 \cdot 6H_2O$ , in which M is ferrous iron, and R is potassium, rubidium, caesium, and ammonium, has at last been successfully and completely accomplished, both morphologically and optically, and the results are presented in this communication. The difficulties which have delayed it are described in a separate memoir, read at the same meeting of the Royal Society and published in the 'Proceedings,'\* together with details of the manner in which these difficulties have been overcome.

The main obstacles were (1) the difficulty of preparing ferrous selenate  $FeSeO_4$ , a salt very much less stable than ferrous sulphate  $FeSO_4$ ; (2) the ready oxidation of its solution in water and of the solutions of the double selenates obtained by the addition of the calculated quantity of the alkali selenate, and (3) the especial difficulty underlying the formation of potassium ferrous selenate, and the fact that even when formed the crystals of this salt decompose and become opaque like porcelain within a very few hours.

There is no record of rubidium or caesium ferrous selenates having ever been previously either prepared or investigated, crystallographically or physically. Ammonium ferrous selenate was prepared by H. TOPSØE,† and its goniometry and a density determination were described by him in his 1870 dissertation; its optics were also to a very limited extent described by him in conjunction with C. CHRISTIANSEN, in their well-known memoir of 1874. Potassium ferrous selenate offered such insuperable difficulties, however, that TOPSØE was only able to obtain four approximate measurements of exterior angles, and no attempt at a density determination was made; for, as he states in his 1870 dissertation, he found that the crystals which he obtained decomposed immediately after their removal from the mother liquor. The salt was consequently never able to be handed over to Prof. CHRISTIANSEN‡ for optical investigation, and is entirely omitted from their joint 1874 memoir.

\* 'Roy. Soc. Proc.,' A, vol. 94, p. 352 (1918).

† 'Krystallogr.-kem. Unders. over de selensure Salte,' Copenhagen, 1870.

‡ 'Ann. Chim. Phys.,' series 5, vol. 1, p. 1 (1874). It is with great regret that the author learns of the death of Prof. CHRISTIANSEN on December 28, 1917.

It has been shown in the separate memoir on the chemistry of these double selenates that a successful and ready method of preparing ferrous selenate in solution, which automatically preserves it in the ferrous condition by retarding oxidation by atmospheric oxygen, is afforded by acting on pure ferrous sulphide in the cold with moderately dilute selenic acid. The especial difficulty of obtaining potassium ferrous selenate from the filtered solution of ferrous selenate, after admixture with the equal molecular proportion of potassium selenate in fairly concentrated solution, has been overcome by making the preparations in the coldest winter weather, the crystals successfully obtained having all been deposited during the four coldest nights of early January, 1918, which were distinguished on Dartmoor for their exceptionally low temperature. The crystallisation occurred in a partial vacuum over oil of vitriol, under the receiver of an air pump. The goniometry and optics were carried through on the succeeding day, immediately after removal from the mother liquor, in each case, during the four or five hours of the transparent life of the crystals and in a very cold room without fire or other artificial heating.

*Potassium Ferrous Selenate*  $K_2Fe(SeO_4)_2 \cdot 6H_2O$ .

The four crops of beautifully clear, transparent, pale green crystals obtained of this remarkable salt were produced during four very cold nights in the manner just described, and given in more detail in the 'Proceedings' memoir on the chemistry of the group (p. 360). They were derived from three separate preparations, only one of which yielded a second crop on the next, also very cold, night. The temperature of the laboratory on all four nights was only just a fraction of a degree above  $0^\circ C.$ , there being from  $8^\circ C.$  to  $10^\circ C.$  of frost outside. Further crops from these preparations, after filtering from oxidised ferric products, and all those derived from the numerous other preparations made in cold, but not such extremely cold, weather, consisted only of very minute crystals, quite unsuitable for goniometrical examination, which corresponded with those which TOPSØE states are produced at ordinary temperatures on moderately mild or warm days, and which he describes as having the composition  $K_2Fe(SeO_4)_2 \cdot 2H_2O$  and as being of probably triclinic symmetry.

According to TOPSØE the decomposition of the crystals of the hexahydrated salt is due to their conversion into this dihydrated salt at a temperature but a few degrees above the freezing point of water. Confirmatory evidence of this will be afforded when the density is discussed, as the author found that the density rises continuously and quite markedly during every half-hour of the life of the crystals after decomposition once starts.

There is no doubt that this potassium salt of the iron group is unstable for the reason that in the regular descent in stability, which the author has shown to be general for all the groups of salts of this hexahydrated series (including the double sulphates), from the caesium salt through the rubidium salt to the potassium salt, the

limit of existence is actually attained in the iron group when the potassium salt is reached, at a temperature which is but very slightly above  $0^{\circ}$  C.

By intensive work on the four cold days succeeding the very cold nights in question—commencing early in the morning, immediately after removing the crystals from their mother liquor and drying them with a soft handkerchief—and by keeping the room cold, it has been found possible to measure completely (1) the whole of the exterior angles of six crystals; (2) to determine the density of a considerable number; (3) to measure the extinction angles and (4) the optic axial angles, and (5) to determine all three refractive indices directly, for the usual range of the seven wavelengths of light employed by the author. The only observations, of the author's usual scheme of work, which have not been possible with this salt are those carried out at higher temperatures, which are obviously out of the question with a salt of such extreme instability at temperatures even somewhat lower than the ordinary. At  $20^{\circ}$  C. to  $30^{\circ}$  C. decomposition is immediate, and even when working in an unpleasantly cold room the life of the crystals does not extend to a second day, even if they be covered by an inert liquid such as benzene, a device which, however, does somewhat prolong their existence, possibly by a couple of hours. On the second day the crystals were as opaque as plaster of Paris. One crystal employed, however, which was of tabular form and mounted between truly plane glass plates in a quickly drying medium of very hard Canada balsam dissolved in benzene, in a manner which entirely enveloped the crystal (all the rest of the air film between the two glass plates being filled up by the balsam) remained transparent for nearly a week. Other attempts at such preservation have not, however, succeeded. Thus 5 to 6 hours' time was the usual limit for work on any crop of crystals. To leave any particular crystal in the mother liquor until ready for work with it proved useless, for the edges became rounded as the temperature of the room inevitably rose slightly during the advance of the morning. The actual temperature of the laboratory, however, never rose above  $6^{\circ}$  C. during all the measurements and determinations, except during the density determinations, when absolutely fresh crystals were employed, surrounded by the usual mixture of methylene iodide and benzene, which preserved them completely free from decomposition during the short time which the Retgers immersion method demands. This work now described would obviously have been quite impossible in summer.

The grinding of section-plates and prisms was avoided as far as possible, because ground surfaces become opaque from decomposition with great rapidity. Special optical methods were employed for most of the work, the crystals being immersed in an inert liquid, cedar oil, which most fortunately happens to possess almost the same refractive index as the mean index of the crystals  $\frac{1}{3}(\alpha + \beta + \gamma)$ , and likewise a very similar dispersion. But the results, although there could thus be no doubt of their accuracy, were confirmed on the last of the four days by the successful grinding of a sufficiently transparent  $60^{\circ}$ -prism from one of the larger crystals obtained, so orientated as to afford direct values for the indices  $\alpha$  and  $\gamma$ , and by the accomplishment

of the determination of these indices therewith before opacity supervened (which occurred within a further hour). The values obtained from this ground prism proved to confirm fully the results previously obtained, and as the third (intermediate) index of refraction  $\beta$  had been afforded twice over absolutely directly by two natural prisms employed, the whole of the optical constants were thus ascertained in a manner which rendered them fully trustworthy.

### Morphology.

*Crystal System.*—Monoclinic. Class No. 5, holohedral-prismatic.

*Ratios of Axes.*—

$a : b : c = 0.7490 : 1 : 0.5044$ . TOPSØE'S approximate values  $0.7407 : 1 : 0.5007$ .

*Axial Angle.*— $\beta = 103^\circ 50'$ . Approximate value of TOPSØE,  $104^\circ 15'$ .

*Forms Observed.*— $a \{100\}$ ,  $b \{010\}$ ,  $c \{001\}$ ,  $p \{110\}$ ,  $p' \{120\}$ ,  $q \{011\}$ ,  $r' \{\bar{2}01\}$ ,  $o' \{\bar{1}11\}$ , and  $n' \{\bar{1}21\}$ . The forms  $a \{100\}$  and  $p' \{120\}$  were not observed by TOPSØE.

*Habit.*—More or less tabular parallel to  $c \{001\}$ , fig. 1, to short prismatic parallel to  $p \{110\}$ , occasionally with especial elongation of one parallel pair of the  $p$ -prism faces only (fig. 2).

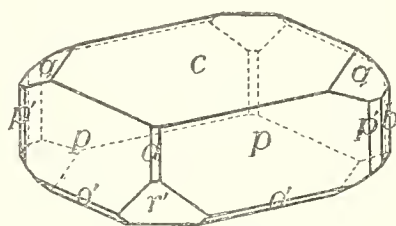


Fig. 1.

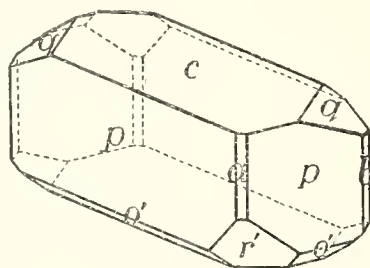


Fig. 2.

The great majority of the crystals obtained were of the tabular type illustrated in fig. 1, and this type proved very useful in the optical work, as the bisectrix of the obtuse angle between the optic axes is nearly identical with the normal to the plate, which latter is parallel to the faces of the basal plane  $c \{001\}$ . The type shown in fig. 2 was represented by one of the finest and largest crystals obtained. In all the crystals the  $c$ -faces and  $p$ -faces predominated, usually the former to the greatest extent. The  $q$ -faces were, as with all the potassium salts of the series, small. The  $r'$ -faces were generally rather large, and sometimes were very prominent indeed, a fact which has been observed to be characteristic of the iron groups of both the double sulphates and double selenates. Three good measurements were obtained from little  $\alpha$ -faces, of a narrow type but excellently reflecting. The faces of  $b \{010\}$ ,  $o' \{\bar{1}11\}$ , and  $n' \{\bar{1}21\}$  were only very minute (usually almost imperceptible lines), and afforded no adequate reflections of the signal. Several little  $p'$ -faces were observed, however, and in two cases good measurements were obtained.

The table of angles is given on the next page, and it is a somewhat surprisingly satisfactory one, considering the circumstances under which these six crystals had to be measured.

INTERFACIAL Angles of Potassium Ferrous Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$ac = (100) : (001)$	3	76 2- 76 16	76 8	76 10	2
$as = (100) : (101)$	—	—	—	46 46	—
$sc = (101) : (001)$	—	—	—	29 24	—
$cr' = (001) : (201)$	11	62 43- 63 1	62 47	62 38	9
$cs' = (001) : (\bar{1}01)$	—	—	—	37 58	—
$s'r' = (\bar{1}01) : (201)$	—	—	—	24 40	—
$r'a = (201) : (\bar{1}00)$	1	—	41 11	41 12	1
$r'c = (201) : (00\bar{1})$	10	117 0-117 30	117 13	117 22	9
$ap = (100) : (110)$	12	35 40- 36 11	36 1	36 1	0
$pp' = (110) : (120)$	2	19 15- 19 34	19 25	19 28	3
$p'b = (120) : (010)$	—	—	—	34 31	—
$pp'' = (110) : (130)$	—	—	—	29 21	—
$p''b = (130) : (010)$	—	—	—	24 38	—
$pb = (110) : (010)$	—	—	—	53 59	—
$pp = (110) : (\bar{1}\bar{1}0)$	9	71 31- 72 21	72 2	*	—
$pp = (110) : (\bar{1}\bar{1}0)$	9	107 39-108 18	107 58	107 58	0
$cq = (001) : (011)$	20	25 45- 26 26	26 6	*	—
$qb = (011) : (010)$	—	—	—	63 54	—
$qq = (011) : (01\bar{1})$	8	127 19-128 27	127 49	127 48	1
$ao = (100) : (111)$	—	—	—	49 59	—
$oq = (111) : (011)$	—	—	—	27 37	—
$aq = (100) : (011)$	—	—	—	77 36	—
$qo' = (011) : (\bar{1}\bar{1}1)$	—	—	—	34 12	—
$o'a = (\bar{1}\bar{1}1) : (\bar{1}00)$	—	—	—	68 12	—
$co = (001) : (111)$	—	—	—	35 9	—
$op = (111) : (110)$	—	—	—	43 42	—
$cp = (001) : (110)$	14	78 44- 79 8	78 51	*	—
$po' = (110) : (11\bar{1})$	—	—	—	56 54	—
$o'e = (11\bar{1}) : (00\bar{1})$	—	—	—	44 15	—
$pe = (110) : (00\bar{1})$	14	100 52-101 30	101 9	101 9	0
$bn = (010) : (121)$	—	—	—	53 41	—
$no = (121) : (111)$	—	—	—	16 8	—
$bo = (010) : (111)$	—	—	—	69 49	—
$os = (111) : (101)$	—	—	—	20 11	—
$bo' = (010) : (\bar{1}\bar{1}1)$	—	—	—	65 17	—
$o's' = (\bar{1}\bar{1}1) : (\bar{1}01)$	—	—	—	24 43	—
$o'o' = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}\bar{1})$	—	—	—	49 26	—
$sq = (101) : (011)$	—	—	—	38 31	—
$qp = (011) : (\bar{1}\bar{1}0)$	13	84 57- 85 27	85 12	85 8	4
$ps = (110) : (\bar{1}0\bar{1})$	—	—	—	56 21	—
$pq = (\bar{1}\bar{1}0) : (0\bar{1}\bar{1})$	14	94 21- 95 8	94 47	94 52	5
$s'q = (\bar{1}01) : (011)$	—	—	—	44 55	—
$qn = (011) : (121)$	—	—	—	27 1	—
$np = (121) : (110)$	—	—	—	37 22	—
$qp = (011) : (110)$	9	64 2- 64 41	64 23	64 23	0
$ps' = (110) : (10\bar{1})$	—	—	—	70 42	—
$pq = (110) : (0\bar{1}\bar{1})$	9	115 19-116 7	115 37	115 37	0
$r'o' = (201) : (\bar{1}\bar{1}\bar{1})$	—	—	—	34 22	—
$o'p = (\bar{1}\bar{1}\bar{1}) : (110)$	—	—	—	93 7	—
$pr' = (110) : (20\bar{1})$	4	52 22- 52 32	52 29	52 31	2
$r'p = (201) : (110)$	4	127 28-127 38	127 31	127 29	2
Total number of measurements .	166				

The forms given in the list other than  $a$  and  $p$  are the same as were observed by TOPSOE. The only four angular measurements which he obtained were as follows:— $pp = (110):(1\bar{1}0) = 71^\circ 21'$ ,  $cp = (001):(\bar{1}10) = 101^\circ 32'$ ,  $cr' = (001):(\bar{2}01) = 63^\circ 1'$ , and  $pq = (\bar{1}10):(011) = 85^\circ 30'$ , all of which he states were only approximate, owing to the crystals becoming dull and decomposed immediately after removal from the mother liquor. They differ considerably from the accurate values now obtained.

*Cleavage.*—It was not possible to determine the cleavage with accuracy, on account of the rapid decomposition of cleaved surfaces, but it would appear that the usual cleavage parallel  $r' \{ \bar{2}01 \}$ , developed throughout the series, is also shared by potassium ferrous selenate.

#### *Volume.*

*Relative Density.*—The following results were obtained in six determinations by the Retgers immersion method. The first four were with crystals belonging to one crop, and were carried out immediately after removal from the mother liquor and careful drying with a soft handkerchief; the last two were carried out on another day, with another of the crops, the crystals used being also transferred directly from the mother liquor to the immersion liquid, after a few moments occupied in the drying with a handkerchief. The results are seen to be eminently concordant. A different room was employed for the work of making the liquid of exactly the same density as the crystal, the temperature of which was higher than that of the laboratory; for it is inadvisable to work at a temperature much more than  $5^\circ$  below  $20^\circ$  C. (the standard temperature of all the author's density comparisons), on account of the large magnitude of the correction for the coefficient of expansion of the crystals which is then involved. The crystals were not at all adversely affected during the rapid work at the temperature of  $13^\circ - 15^\circ$ , as they were immersed in the heavy protective liquid, being quite as transparent at the finish as when immersed, and several of them were employed immediately afterwards in the goniometrical work.

I.	Density for $13^\circ 0/4^\circ$	. . .	2.4931	For $20^\circ/4^\circ$	. . .	2.4914	}	Mean		
II.	„	$15^\circ 0/4^\circ$	. . .	2.4944	„	$20^\circ/4^\circ$			. . .	2.4932
III.	„	$13^\circ 3/4^\circ$	. . .	2.4930	„	$20^\circ/4^\circ$			. . .	2.4913
IV.	„	$14^\circ 4/4^\circ$	. . .	2.4939	„	$20^\circ/4^\circ$			. . .	2.4925
V.	„	$13^\circ 6/4^\circ$	. . .	2.4955	„	$20^\circ/4^\circ$	. . .	2.4939	}	2.4941
VI.	„	$15^\circ 4/4^\circ$	. . .	2.4953	„	$20^\circ/4^\circ$	. . .	2.4942		
Mean . . .								2.4928		

As it is probable that the higher mean value for the second of the two different preparations is nearer the truth for cavity-free crystals, the value accepted for  $20^\circ/4^\circ$  is 2.494.

*Molecular Volume.*— $\frac{M}{d} = \frac{524.72}{2.494} = 210.39.$

*Molecular Distance Ratios (topic axial ratios).*—

$$\chi : \psi : \omega = 6.2230 : 8.3085 : 4.1908.$$



In addition to the above determinations of density with clear, transparent, absolutely fresh crystals, a number of further determinations were made with crystals in the act of decomposing, employing some that were only just showing the first signs when placed in the immersion liquid, and continuing with the same crystals, a fresh determination of their density being made each half-hour. The temperatures of the liquid only varied from  $13^{\circ}7$  to  $14^{\circ}5$ , and the results for  $20^{\circ}/4^{\circ}$  of seven successive determinations at the half-hour intervals were 2.5211, 2.5238, 2.5296, 2.5442, 2.5551, 2.5622, and 2.5726. It is thus obvious that the crystals became denser as decomposition proceeded. This would appear to agree with the conclusion of TOPSØE that the monoclinic crystals of the hexahydrated salt  $\text{K}_2\text{Fe}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ , which are only stable up to a temperature but slightly above  $0^{\circ}\text{C}$ ., break down at ordinary temperatures into microscopic triclinic crystals of the dihydrated salt  $\text{K}_2\text{Fe}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

#### *Optics.*

The author's usual procedure—including the grinding of two section-plates parallel to the symmetry plane for extinction determinations of six section-plates (three perpendicular to each of the two median lines) for optic axial angle measurements, and of six  $60^{\circ}$ -prisms for refractive index determinations—was not possible with this unstable salt. As already mentioned, only four crops of the crystals were obtained, and the life of any one crystal was not more than six hours, after which it had usually become hopelessly opaque from decomposition. Hence, very rapid methods of work and avoidance of the grinding of many surfaces (which become much more rapidly opaque than natural ones) were essential, for the time lost in grinding a plate or prism, which when finished was useless, could much more profitably be spent in making confirmatory measurements with other natural crystals.

All the optical work, therefore, was carried out with three natural plates, tabular crystals parallel to the basal plane  $c\{001\}$ , two natural prisms formed by a pair of  $p$ -faces (inclined at  $72^{\circ}2'$ ) and a pair of  $q$ -faces (inclined at  $52^{\circ}12'$ ), and one ground prism (of  $60^{\circ}$ ) only, the latter from the largest of the crystals obtained and ground accurately to afford the  $\alpha$  and  $\gamma$  indices, the grinding of which was fortunately accomplished and the measurements obtained with it just before opacity supervened.

Each of the three crystal plates was mounted with hard balsam in benzene on a truly plane glass plate (one of the circular ones a centimetre diameter provided with the cutting and grinding goniometer) and covered with a small piece of thin cover glass, the crystal being completely protected by the balsam and its life thereby lengthened by an hour or two (in one exceptional case longer). Each crystal plate was rhombus-shaped (see fig. 1), the four  $p$ -faces being the main rhombus-determining edge faces. It was suspended by its circular glass mount-plate truly vertically from the adjusting apparatus of the polariscopical goniometer, so that the shorter diagonal of the rhombus (from front to back in fig. 1), the trace of the symmetry plane  $b\{010\}$ , was horizontal; it was also adjusted so that the centre of the rhombus-like  $c$ -face was in the optical axis

of the polariscope. On raising into position the cell containing the immersion liquid, cedar oil, of similar refractive index ( $\mu = 1.5102$  for Na-light) to the mean index of the crystals,\* so that the crystal occupied the centre of the cell, and then rotating the goniometer circle (with the crystal-carrying axis rigidly fixed to it) first on one side and then on the other, the optic axial interference figure was seen, with the optic axes separated at their true obtuse angle, the more accurately true the more nearly identical the refractive indices of the liquid and the crystal. For *the plane of the optic axes is the symmetry plane*  $b\{010\}$ , which had been horizontally adjusted; and the second median line, the obtuse bisectrix and axis  $\alpha$  of the optical indicatrix as *the sign of the double refraction is positive*, is very nearly perpendicular to the basal plane  $c\{001\}$ , the plane of the crystal plate.

Three different constants were then determinable:—(1) the exact position of the second median line with reference to the normal to the basal plane  $c\{001\}$ , which is the same as the normal to the glass mount-plate, for the circle reading for this normal could be directly observed; (2) the true acute optic axial angle  $2V_a$ , for this is the supplement of the true obtuse angle  $2V_o$ , directly measurable, and is indeed itself directly measurable by further rotation of the circle; (3) the dispersion of the median lines. The course of these operations was as follows.

The crystal plate was first adjusted so that the plane of the plate and of its mount-plate was approximately truly vertical, parallel to the goniometer axis, and the circle reading of the polariscopical goniometer was determined for the position when the plane of the plate was exactly normal to the axis of the polariscope, the crystal-holder and the steel axis carrying it and its adjustments being locked immovably to the circle axis. This adjustment of the plate to normality was rendered readily possible by use of the Becker transparent mirror-and-lens fitting, described on p. 34 and illustrated in fig. 13 of the author's "Crystallography and Practical Crystal Measurement" (Macmillan), the fitting being placed close up in front of the analysing Nicol of the polariscope. This combination, of a glass plate transparent mirror arranged at  $45^\circ$  and a lens fitted in an elbow side-tube, permitted the light from a goniometer electric lamp (provided with a copper cylindrical shade perforated by a suitable circular aperture and arranged to one side of the goniometer) to be reflected along the axis of the analysing tube of the polariscope to the glass mount-plate (the crystal being behind the plate during these operations), from which it was reflected back again to the Becker fitting, and passed through the transparent mirror and the small observing aperture in the front of the fitting to the observer's eye. The images of the cross spider-lines of the analysing tube, a parallel pair of vertical lines and a single horizontal line, could be plainly seen with the aid of this fitting,

\* It was possible to forecast with considerable accuracy the optical constants of this salt from the general principles already established for the relations of the three alkali-metallic salts of each group. To be adequately certain as regards the refractive index, one of the two natural prisms was used for a determination of the intermediate index  $\beta$  before proceeding with the plates, as will be described later.

reflected from the mount-plate, and they were readily brought by slight rotation of the circle and plate to coincidence with the spider-lines seen directly, any slight vertical displacement being readily corrected with the aid of the appropriate (back to front) movable segment of the crystal-adjusting apparatus. When the adjustment to coincidence was perfect the reading of the circle was taken, this reading then corresponding to the identity of the normal to the plate and to the crystal face  $c\{001\}$  with the axis of the polariscope. The cell containing the immersion liquid, cedar oil, was then raised into position so that the crystal occupied its centre. The crystal plate was next adjusted, by slight rotation in its own plane, using white light, so that the optic axial plane  $b\{010\}$ , the symmetry plane, was strictly horizontal if not already so adjusted. This was effected by viewing and adjusting the interference figure in convergent polarised light (the Nicols being crossed at  $45^\circ$  and  $135^\circ$ ); the correct position was attained when the optic axial "eyes" (the very small innermost rings and sharp vertices of the hyperbolic brushes) to the right and left of the normal position, as the circle was rotated, first one way and then the other, moved exactly along the horizontal cross-spider-line, by which they were bisected. The conditions were then attained for the measurement of the optic axial angle for the usual series of six wave-lengths of light, the crystal plate remaining locked to the circle throughout the measurements. These measurements were then carried out with the aid of the spectroscopic monochromatic illuminator, the vertices of the optic "eyes" being brought to the centre of the pair of vertical spider-lines for each wave-length in turn. Not only were readings for each of the two "eyes" to right and left of the normal taken, but also the readings for the other two optic "eyes" observed on rotating through the whole circle. By this means duplicate readings  $180^\circ$  apart were obtained for both the obtuse and acute true optic axial angles  $2V_o$  and  $2V_a$ , the plate being immersed in a liquid of similar index of refraction and consequently affording not merely an apparent angle in oil but the real optic axial angle within the crystal. For as the plate was rotated through a complete circle four optic eyes were met with in succession, each at its correct position as within the crystal. The mean (half-way) positions  $90^\circ$  apart for any one colour of light were those of the two median lines, perpendicular to each other, the axes  $\alpha$  and  $\gamma$  of the optical indicatrix. The procedure will be rendered clear from the following record of the observations with Plate 1; fig. 3 will also assist in elucidating the arrangements, A representing the crystal and B the glass mount-plate,

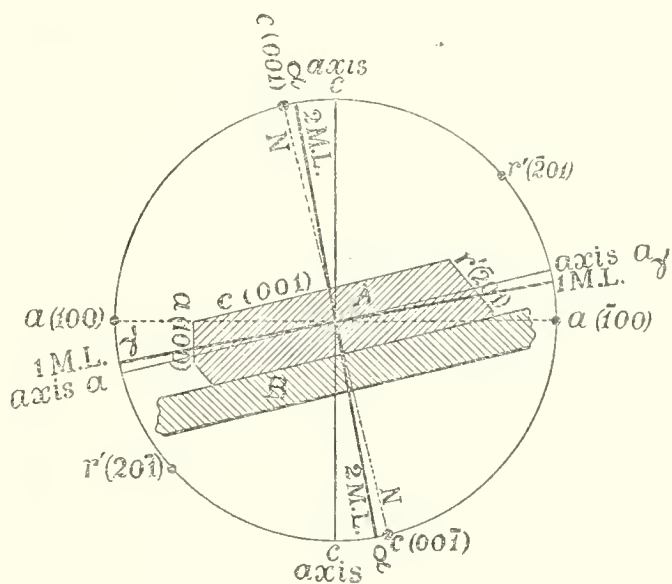


Fig. 3.

The mean (half-way) positions  $90^\circ$  apart for any one colour of light were those of the two median lines, perpendicular to each other, the axes  $\alpha$  and  $\gamma$  of the optical indicatrix. The procedure will be rendered clear from the following record of the observations with Plate 1; fig. 3 will also assist in elucidating the arrangements, A representing the crystal and B the glass mount-plate,

*Crystal Plate 1, Parallel c {001}.*

Circle reading for normal (N in fig. 3) to  $c(001)$ , determined by coincidence of spider-lines with their own reflections . . .  $214^{\circ} 18'$ .

## PLATE Arranged with Crystal Behind (as in fig. 3).

Light.	Observed left vertex.	Calculated 2 M.L.*	Observed right vertex.	$2V_o$ .
Li . . . . .	276 1	217 36	159 11	116 50
C . . . . .	276 0	217 35.5	159 11	116 49
Na . . . . .	275 59	217 37	159 15	116 44
Tl . . . . .	275 58	217 37.5	159 17	116 41
Cd . . . . .	275 57	217 38.5	159 20	116 37
F . . . . .	275 55	217 39.5	159 24	116 31
Dispersion (Li ~ F) .	0 6	0 3.5	0 13	

\* The midway position between the observed left and right vertex readings.

## PLATE Arranged with Crystal in Front.

Light.	Observed left vertex.	Calculated 2 M.L.	Observed right vertex.	$2V_o$ .
Li . . . . .	96 3	37 38	339 13	116 50
C . . . . .	96 3	37 38.5	339 14	116 49
Na . . . . .	96 2	37 41.5	339 21	116 41
Tl . . . . .	96 0	37 43.5	339 27	116 33
Cd . . . . .	95 57	37 43	339 29	116 28
F . . . . .	95 55	37 42.5	339 30	116 25
Dispersion (Li ~ F) .	0 8	0 4.5	0 17	

Light.	Mean $2V_o$ .	Mean $2V_a$ .	Mean 2 M.L.
Li . . . . .	116 50	63 10	217 37
C . . . . .	116 49	63 11	217 37
Na . . . . .	116 43	63 17	217 39
Tl . . . . .	116 37	63 23	217 40
Cd . . . . .	116 33	63 27	217 41
F . . . . .	116 28	63 32	217 41
Dispersion (Li ~ F) . . . .			0 4

The extreme readings, for red Li and greenish blue F light, were repeated and confirmed several times, and the fact definitely established that the optic axis emerging to the left of the normal to the plate was dispersed  $7'$  (within the error of experiment, which even with the beautifully small innermost rings and very sharp hyperbolic vertices obtained amounts to possibly  $2'$ ), while the right-hand optic axis was dispersed double this amount,  $15'$ . That the extreme outside reading in each case (the highest on the left and the lowest on the right) was for red was clearly apparent, and was confirmed by the colours bordering the vertices when seen in white light, the inner margins of both being tinted red, and the left one more faintly than the right. Hence, it can be accepted with confidence that the second median line was dispersed to the extent of  $\frac{15'-7'}{2}$ , that is  $4'$ . This is also clearly shown by the mean readings for the position of the second median line, given in the last column at the foot of the table, the difference between these mean readings for Li and F light being  $4'$ . The  $2'$  possible error in the readings of the positions for the right and left vertices for any one wave-length is eliminated in taking this mean value, and also the mean of the two separate sets of observations (crystal behind and crystal in front of the mount plate),  $3'5$  and  $4'5$ , is also obviously  $4'$ . Hence, the amount of the dispersion of the median lines is undoubtedly  $4'$ , with a possible error of only one minute on each side.

In mounting the crystal on the glass plate great care was taken to observe the orientation of the crystal, as regards particularly the direction of the little strip-face of  $a$  (100) replacing the  $pp$  edge, and that of the two faces of  $r'$   $\{201\}$ . The former lay to the left and the larger of the two latter to the right, as shown in fig. 3, when the crystal was behind the glass plate. The edge-face  $a$  (100) is parallel to the vertical crystal axis  $c$ , and this axis emerged  $13^\circ 50'$  to the left of the normal N to  $c$  (001), for the plane of the latter face is parallel to the inclined crystal axis  $a$ , and the crystal axial angle  $\beta = ac = 76^\circ 10'$ . Now the reading for the normal N was  $214^\circ 18'$  (see top of table), from the observation taken before the plate was wetted with the immersion liquid (cedar oil), and the readings for the second median line (the half-way positions between those of the observed left and right optic eye vertices) were shown to be  $217^\circ 37'-41'$  according to the wave-length (from Li to F). These latter readings were also to the left of the normal. Hence, the second median line is inclined from the normal to  $c$  (001) towards the left, that is, towards the vertical crystal axis  $c$ , to an extent which increases regularly from  $3^\circ 19'$  for red Li light to  $3^\circ 23'$  for greenish blue F hydrogen light. Thus the second median line is nearer to the vertical axis  $c$  by  $4'$  for F light than for C light. The mean,  $3^\circ 21'$ , is the inclination for yellow sodium light of the second median line to the normal to  $c$  (001), and is the extinction angle which the author generally determines on the stauroscope, with a couple of section-plates parallel to the symmetry plane  $b$   $\{010\}$ .

The first median line, the direction of the  $\gamma$  axis of the indicatrix, is, of course,

always perpendicular to the second median line, which in this substance corresponds to the  $\alpha$  axis of the indicatrix.

The order of dispersion for the first median line is, therefore, that the latter is nearer to the inclined axis  $\alpha$  by four minutes for red C light than it is for greenish blue F light. The third axis of the indicatrix, the intermediate axis  $\beta$ , is identical with the crystal axis  $b$ , the symmetry axis of the monoclinic crystals, normal to the paper in fig. 3.

These measurements with Plate 1, which have afforded all the data concerning the orientation of the axes of the optical indicatrix and of the optic axes, were supplemented by similar ones derived by the use of two other tabular crystals parallel  $c$  {001}, Plates 2 and 3. The results as regards the dispersion of the median lines were identical in both cases with that derived from Plate 1, namely, that the first median line is nearer by 4' to the inclined axis  $\alpha$  for red C light than it is for greenish blue F light.

The *Extinction Angles with the Normal to  $c$  (001)*, behind that normal towards the direction of the vertical axis  $c$ , derived from Plates 2 and 3, were  $2^\circ 11'$  from Plate 2 and  $4^\circ 39'$  from Plate 3. The two plates were not quite so perfectly developed as Plate 1, as regards the planeness and perfection of surface of the two  $c$ -faces, Plate 1 having been a remarkably perfect crystal. But the mean value of the extinction angle for sodium light for the Plates 2 and 3 is  $3^\circ 25'$ , only 4' removed from the excellent value derived from Plate 1, which was  $3^\circ 21'$  for sodium light. Hence the mean value of the results from all three plates,  $3^\circ 23'$ , may be taken with confidence as very near the truth, quite as near as is possible in the cases of the ordinary extinction angle determinations in sodium light with the stauroscope.

The final result for *the orientation of the optical ellipsoid* is therefore as follows. The crystallographic axial angle  $ac$  being  $76^\circ 10'$ , the angle between the normal to the  $c$ -face (001) and the vertical axis  $c$  is  $13^\circ 50'$ . The second median line (axis  $\alpha$  of ellipsoid) is inclined  $10^\circ 27'$  for sodium light from and in front of the vertical axis  $c$ , and  $3^\circ 23'$  behind the normal to  $c$  (001). The first median line (axis  $\gamma$ ) lies  $3^\circ 23'$  above the inclined axis  $\alpha$  of the crystal and  $10^\circ 37'$  below the normal to  $\alpha$  (100). Both median lines thus lie in the obtuse crystal-axial angle  $ac$ . These positions will be clear from fig. 3.

The values for the optic axial angle derived from Plates 2 and 3 were as under:—

Light.	Plate 2.	Plate 3.	Mean $2V_c$ .	Mean $2V_a$ .
Li . . . . .	116 28	117 8	116 48	63 12
C . . . . .	116 27	117 7	116 47	63 13
Na. . . . .	116 18	117 1	116 40	63 20
Tl . . . . .	116 12	116 52	116 32	63 28
Cd . . . . .	116 8	116 45	116 27	63 33
F . . . . .	116 2	116 38	116 20	63 40

The mean result for these two plates, the adjustments for which were not quite so perfect as for Plate 1, on account of less true-planeness of the  $c$ -faces, is so close to that for Plate 1 that the mean of the two results, given in the next table, may confidently be accepted as very near the truth.

## OPTIC Axial Angle of KFe Selenate.

Light.	$2V_o$ .	$2V_a$ in cedar oil.	True $2V_a$ (corrected for difference of refraction).
Li . . . . .	116 49	63 11	64 11
C . . . . .	116 48	63 12	64 12
Na . . . . .	116 42	63 18	64 18
Tl . . . . .	116 35	63 25	64 25
Cd . . . . .	116 30	63 30	64 30
F . . . . .	116 24	63 36	64 36

If the refractive index of the immersion liquid, cedar oil, were absolutely identical with the mean index of the crystals ( $1/3 (\alpha + \beta + \gamma) = 1.5207$  for sodium light), and the two dispersions were also identical, we could be content with the final value of  $2V_a$  given in the third column. After the completion of the work on these unstable crystals, however, when time was no longer so important, the refractive index of the cedar oil employed was carefully determined, with the following result:—

## REFRACTIVE Indices of Cedar Oil.

Li . . . . .	1.5064	Na . . . . .	1.5102	F . . . . .	1.5175
C . . . . .	1.5068	Tl . . . . .	1.5135	G . . . . .	1.5238
		Cd . . . . .	1.5153		

The index for Na-light is thus 0.0105 lower than the mean crystal index, but the dispersion between Li and G-light is practically identical (0.0174) with that of the crystals 0.0171. Another liquid, monochlorbenzene, has the index 1.5248 for Na-light, 0.0041 higher than the mean crystal index. But it has the disadvantage of dissolving the cementing balsam, which cedar oil does not. The angle  $2V_o$  as observed in cedar oil would thus be slightly too large, while if observed in monochlorbenzene it would appear still more slightly too small. It has been possible to calculate the exact amount of the desirable correction, from observations made in both liquids at leisure, with the permanent crystals of rubidium ferrous selenate, the mean refractive index of which is almost identical (1.5220) with that of potassium ferrous selenate. The measurement of  $2V_a$  for Na-light was  $74^\circ 28'$  in cedar oil and  $73^\circ 4'$  in monochlorbenzene; the true value, as calculated from  $2H_a$  and  $2H_o$  in bromonaphthalene, was

73° 28'. The angle in cedar oil was thus 1° 24' greater than that in monochlorobenzene, and we can consider this result as also applicable to potassium ferrous selenate, the conditions being so nearly alike. The difference between the indices of the two liquids is 0·0146, and between those of cedar oil and the crystals of KFe selenate 0·0105. Hence, the correction, to be subtracted from the angle  $2V_o$ , as observed in cedar oil in order to give the true angle  $2V_a$ , within the crystal, is

$$\frac{84' \times 0\cdot0105}{0\cdot0146} = 60'.$$

The values in the last column of the table have, therefore, been obtained by adding exactly one degree to those for  $2V_a$  in the third column, which corresponds to the subtraction of a degree from the observed values of  $2V_o$  in column 2, as  $2V_a$  is the supplement of  $2V_o$ . This final corrected value for  $2V_a$  is certainly very close to the truth, quite as close indeed as if the ordinary procedure of observing  $2H_a$  and  $2H_o$  in bromonaphthalene, with section-plates perpendicular to the first and second median lines respectively, had been employed.

For the true optic axial angles in different crystals of the same substance frequently differ more than the few minutes of any possible error in these determinations.

In confirmation, however, the true angle  $2V_a$  may also be calculated, now that the exact refractive index  $n$  of the immersion liquid is known, with the aid of the intermediate refractive index  $\beta$  of the crystals, from the observed value of the obtuse angle  $2V_o$ , considered as  $2H_o$ , by means of the well-known formula:—

$$\cos V_a = \frac{n}{\beta} \sin H_o.$$

Inserting the values for sodium light and making the calculation we have:—

$$\cos V_a = \frac{1\cdot5102}{1\cdot5182} \sin 58^\circ 21',$$

from which

$$V_a = 32^\circ 8' \text{ and } 2V_a = 64^\circ 16'.$$

This result differs by only 2' from the corrected value given in the last column of the table, thus affording a most satisfactory confirmation of the final column of values in the table.

*Refractive Indices.*—A series of measurements of refractive index with a natural prism affording directly the index  $\beta$  had been carried out previous to the work just described with the plates, in order to obtain the necessary exact knowledge of the refractive power of the crystals to enable a proper choice to be made of an immersion liquid of like refractive index, for use with those plates. The index  $\beta$  is but slightly higher than the mean index of the crystals,  $\frac{\alpha + \beta + \gamma}{3}$ , and so enabled the



choice of cedar oil to be made. The prism in question was one formed by two excellent faces of  $p$  {110}, the pair which form the acute angle  $72^\circ 2'$ , and the edge between which is often replaced by a strip-face of  $b$  {010}. To preserve it fully transparent during the rather prolonged measurements with seven wave-lengths of light from the spectroscopic monochromatic illuminator, the two  $p$ -faces in question were covered with miniature glass plates cemented by quickly drying hard balsam in benzene. The edge of such a prism is parallel to the vertical crystal axis  $c$ , and is not very far ( $10^\circ 27'$ ) from parallel to the second median line, the  $\alpha$  axis of the optical ellipsoid, light vibrating parallel to which affords the  $\alpha$  index of refraction. The index corresponding to rays vibrating parallel to the prism edge would, therefore, have a value not far removed from  $\alpha$ . The other direction of vibration of rays passing through the prism at minimum deviation was that of the symmetry axis  $b$  of the crystal, and as this is absolutely identical for all wave-lengths with the intermediate axis  $\beta$  of the optical ellipsoid it furnishes the refractive index  $\beta$  directly with absolute accuracy. The object of this set of measurements was thus to determine  $\beta$ , the image of the slit corresponding to this index being that transmitted when the Nicol prism in front of the eyepiece of the goniometer-spectrometer was arranged at  $0^\circ$ ; the image obtained when the Nicol was at  $90^\circ$  corresponded to vibrations parallel to the prism edge and thus afforded a value slightly higher than that of the minimum index  $\alpha$ .

A second natural prism was subsequently employed in a similar manner; it was formed by two excellent faces of  $q$  {011}, those between which also comes the narrow line-face  $b$  (010) when developed. The prism angle in this case is  $52^\circ 12'$ . The edge of such a prism is parallel to the inclined crystal axis  $a$ , and only  $3^\circ 23'$  removed from the  $\gamma$  axis of the ellipsoid, so that vibrations parallel to it (those transmitted with the Nicol at  $90^\circ$ ) afford almost exactly the  $\gamma$  indices. The other rectangular vibration direction of the prism, like that of the first prism, was that of the symmetry crystal axis  $b$ , so that this prism also afforded directly and accurately the intermediate refractive index  $\beta$ , the image corresponding to it being that observed when the Nicol was at the  $0^\circ$  position.

The two values of  $\beta$  obtained from these two natural prisms, and their mean value, are as follows:—

Light.	$p$ -faced prism.	$q$ -faced prism.	Mean $\beta$ .
Li . . . . .	1.5136	1.5152	1.5144
C . . . . .	1.5141	1.5158	1.5149
Na . . . . .	1.5173	1.5191	1.5182
Tl . . . . .	1.5207	1.5223	1.5215
Cd . . . . .	1.5225	1.5242	1.5234
F . . . . .	1.5244	1.5262	1.5253
G . . . . .	1.5307	1.5321	1.5314

The approximate values obtained for  $\alpha$  from the  $p$ -faced prism and for  $\gamma$  from the  $q$ -faced prism, were as under :—

Light.	Approximate $\alpha$ .	Approximate $\gamma$ .
Li . . . . .	1·5078	1·5307
C . . . . .	1·5083	1·5312
Na . . . . .	1·5113	1·5345
Tl . . . . .	1·5145	1·5381
Cd . . . . .	1·5163	1·5400
F . . . . .	1·5182	1·5422
G . . . . .	1·5242	1·5484

As the direction for which this approximate value for  $\gamma$  was determined was only  $3\frac{1}{2}^\circ$  from the exact direction for the  $\gamma$  axis of the ellipsoid, it is probable that the above value for  $\gamma$  is practically correct. The approximate value for  $\alpha$  was determined for a direction  $10\frac{1}{2}^\circ$  removed from the true direction for the  $\alpha$  (minimum) axis of the ellipsoid, and its value is therefore somewhat too high, probably by about 0·001 to 0·002.

Finally, in the fourth and last crop of crystals obtained there was a crystal large and transparent enough to suggest an attempt at grinding a prism to afford  $\alpha$  and  $\gamma$  directly. One was therefore ground in the correct orientation to afford these indices directly and absolutely. The refracting edge was parallel to the second median line, (the  $\alpha$  axis of the ellipsoid), so that vibrations affording the signal image when the Nicol was at  $90^\circ$  corresponded to the  $\alpha$  index. The two faces of the prism were symmetrical to (inclined  $30^\circ$  on each side of) the symmetry plane  $b$  {010}, so that the other rectangular direction of vibration within that plane, corresponding to the image transmitted when the Nicol was at  $0^\circ$ , was parallel to the  $\gamma$  axis of the ellipsoid and afforded the index  $\gamma$ . By working very rapidly and keeping the crystal covered with the lubricating oil after its goniometrical adjustment to the correct desired orientation, and as soon as the grinding and polishing were completed covering the prepared surfaces with balsam-cemented glass plates, the prism was completed before any serious loss of transparency had occurred; an hour was permitted for the drying of the hard balsam in benzene, and the transparency was then still such as enabled the refractive indices  $\alpha$  and  $\gamma$  to be determined for all wave-lengths from Li red as far as greenish blue F of the spectrum, only the G-images being too weak for accurate allocation to the cross wires. The results are given below.

Light.	$\alpha$ .	$\gamma$ .
Li . . . . .	1·5059	1·5306
C . . . . .	1·5064	1·5311
Na . . . . .	1·5095	1·5345
Tl . . . . .	1·5127	1·5379
Cd . . . . .	1·5145	1·5399
F . . . . .	1·5164	1·5421

It is obvious that, as expected, the approximate values for  $\gamma$  afforded by the  $q$ -faced prism were the true values within the limits of experiment (0.0002); and that the approximate  $\alpha$  values derived from the  $p$ -faced prism were slightly higher than the true  $\alpha$ .

It is thus now possible to give with all confidence the true values of  $\alpha$ ,  $\beta$  and  $\gamma$ , all obtained directly. They are as under, the G-values for  $\alpha$  and  $\beta$  being included from the evidence of their difference from the F-values afforded by the approximate determinations with the natural prisms.

REFRACTIVE INDICES of Potassium Ferrous Selenate.

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Li . . . . .	1.5059	1.5144	1.5306
C . . . . .	1.5064	1.5149	1.5311
Na . . . . .	1.5095	1.5182	1.5345
Tl . . . . .	1.5127	1.5215	1.5379
Cd . . . . .	1.5145	1.5234	1.5399
F . . . . .	1.5164	1.5253	1.5421
G . . . . .	1.5224	1.5314	1.5483

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.5207.

$\alpha$  = Vibration direction parallel to second median line, 10° 27' in front of axis  $c$ .

$\beta$  = " " " " symmetry axis  $b$ .

$\gamma$  = " " " " first median line, 3° 23' above axis  $a$ .

Double refraction,  $\text{Na}_{\gamma-\alpha} = 0.0250$ .

General formula for  $\beta$ , for any wave-length  $\lambda$ , corrected to a vacuum (correction + 0.0004):—

$$\beta = 1.4984 + \frac{838\,265}{\lambda^2} - \frac{4\,754\,500\,000\,000}{\lambda^4} + \dots$$

The  $\alpha$  indices are also reproduced if the constant 1.4984 be diminished by 0.0087, and the  $\gamma$  indices if the constant is increased by 0.0163.

*Axial Ratios of the Optical Ellipsoid.*—These values work out as under:—

Indicatrix . . . .  $\alpha : \beta : \gamma = 0.9943 : 1 : 1.0107$ .

Velocity ellipsoid . .  $a : b : c = 1.0058 : 1 : 0.9894$ .

*Molecular Optical Constants.*—The values of these constants, calculated by both the formulæ of LORENZ and of GLADSTONE and DALE, are given in the next table.

	Axis of optical indicatrix . . . .	$\alpha$ .	$\beta$ .	$\gamma$ .	
LORENZ	Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$ . . . . .	C	0.1192	0.1209	0.1241
		G	0.1224	0.1241	0.1274
"	Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$ . . . . .	C	62.55	63.43	65.10
		G	64.21	65.13	66.85
"	Specific dispersion, $n_G - n_C$ . . . . .		0.0032	0.0032	0.0033
			1.66	1.70	1.75
GLADSTONE	Molecular refraction, $\frac{n - 1}{d} M$ . . . . .	C	106.54	108.33	111.74

Mean molecular refraction (GLADSTONE),  $\frac{1}{3}(\alpha + \beta + \gamma) = 108.87$ .

*Rubidium Ferrous Selenate*,  $\text{Rb}_2\text{Fe}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ .*Morphology.*

This substance has not been previously investigated, either goniometrically or optically. It forms beautifully transparent and, considering its composition (as containing ferrous iron), remarkably permanent crystals of a very pale bluish green colour.

Ten crystals were measured, selected from the three best crops of the several prepared. The ferrous selenate employed in one case had been prepared by the action of selenic acid on iron wire. An equivalent of pure rubidium selenate, prepared by the action of selenic acid on rubidium carbonate, was dissolved in only slightly more than the minimum amount of water required for solution at the ordinary temperature, and added to the cold solution of ferrous selenate immediately after the filtration from the precipitated selenium, in order to avoid the somewhat rapid decomposition (oxidation) which solutions of ferrous selenate suffer. Crystallisation occurred under the receiver of an air pump, under reduced pressure. Several crops of remarkably transparent and permanent crystals of rubidium ferrous selenate were also obtained by the method described in the introduction.

*Crystal System.*—Monoclinic. Class No. 5, holohedral-prismatic.

*Ratios of Axes.*—

$$a : b : c = 0.7424 : 1 : 0.5000.$$

*Axial Angle.*— $\beta = 104^\circ 57'$ .

*Forms Observed.*— $a \{100\}$ ,  $b \{010\}$ ,  $c \{001\}$ ,  $p \{110\}$ ,  $p' \{120\}$ ,  $q \{011\}$ ,  $r' \{\bar{2}01\}$ ,  $o' \{\bar{1}11\}$ , and  $n' \{\bar{1}21\}$ .

*Habit.*—Thick blocks, more or less tabular, parallel to  $c \{001\}$ . A typical crystal is shown in fig. 4.

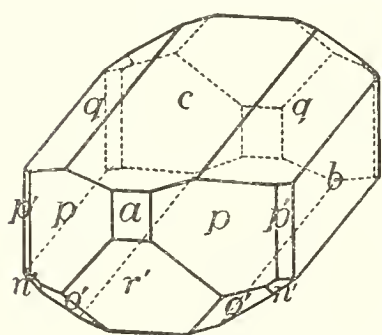


Fig. 4.

The crystals exhibited the usual characteristic relative development of the faces of the basal plane  $c \{001\}$  and  $q \{011\}$  common to all the rubidium salts of the series, namely, the  $c$ -faces predominated, but the  $q$ -faces were also well developed as fairly broad bevellings. The faces of the clinopinakoid  $b \{010\}$  were also frequently quite large on this salt, forming the two sides of the blocks. The ends of the blocks were formed by the faces of the primary prism  $p \{110\}$  and the orthopinakoid  $r' \{\bar{2}01\}$ , which latter were often relatively very large, forming the two predominating end planes. Good little faces of the primary orthopinakoid  $a \{100\}$  were usually present, and indeed large crystals often showed the  $a$ -faces quite considerably developed. There were also usually several faces of the hemipyramid  $o' \{\bar{1}11\}$  present, but their reflections were poor. Excellent, although narrow faces of the prism  $p' \{120\}$  were also observed on two of the crystals measured. Minute faces of the hemipyramid

INTERFACIAL Angles of Rubidium Ferrous Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$\left\{ \begin{array}{l} ac = (100) : (001) \\ as = (100) : (101) \\ sc = (101) : (001) \\ cr' = (001) : (201) \\ cs' = (001) : (\bar{1}01) \\ s'r' = (\bar{1}01) : (201) \\ r'a = (\bar{2}01) : (\bar{1}00) \\ r'c = (\bar{2}01) : (00\bar{1}) \end{array} \right.$	3 — — 19 — — 2 17	$\overset{\circ}{75} \overset{\prime}{2} - \overset{\circ}{75} \overset{\prime}{9}$ — — 63 29- 63 49 — — 41 22- 41 26 116 17-116 28	$\overset{\circ}{75} \overset{\prime}{6}$ — — 63 37 — — 41 24 116 23	$\overset{\circ}{75} \overset{\prime}{3}$ 46 2 29 1 63 24 38 15 25 9 41 33 116 36	$\overset{\prime}{3}$ — — 13 — — 9 13
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp' = (110) : (120) \\ p'b = (120) : (010) \\ pp''' = (110) : (130) \\ p''b = (130) : (010) \\ pb = (110) : (010) \\ pp = (110) : (\bar{1}\bar{1}0) \\ pp = (110) : (\bar{1}10) \end{array} \right.$	8 3 3 — — 36 16 17	35 31- 35 48 19 24- 19 29 34 42- 34 54 — — 54 11- 54 30 71 12- 71 33 108 25-108 44	35 41 19 27 34 49 — — 54 21 71 23 108 35	35 39 19 28 34 53 29 25 24 56 * 71 18 108 42	2 1 4 — — — 5 7
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qb = (011) : (010) \\ qq = (011) : (01\bar{1}) \end{array} \right.$	38 38 15	25 21- 25 59 64 0- 64 28 128 12-128 38	25 47 64 13 128 25	* 64 13 128 26	— 0 1
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \\ aq = (100) : (011) \\ qo' = (011) : (\bar{1}11) \\ o'a = (\bar{1}11) : (\bar{1}00) \end{array} \right.$	— — — — —	— — — — —	— — — — —	49 13 27 21 76 34 34 28 68 58	— — — — —
$\left\{ \begin{array}{l} co = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \\ po' = (110) : (11\bar{1}) \\ o'c = (11\bar{1}) : (00\bar{1}) \\ pc = (110) : (00\bar{1}) \end{array} \right.$	— — 40 13 14 39	— — 77 47- 78 8 57 20- 57 46 44 25- 44 47 101 46-102 20	— — 77 54 57 30 44 38 102 6	34 38 43 16 * 57 39 44 27 102 6	— — — 9 11 0
$\left\{ \begin{array}{l} bi = (010) : (121) \\ no = (121) : (111) \\ bo = (010) : (111) \\ os = (111) : (101) \end{array} \right.$	— — — —	— — — —	— — — —	54 15 15 57 70 12 19 48	— — — —
$\left\{ \begin{array}{l} bo' = (010) : (\bar{1}11) \\ o's' = (\bar{1}11) : (\bar{1}01) \\ o'o' = (\bar{1}11) : (\bar{1}\bar{1}1) \end{array} \right.$	18 — 6	65 5- 65 21 — 49 24- 49 35	65 13 — 49 31	65 20 24 40 49 21	7 — 10
$\left\{ \begin{array}{l} sq = (101) : (011) \\ qp = (011) : (\bar{1}10) \\ ps = (\bar{1}10) : (\bar{1}0\bar{1}) \\ pq = (\bar{1}10) : (0\bar{1}\bar{1}) \end{array} \right.$	— 35 — 36	— 86 1- 86 27 — 93 29- 94 3	— 86 11 — 93 49	38 3 86 17 55 40 93 43	— 6 — 6
$\left\{ \begin{array}{l} s'q = (\bar{1}01) : (011) \\ qn = (011) : (121) \\ np = (121) : (110) \\ qp = (011) : (110) \\ ps' = (110) : (10\bar{1}) \\ pq = (110) : (0\bar{1}\bar{1}) \end{array} \right.$	— — — 35 — 34	— — — 63 32- 63 59 — 116 2-116 28	— — — 63 47 — 116 13	45 0 26 43 37 2 63 45 71 15 116 15	— — — 2 — 2
$\left\{ \begin{array}{l} r'o' = (\bar{2}01) : (\bar{1}11) \\ o'p = (\bar{1}11) : (110) \\ pr' = (110) : (20\bar{1}) \\ r'p = (\bar{2}01) : (110) \end{array} \right.$	21 20 37 36	34 28- 34 56 92 45- 93 6 52 14- 52 31 127 33-127 55	34 43 92 56 52 23 127 37	34 39 92 48 52 33 127 27	4 8 10 10
Total number of measurements .	599				

$n'\{\bar{1}21\}$  were also shown, but the reflections of the signal were too faint for accurate allocation to the spider-lines.

The faces of the forms  $p\{110\}$  and  $c\{001\}$  on the crystals of this salt were more than usually affected by striation, and only two crops were obtained sufficiently free from the defect for the purpose of the measurements. Even the 10 apparently excellent crystals selected from these crops have afforded results which show in the cases of certain angles greater differences between the calculated and observed angles than usual, compared with the salts of the series previously measured. The differences, however, are not sufficiently great to affect any of the conclusions drawn from the comparison of the results with those for the other members of the iron group of double selenates.

A table of angles is given on the previous page.

*Cleavage*.—There is a good cleavage developed parallel to  $r'\{\bar{2}01\}$ .

*Relative Density*.—Six determinations by the immersion method gave the following results:—

I.	Density for $16^\circ 6/4^\circ$	. . .	2·8034	For $20^\circ/4^\circ$	. . .	2·8025
II.	„ $16^\circ 2/4^\circ$	. . .	2·7986	„ $20^\circ/4^\circ$	. . .	2·7975
III.	„ $16^\circ 4/4^\circ$	. . .	2·8018	„ $20^\circ/4^\circ$	. . .	2·8008
IV.	„ $16^\circ 1/4^\circ$	. . .	2·7985	„ $20^\circ/4^\circ$	. . .	2·7974
V.	„ $16^\circ 1/4^\circ$	. . .	2·8031	„ $20^\circ/4^\circ$	. . .	2·8020
VI.	„ $16^\circ 2/4^\circ$	. . .	2·8002	„ $20^\circ/4^\circ$	. . .	2·7991
				Mean	. . .	2·7999

The value accepted for  $20^\circ/4^\circ$  is 2·800.

*Molecular Volume*.— $\frac{M}{d} = \frac{616\cdot82}{2\cdot800} = 220\cdot29$ .

*Molecular Distance Ratios (topic axial ratios)*.—

$$\chi : \psi : \omega = 6\cdot3109 : 8\cdot5006 : 4\cdot2503.$$

### Optics.

*Nature and Orientation of the Optical Ellipsoid*.—The plane of the optic axes is the symmetry plane  $b\{010\}$ . The double refraction is positive, the first median line corresponding to the refractive index  $\gamma$  and the second median line to  $\alpha$ . Extinction determinations with two plates parallel to the symmetry plane gave the following positions for one of the extinction directions with respect to the normal to  $c\{001\}$ .

#### *Extinction Direction in the Symmetry Plane.*

Plate 1	. . .	$1^\circ 44'$ ,	Plate 2	. . .	$0^\circ 56'$ ,
Mean	. . .	$1^\circ 20'$	with normal to $c\{001\}$ .		

The direction is behind the normal, towards the vertical axis  $c$ . It is the second median line and corresponds to the  $\alpha$  index. As the angle between the normal to  $c\{001\}$  and the axis  $c$  is  $14^\circ 57'$  (the angle  $ac = (100) : (001) = 75^\circ 3'$ ), this second median line is inclined  $13^\circ 37'$  to (in front of) the axis  $c$ . The first median line is consequently inclined  $1^\circ 20'$  to (above) the axis  $a$ , and lies  $13^\circ 37'$  below the normal to  $a(100)$ . Both median lines are in the obtuse angle of the crystal axes  $ac$ . The conditions are clearly shown in the diagram given in fig. 5.

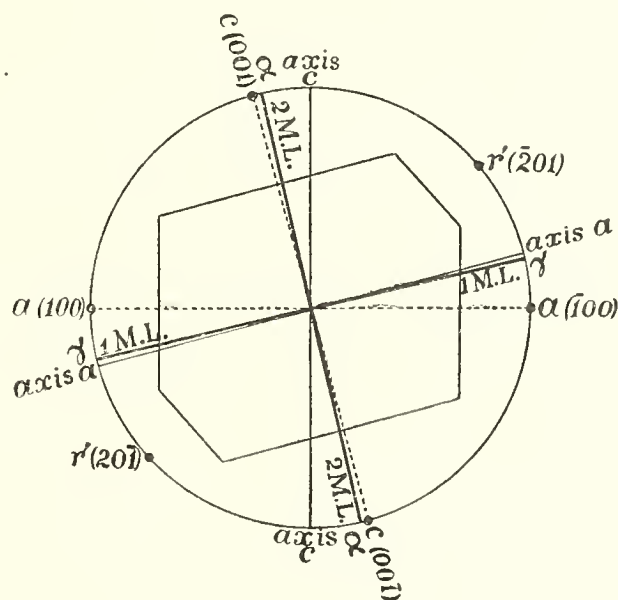


Fig. 5.

*Optic Axial Angle.*—Three pairs of section-plates were ground, perpendicular to the first and second median lines, and afforded the values for  $2E$ ,  $2H_a$  and  $2H_o$ , recorded in the two following tables. The angle in air  $2E$  is very large, and only Plates 1 and 3 of the three perpendicular to the first median line afforded it satisfactorily clearly. Monobromonaphthalene was the immersion liquid employed for the measurements of  $2H_a$  and  $2H_o$ , for which very clear and suitable interference figures were obtained.

APPARENT Optic Axial Angle in Air,  $2E$ , of  $RbFe$  Selenate.

Light.	Plate 1.	Plate 3.	Mean $2E$ .
Li . . . . .	130 18	130 35	130 27
C . . . . .	130 23	130 40	130 32
Na . . . . .	131 3	131 7	131 5
Tl . . . . .	131 34	131 41	131 38
Cd . . . . .	131 59	132 1	132 0
F . . . . .	132 36	132 30	132 33

## DETERMINATION of True Optic Axial Angle in Bromonaphthalene of RbFe Selenate.

Light.	No. of plate perp. 1 M.L.	Observed 2H <sub>a</sub> .	No. of plate perp. 2 M.L.	Observed 2H <sub>o</sub> .	Calculated 2V <sub>a</sub> .	Mean 2V <sub>a</sub> .
Li . . . . .	1	66 33	1a	94 31	73 32	73 35
	2	66 38	2a	94 30	73 36	
	3	66 38	3a	94 29	73 36	
C . . . . .	1	66 31	1a	94 29	73 31	73 34
	2	66 34	2a	94 25	73 35	
	3	66 36	3a	94 25	73 36	
Na . . . . .	1	66 15	1a	94 9	73 28	73 32
	2	66 17	2a	94 1	73 33	
	3	66 20	3a	94 5	73 34	
Tl . . . . .	1	65 58	1a	93 47	73 26	73 30
	2	65 57	2a	93 32	73 32	
	3	66 2	3a	93 38	73 32	
Cd . . . . .	1	65 45	1a	93 30	73 24	73 28
	2	65 47	2a	93 16	73 31	
	3	65 49	3a	93 21	73 30	
F . . . . .	1	65 30	1a	93 15	73 20	73 26
	2	65 35	2a	92 58	73 30	
	3	65 36	3a	93 5	73 28	

*Dispersion of the Median Lines.*—This was determined by observations of the approximate true optic axial angle in cedar oil ( $\mu = 1.5200$ ) and monochlorbenzene ( $\mu = 1.5248$ ), the refractive indices of which liquids are respectively just lower and just higher than the mean index of the crystals. The dispersion proved to be very small, only 10' between red C-light and green Tl-light, and is such that the first median line is nearer to the axis  $a$  by 10' for red C-light than for green Tl-light.

*Effect of Temperature on the Optical Axial Angle.*—Measurements of the apparent optic axial angle in air 2E at 85° C. showed that this angle increases almost exactly two degrees for 70° C. rise of temperature (from 15° to 85°).

*Refractive Indices.*—Six excellent 60°-prisms were ground, each symmetrical to a principal plane of the optical ellipsoid and with the refracting edge parallel to one of the axes, so as to afford directly two of the three indices  $\alpha, \beta, \gamma$ . The separate results for each index were satisfactorily concordant, and the mean values are given in the next table.



REFRACTIVE INDICES of Rubidium Ferrous Selenate.

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Li . . . . .	1.5099	1.5165	1.5290
C . . . . .	1.5104	1.5170	1.5295
Na . . . . .	1.5133	1.5200	1.5328
Tl . . . . .	1.5165	1.5233	1.5363
Cd . . . . .	1.5184	1.5252	1.5382
F . . . . .	1.5202	1.5272	1.5404
G . . . . .	1.5264	1.5334	1.5467

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.5220.

$\alpha$  = Vibration direction parallel to second median line, 13° 37' in front of axis  $c$ .

$\beta$  = " " " " symmetry axis  $b$ .

$\gamma$  = " " " " first median line, 1° 20' above axis  $a$ .

Double refraction,  $N_{\alpha-\gamma} = 0.0195$ .

General formula for  $\beta$ , corrected to a vacuum :—

$$\beta = 1.5048 + \frac{546\ 205}{\lambda^2} - \frac{160\ 200\ 000\ 000}{\lambda^4} + \dots$$

The  $\alpha$  indices are also very closely reproduced by the formula if the constant 1.5048 be diminished by 0.0067, and the  $\gamma$  indices also if the constant be increased by 0.0128.

Observations at 65° indicated that the refractive indices are diminished by about 0.0016 for  $\alpha$ , 0.0018 for  $\beta$ , and 0.0021 for  $\gamma$ , by a rise of temperature of 50° C. (from 15° to 65°).

Axial Ratios of the Optical Ellipsoid.—The values for the optical indicatrix and optical velocity ellipsoid are respectively as follows :—

$$\alpha : \beta : \gamma = 0.9956 : 1 : 1.0084.$$

$$a : b : c = 1.0044 : 1 : 0.9916.$$

Molecular Optical Constants.—The values of these constants, calculated by both the formulæ of LORENZ and of GLADSTONE and DALE, are given in the next table.

	Axis of optical indicatrix . . . .	$\alpha$ .	$\beta$ .	$\gamma$ .	
LORENZ	Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$ . . . .	C	0.1069	0.1080	0.1102
		G	0.1097	0.1109	0.1132
"	Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$ . . . .	C	65.93	66.65	68.00
		G	67.66	68.41	69.83
"	Specific dispersion, $n_G - n_C$ . . . . .		0.0028	0.0029	0.0030
			1.73	1.76	1.83
GLADSTONE	Molecular refraction, $\frac{n - 1}{d} M$ . . . . . C	112.44	113.89	116.65	

Mean molecular refraction (GLADSTONE),  $\frac{1}{3}(\alpha + \beta + \gamma) = 114.33$ .

*Cæsium Ferrous Selenate*,  $\text{Cs}_2\text{Fe}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ .*Morphology.*

The salt was prepared in the manner described in the introduction, the ferrous selenate being prepared by the action of selenic acid on ferrous sulphide, and the cæsium selenate by the action of selenic acid on pure cæsium carbonate.

Ten crystals were measured, selected from four different crops, all of which were composed of excellent transparent single crystals, sometimes grown to a considerable size, and of a pale (almost colourless) bluish green colour containing more yellow than the crystals of rubidium ferrous selenate.

*Crystal System.*—Monoclinic. Class No. 5, holohedral-prismatic.

*Ratios of Axes.*— $a : b : c = 0.7308 : 1 : 0.4979$ .

*Axial Angle.*— $\beta = 106^\circ 2'$ .

*Forms Observed.*— $b \{010\}$ ,  $c \{001\}$ ,  $p \{110\}$ ,  $q \{011\}$ ,  $r' \{\bar{2}01\}$ , and  $o' \{\bar{1}11\}$ .

*Habit.*—Prismatic parallel to the inclined axis  $a$ .

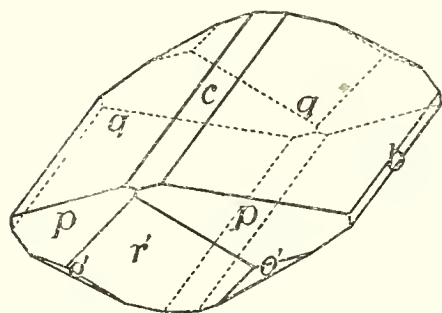


Fig. 6.

A typical crystal is represented in fig. 6.

The crystals were usually very definitely of this habit, which is distinguished by narrow faces of  $c \{001\}$  and broad faces of  $q \{011\}$ , and which is very characteristic of the cæsium salts of the series. In a few crops the  $c$ -faces were somewhat broader, and almost conferred a tabular habit on the crystals. As in several of the double sulphates containing iron, notably ammonium ferrous sulphate, the faces of the orthopinakoid  $r' \{\bar{2}01\}$  were usually more prominent than those of the primary prism  $p \{110\}$ , and in many cases practically formed the ends of the prisms, the  $p$ -faces being very small. The faces of the clinopinakoid  $b \{010\}$  and of the hemipyramid  $o' \{\bar{1}11\}$  were only occasionally present, and then were very subsidiary, although some good reflections were obtained from them.

*Cleavage.*—There is an excellent cleavage parallel to  $r' \{\bar{2}01\}$ .

*Volume.*

*Relative Density.*—Four determinations by the immersion method yielded the following values :—

I.	Density for $15^\circ 9/4^\circ$	. . .	3.0497	For $20^\circ/4^\circ$	. . .	3.0484
II.	„ $15^\circ 7/4^\circ$	. . .	3.0485	„ $20^\circ/4^\circ$	. . .	3.0472
III.	„ $16^\circ 2/4^\circ$	. . .	3.0495	„ $20^\circ/4^\circ$	. . .	3.0483
IV.	„ $16^\circ 1/4^\circ$	. . .	3.0504	„ $20^\circ/4^\circ$	. . .	3.0492
				Mean	. . .	3.0483

Accepted value for  $20^\circ/4^\circ$ , 3.048.

INTERFACIAL Angles of Cæsium Ferrous Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$ac = (100):(001)$	—	—	—	73 58	—
$as = (100):(101)$	—	—	—	45 9	—
$sc = (101):(001)$	—	—	—	28 49	—
$cr' = (001):(201)$	22	64 16- 64 43	64 32	64 29	3
$cs' = (001):(\bar{1}01)$	—	—	—	38 51	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	25 38	—
$r'a = (\bar{2}01):(\bar{1}00)$	—	—	—	41 33	—
$r'c = (\bar{2}01):(00\bar{1})$	22	115 17-115 45	115 28	115 31	3
$ap = (100):(110)$	—	—	—	35 7	—
$pp' = (110):(120)$	—	—	—	19 28	—
$p'b = (120):(010)$	—	—	—	35 25	—
$pp''' = (110):(130)$	—	—	—	29 31	—
$p''b = (130):(010)$	—	—	—	25 22	—
$pb = (110):(010)$	8	54 43- 55 1	54 52	54 53	1
$pp = (110):(\bar{1}\bar{1}0)$	19	70 6- 70 23	70 14	*	—
$pp = (110):(\bar{1}\bar{1}0)$	19	109 35-109 57	109 46	109 46	0
$cq = (001):(011)$	37	25 20- 25 42	25 34	*	—
$qb = (011):(010)$	8	64 23- 64 39	64 28	64 26	2
$qq = (011):(01\bar{1})$	18	128 44-129 2	128 52	128 52	0
$ao = (100):(111)$	—	—	—	48 19	—
$oq = (111):(011)$	—	—	—	27 16	—
$aq = (100):(011)$	—	—	—	75 35	—
$qo' = (011):(\bar{1}\bar{1}1)$	—	—	—	35 3	—
$o'a = (\bar{1}\bar{1}1):(\bar{1}00)$	—	—	—	69 22	—
$co = (001):(111)$	—	—	—	34 18	—
$op = (111):(110)$	—	—	—	42 39	—
$cp = (001):(110)$	40	76 48- 77 4	76 57	*	—
$po' = (110):(111)$	4	58 3- 58 15	58 11	58 7	4
$o'c = (11\bar{1}):(\bar{0}0\bar{1})$	4	44 46- 44 57	44 52	44 56	4
$pc = (110):(00\bar{1})$	40	102 50-103 13	103 3	103 3	0
$bn = (010):(121)$	—	—	—	54 47	—
$no = (121):(111)$	—	—	—	15 47	—
$bo = (010):(111)$	—	—	—	70 34	—
$os = (111):(101)$	—	—	—	19 26	—
$bo' = (010):(\bar{1}\bar{1}1)$	2	65 21- 65 27	65 24	65 21	3
$o's' = (\bar{1}\bar{1}1):(\bar{1}01)$	—	—	—	24 39	—
$o'o' = (\bar{1}\bar{1}1):(\bar{1}\bar{1}1)$	1	—	49 14	49 18	4
$sq = (101):(011)$	—	—	—	37 47	—
$qp = (011):(\bar{1}\bar{1}0)$	40	87 21- 87 43	87 30	87 27	3
$ps = (\bar{1}\bar{1}0):(\bar{1}0\bar{1})$	—	—	—	54 46	—
$pq = (\bar{1}\bar{1}0):(0\bar{1}\bar{1})$	40	92 19- 92 37	92 30	92 33	3
$s'q = (\bar{1}01):(011)$	—	—	—	45 22	—
$qn = (011):(121)$	—	—	—	26 33	—
$np = (121):(110)$	—	—	—	36 35	—
$qp = (011):(110)$	40	62 49- 63 13	63 6	63 8	2
$ps' = (110):(10\bar{1})$	—	—	—	71 30	—
$pq = (110):(0\bar{1}\bar{1})$	40	116 44-117 4	116 54	116 52	2
$r'o' = (\bar{2}01):(\bar{1}\bar{1}1)$	6	34 51- 35 14	34 58	34 59	1
$o'p = (\bar{1}\bar{1}1):(110)$	6	92 40- 92 51	92 45	92 46	1
$pr' = (110):(20\bar{1})$	40	52 1- 52 28	52 16	52 15	1
$r'p = (\bar{2}01):(110)$	39	127 32-127 56	127 44	127 45	1
Total number of measurements . .	495				

*Molecular Volume.*—  $\frac{M}{d} = \frac{710.82}{3.048} = 233.21.$

*Molecular Distance Ratios (topic axial ratios).*—

$$\chi : \psi : \omega = 6.3847 : 8.7366 : 4.3499.$$

*Optics.*

*Nature and Orientation of Optical Ellipsoid.*—The symmetry plane  $b\{010\}$  is the plane of the optic axes. The double refraction is positive, so that the first median line corresponds to  $\gamma$  and the second median line to  $\alpha$ . Extinction determinations with two section-plates ground parallel to the symmetry plane afforded the following positions for one of the extinction directions which lies nearly normal to the basal plane  $c\{001\}$  :—

*Extinction Direction in the Symmetry Plane.*

Plate 1 . . . .	4° 47',	Plate 2 . . . .	5° 16',
Mean . . . .	5° 2' with normal to $c\{001\}$ .		

The direction is in front of the normal, further away than the latter from the vertical axis  $c$ ; it is the second median line and corresponds to the refractive index  $\alpha$ . As the angle between the normal to  $c\{001\}$  and the vertical axis is  $16^\circ 2'$  ( $ac = 73^\circ 58'$ ), the angle between the vertical axis  $c$  and the second median line is  $21^\circ 4'$  in front of the axis. The first median line lies  $5^\circ 2'$  below the inclined axis  $\alpha$ , and thus lies in

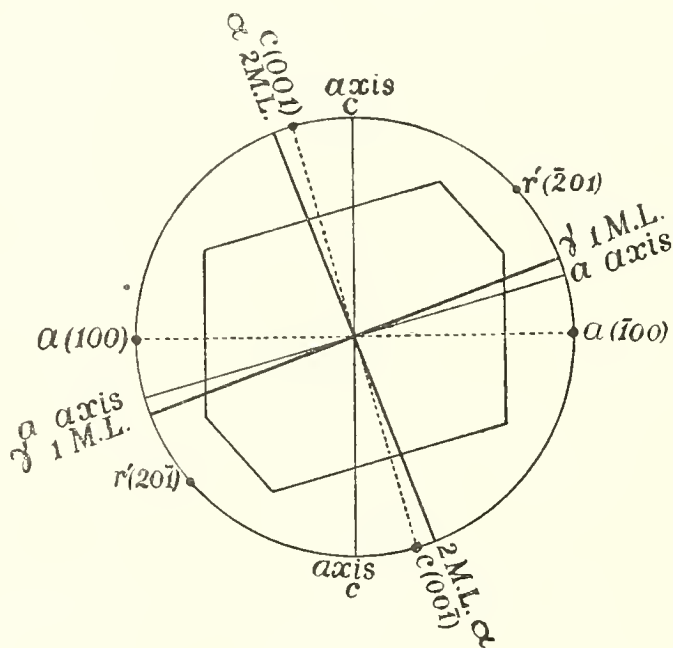


Fig. 7.

the acute crystallographic axial angle  $ac$ , while the second median line lies in the obtuse angle  $\beta$  between the crystal axes  $a$  and  $c$  lying in the symmetry plane. The conditions are graphically shown in fig. 7.

*Optic Axial Angle.*—Three pairs of section-plates were ground, 1, 2, and 3 perpendicular to the first median line and  $1a$ ,  $2a$ , and  $3a$  perpendicular to the second median line. The optic axial angle in air 2E is so large that it could not be measured, it being impossible to get the hyperbolic brush-vertices quite to the cross-wires before disappearance. In monobromonaphthalene excellent measurements of  $2H_a$  with sections 1, 2, and 3, and of  $2H_o$  with sections  $1a$ ,  $2a$ , and  $3a$  were obtained, the central rings being small and the brush-vertices very sharp. The values obtained, and those of the true optic axial angle  $2V_a$  calculated therefrom, together with the mean  $2V_a$ , are given in the next table.

DETERMINATION of True Optic Axial Angle, in Bromonaphthalene, of CsFe Selenate.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp. 2 M.L.	Observed $2H_o$ .	Calculated $2V_a$ .	Mean $2V_a$ .
Li . . . . .	1	75 38	$1a$	87 18	83 14	82 58
	2	75 25	$2a$	87 48	82 50	
	3	75 21	$3a$	87 44	82 50	
C . . . . .	1	75 33	$1a$	87 15	83 12	82 56
	2	75 20	$2a$	87 46	82 48	
	3	75 17	$3a$	87 42	82 48	
Na . . . . .	1	75 2	$1a$	87 8	82 56	82 47
	2	75 0	$2a$	87 32	82 42	
	3	74 59	$3a$	87 25	82 44	
Tl . . . . .	1	74 27	$1a$	86 51	82 42	82 33
	2	74 25	$2a$	87 16	82 28	
	3	74 25	$3a$	87 12	82 30	
Cd . . . . .	1	74 8	$1a$	86 43	82 34	82 25
	2	74 8	$2a$	87 8	82 20	
	3	74 6	$3a$	87 4	82 22	
F . . . . .	1	73 53	$1a$	86 34	82 28	82 20
	2	73 50	$2a$	87 0	82 13	
	3	73 56	$3a$	86 52	82 20	

*Dispersion of the Median Lines.*—The mean refractive index of the crystals for sodium light will be shown to be 1.5357. Methylsalicylate has almost exactly the same refractive index for sodium light, 1.5363, so that this substance was employed as the immersion liquid for the determination of the dispersion of the median lines, with the two best sections 1 and 3 perpendicular to the first median line. The first median line proves to lie very slightly nearer to the inclined axis  $a$  for greenish blue F-light than for red Li-light, the amount indicated by section 1 being  $11'$ , and that indicated by the measurements with section 3 being  $13'$ , the results thus in the mean affording the amount  $12'$ . The mean values of the true optic axial angle  $2V_a$ , afforded by

these observations in a liquid of so very nearly the same refraction as the crystals, were  $82^{\circ} 41'$  for Li-light and  $81^{\circ} 33'$  for F-light, direct observations which amply confirm both the actual values given in the table for the true angle, by calculation from  $2H_a$  and  $2H_o$ , and the order of the dispersion.

*Refractive Indices.*—The refractive indices were determined with six prisms of about  $60^{\circ}$  angle, ground so that the faces were symmetrical to the principal planes and the refracting edges parallel to the axes of the optical ellipsoid, so that each prism yielded two of the three refractive indices  $\alpha$ ,  $\beta$ ,  $\gamma$  directly. The results for the same index from the different prisms were all remarkably concordant, and the mean values are given in the next table.

REFRACTIVE INDICES of Cæsium Ferrous Selenate.

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Li . . . . .	1.5269	1.5317	1.5379
C . . . . .	1.5274	1.5322	1.5384
Na . . . . .	1.5306	1.5352	1.5414
Tl . . . . .	1.5339	1.5385	1.5450
Cd . . . . .	1.5359	1.5405	1.5470
F . . . . .	1.5379	1.5425	1.5491
G . . . . .	1.5442	1.5488	1.5555

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.5357.

$\alpha$  = Vibration direction parallel to second median line,  $21^{\circ} 4'$  in front of axis  $c$ .

$\beta$  = " " " " symmetry axis  $b$ .

$\gamma$  = " " " " first median line,  $5^{\circ} 2'$  below axis  $a$ .

Double refraction,  $N_{\gamma-a} = 0.0108$ .

General formula for the intermediate refractive index  $\beta$ , corrected to a vacuum (correction + 0.0004) :—

$$\beta = 1.5200 + \frac{546\,452}{\lambda^2} - \frac{170\,930\,000\,000}{\lambda^4} + \dots$$

The  $\alpha$  indices are also reproduced by the formula if the constant 1.5200 be diminished by 0.0047, and the  $\gamma$  indices if the constant be increased by 0.0063.

*Observations of refractive index at  $65^{\circ}$*  with one of the prisms indicated the usual slight diminution of refraction with rise of temperature, the amount indicated for  $50^{\circ}$  C. of rise of temperature (from  $15^{\circ}$  to  $65^{\circ}$ ) being about 0.0012.

*Axial Ratios of the Optical Ellipsoid.*—The values of these constants for the two types of ellipsoid are as under :—

$$\alpha : \beta : \gamma = 0.9970 : 1 : 1.0040.$$

$$a : b : c = 1.0030 : 1 : 0.9960.$$

*Molecular Optical Constants.*—These work out as under:—

	Axis of optical indicatrix . . .	$\alpha$ .	$\beta$ .	$\gamma$ .	
LORENZ	Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$ . . .	C	0·1009	0·1017	0·1027
		G	0·1036	0·1043	0·1054
„	Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$ . . .	C	71·74	72·29	72·99
		G	73·64	74·16	74·91
„	Specific dispersion, $n_G - n_C$ . . . . .		0·0027	0·0026	0·0027
„	Molecular dispersion, $m_G - m_C$ . . . . .		1·90	1·87	1·92
GLADSTONE	Molecular refraction, $\frac{n - 1}{d} M$ . . . . .	C	122·99	124·11	125·56

Mean molecular refraction (GLADSTONE),  $\frac{1}{3}(\alpha + \beta + \gamma) = 124·22$ .

*Ammonium Ferrous Selenate*  $(NH_4)_2 Fe (SeO_4)_2 \cdot 6H_2O$ .

*Morphology.*

An investigation of ammonium ferrous selenate, as regards goniometry and specific gravity only, was carried out by HALDOR TOPSØE\* in the year 1870, and as regards the optics of the crystals by TOPSØE and CHRISTIANSEN† in 1874.

The crystals employed in the present investigation were prepared by the method described in the introduction, the ferrous selenate being prepared by the action of selenic acid on ferrous sulphide. They were clear and transparent, and of a very pale yellowish green colour. Ten excellent little crystals were measured, belonging to eight different crops.

*Crystal System.*—Monoclinic. Class No. 5, holohedral-prismatic.

*Ratios of Axes.*— $a : b : c = 0·7433 : 1 : 0·5019$ . Values of TOPSØE,  $0·7405 : 1 : 0·5012$ .

*Axial Angle.*— $\beta = 106^\circ 9'$ . Value of TOPSØE,  $106^\circ 13'$ .

*Forms Observed.*— $b \{010\}$ ,  $c \{001\}$ ,  $p \{110\}$ ,  $q \{011\}$ ,  $r' \{\bar{2}01\}$ , and  $o' \{\bar{1}11\}$ . The same forms, and these only, were observed by TOPSØE.

*Habit.*—From somewhat (thick) tabular parallel to  $c \{001\}$ , to short prismatic parallel to  $p \{110\}$  and the vertical axis  $c$ , and with  $r' \{\bar{2}01\}$  more prominent than usual in the series.

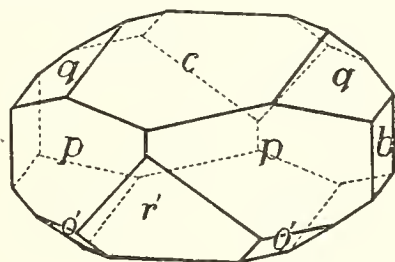


Fig. 8.

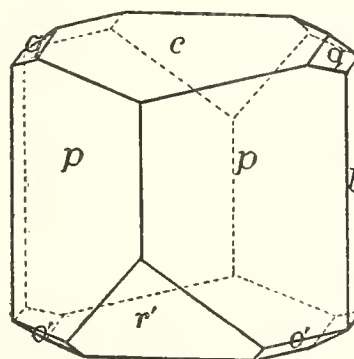


Fig. 9.

A typical crystal of the first type is represented in fig. 8, and one of the second type in fig. 9.

\* 'Kryst.-kem. Unders. o. d. selens. Salte, Dissertation,' Copenhagen, 1870.

† 'Ann. Chim. Phys.' (1874), series 5, vol. 1, p. 83.

## INTERFACIAL Angles of Ammonium Ferrous Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of TOPSØE.
$ac = (100) : (001)$	—	—	—	73 51	—	—
$as = (100) : (101)$	—	—	—	45 13	—	—
$sc = (101) : (001)$	—	—	—	28 38	—	—
$cr' = (001) : (201)$	19	64 16- 64 26	64 22	64 17	5	64 24
$cs' = (001) : (\bar{1}01)$	—	—	—	38 36	—	—
$s'r' = (\bar{1}01) : (201)$	—	—	—	25 41	—	—
$r'a = (201) : (\bar{1}00)$	—	—	—	41 52	—	—
$r'c = (201) : (00\bar{1})$	19	115 33-115 50	115 38	115 43	5	—
$ap = (100) : (110)$	—	—	—	35 30	—	—
$pp' = (110) : (120)$	—	—	—	19 28	—	—
$p'b = (120) : (010)$	—	—	—	35 2	—	—
$pp''' = (110) : (130)$	—	—	—	29 27	—	—
$p'''b = (130) : (010)$	—	—	—	25 3	—	—
$pb = (110) : (010)$	12	54 27- 54 44	54 33	54 30	3	54 28
$pp = (110) : (\bar{1}\bar{1}0)$	20	70 46- 71 13	71 0	*	—	70 50
$pp = (110) : (\bar{1}\bar{1}0)$	20	108 41-109 17	109 0	109 0	0	—
$cq = (001) : (011)$	35	25 37- 25 56	25 44	*	—	25 42
$qb = (011) : (010)$	11	64 11- 64 24	64 17	64 16	1	64 19
$qq = (011) : (01\bar{1})$	17	128 19-128 36	128 31	128 32	1	—
$ao = (100) : (111)$	—	—	—	48 25	—	—
$oq = (111) : (011)$	—	—	—	27 5	—	—
$aq = (100) : (011)$	—	—	—	75 30	—	—
$qo' = (011) : (\bar{1}\bar{1}1)$	—	—	—	34 48	—	34 34
$o'a = (\bar{1}\bar{1}1) : (\bar{1}00)$	—	—	—	69 42	—	—
$co = (001) : (111)$	—	—	—	34 14	—	—
$op = (111) : (110)$	—	—	—	42 41	—	—
$cp = (001) : (110)$	40	76 47- 77 2	76 55	*	—	76 54
$po' = (110) : (\bar{1}\bar{1}\bar{1})$	6	58 0- 58 20	58 10	58 13	3	57 59
$o'c = (\bar{1}\bar{1}\bar{1}) : (00\bar{1})$	7	44 41- 45 6	44 55	44 52	3	—
$pc = (110) : (00\bar{1})$	40	102 55-103 15	103 5	103 5	0	103 9
$bn = (010) : (121)$	—	—	—	54 33	—	—
$no = (121) : (111)$	—	—	—	15 51	—	—
$bo = (010) : (111)$	—	—	—	70 24	—	—
$os = (111) : (101)$	—	—	—	19 36	—	—
$bo' = (010) : (\bar{1}\bar{1}\bar{1})$	4	65 2- 65 20	65 11	65 7	4	—
$o's' = (\bar{1}\bar{1}\bar{1}) : (\bar{1}01)$	—	—	—	24 53	—	—
$o'o' = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1})$	1	—	49 47	49 46	1	49 42
$sq = (101) : (011)$	—	—	—	37 45	—	—
$qp = (011) : (\bar{1}\bar{1}0)$	31	87 10- 87 22	87 16	87 15	1	87 27
$ps = (\bar{1}\bar{1}0) : (\bar{1}0\bar{1})$	—	—	—	55 0	—	—
$pq = (\bar{1}\bar{1}0) : (0\bar{1}\bar{1})$	31	92 39- 92 52	92 44	92 45	1	—
$s'q = (\bar{1}01) : (011)$	—	—	—	45 15	—	—
$qn = (011) : (121)$	—	—	—	26 23	—	—
$np = (121) : (110)$	—	—	—	36 29	—	—
$qp = (011) : (110)$	33	62 45- 63 1	62 53	62 52	1	62 51
$ps' = (110) : (10\bar{1})$	—	—	—	71 53	—	—
$pq = (110) : (0\bar{1}\bar{1})$	33	116 59-117 22	117 8	117 8	0	—
$r'o' = (201) : (\bar{1}\bar{1}\bar{1})$	7	35 5- 35 13	35 9	35 9	0	34 56
$o'p = (\bar{1}\bar{1}\bar{1}) : (110)$	5	91 52- 92 21	92 12	92 10	2	—
$pr' = (110) : (20\bar{1})$	34	52 28- 52 46	52 36	52 41	5	52 35
$r'p = (201) : (110)$	34	127 15-127 33	127 24	127 19	5	—
Total number of measurements . .	459					



Although the crystals were largely of the two principal types just mentioned, and shown in the figures, practically all the types of crystals met with in this large series of double sulphates and double selenates were observed. That is, crystals were found of the three main types (and also of all intermediate varieties) which have been shown in previous communications to be characteristic respectively of the potassium, rubidium, and caesium salts of the series; namely, for the potassium salts prismatic parallel  $p\{110\}$  with large broad  $c\{001\}$ , and very small  $q\{011\}$ , for the caesium salts prismatic parallel  $q\{011\}$  with narrow  $c\{001\}$ , and for the rubidium salts the midway type with only moderately prominent  $c\{001\}$  faces and with  $q\{011\}$  faces relatively smaller than the immense ones of the caesium salts yet larger than the very small ones of the potassium salts. One prominent characteristic was noticeable, however, on these crystals of ammonium ferrous selenate, namely, the very pronounced development of the orthopinakoid  $r'\{\bar{2}01\}$ . This form is characteristically well and often obtrusively developed in all the iron salts of this grand series, both those of the double sulphates and those of the double selenates, and is remarkably so in the common well-known salt ferrous ammonium sulphate, which ferrous ammonium selenate closely resembles.

The reflections from the crystals measured were of general excellence, and relatively but little trouble was experienced from striation of the  $c$  and  $p$ -faces. Certain crops rarely showed any traces of the faces of  $b\{010\}$  and  $o'\{\bar{1}11\}$ , while on the crystals of other crops these faces were quite well developed.

*Cleavage.*—A good cleavage was observed parallel to  $r'\{\bar{2}01\}$ , the cleavage direction common to the whole series. No trace could be discovered of cleavage parallel to  $b\{010\}$ , which has been observed to be developed in some of the ammonium salts of the series.

#### *Volume.*

*Relative Density.*—Four determinations by the immersion method yielded the following values:—

I. Density for $17^{\circ}9/4^{\circ}$ . . .	2.1915	For $20^{\circ}/4^{\circ}$ . . .	2.1910
II. „ „ $19^{\circ}0/4^{\circ}$ . . .	2.1904	„ $20^{\circ}/4^{\circ}$ . . .	2.1902
III. „ „ $19^{\circ}1/4^{\circ}$ . . .	2.1914	„ $20^{\circ}/4^{\circ}$ . . .	2.1912
IV. „ „ $18^{\circ}8/4^{\circ}$ . . .	2.1914	„ $20^{\circ}/4^{\circ}$ . . .	2.1911
		Mean . . .	2.1909

Accepted value for  $20^{\circ}/4^{\circ}$ , **2.191**.

The value 2.160 was obtained by TOPSØE.

*Molecular Volume.*— $\frac{M}{d} = \frac{482.88}{2.191} = 220.39$ .

*Molecular Distance Ratios (topic axial ratios).*—

$$\chi : \psi : \omega = 6.3212 : 8.5043 : 4.2684.$$

*Optics.*

*Nature and Orientation of the Optical Ellipsoid.*—The optic axes lie in the symmetry plane  $b\{010\}$ . The sign of the double refraction is positive, the first median line corresponding to the refractive index  $\gamma$ , and the second median line to  $\alpha$ .

Extinction determinations with two section-plates ground parallel to the symmetry plane afforded the following results with respect to the normal to  $c\{001\}$ .

*Extinction Direction in the Symmetry Plane.*

Plate 1 . . .	$11^\circ 2'$ ,	Plate 2 . . .	$10^\circ 28'$ .
Mean . . .	$10^\circ 45'$ , behind the normal to $c\{001\}$ .		

This direction, between the normal to  $c\{001\}$  and the vertical axis  $c$ , is the second median line. As the angle between the normal to  $c\{001\}$  and the vertical axis is  $16^\circ 9'$  (the acute axial angle  $ac$  being  $73^\circ 51'$ ), the inclination of the second median line to and in front of the vertical axis  $c$  is  $5^\circ 24'$ . The rectangular direction (the other axis of the optical ellipsoid also lying in the symmetry plane) is the first median line, and is inclined  $10^\circ 45'$  to and above the inclined axis  $\alpha$ . Both median

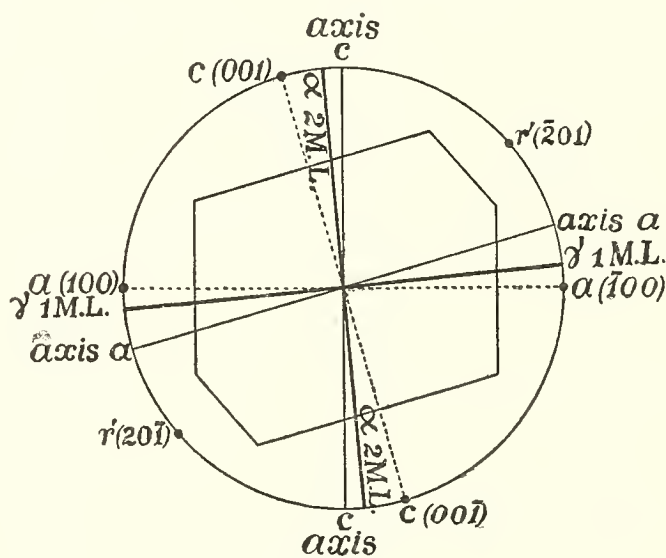


Fig. 10.

lines thus lie in the obtuse axial angle  $ac$ , and the positions will be rendered clear by a reference to fig. 10.

TOPSØE and CHRISTIANSEN (*loc. cit.*) give  $6^\circ 50'$  and  $9^\circ 23'$  for the two extinction positions, axis  $c$ : second median line, and axis  $\alpha$ : first median line, respectively.

*Optic Axial Angle.*—Three pairs of section plates, ground perpendicular to the first and second median lines respectively, afforded the values given in the two following tables for the apparent optic axial angle in air 2E, and the apparent acute and obtuse optic axial angles in monobromonaphthalene  $2H_a$  and  $2H_o$ . The values of

the true optic axial angle  $2V_a$  from these two latter determinations are given in the penultimate column of the second table, and the mean  $2V_a$  in the last column.

APPARENT Optic Axial Angle in Air,  $2E$ , of AmFe Selenate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean $2E$ .
	° /	° /	° /	° /
Li . . . . .	145 35	145 50	145 37	145 41
C . . . . .	145 53	146 18	145 51	146 1
Na . . . . .	148 56	149 4	147 46	148 35
Tl . . . . .	149 21	149 40	149 10	149 24
Cd . . . . .	151 8	150 7	150 18	150 31
F . . . . .	152 10	151 0	151 20	151 30

DETERMINATION of True Optic Axial Angle, in Bromonaphthalene, of AmFe Selenate.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp. 2 M.L.	Observed $2H_o$ .	Calculated $2V_a$ .	Mean $2V_a$ .
		° /		° /	° /	° /
Li . . . . .	1	70 28	1a	91 45	77 34	77 36
	2	70 32	2a	91 47	77 36	
	3	70 32	3a	91 42	77 38	
C . . . . .	1	70 27	1a	91 43	77 35	77 37
	2	70 31	2a	91 44	77 37	
	3	70 30	3a	91 39	77 39	
Na . . . . .	1	70 14	1a	91 10	77 42	77 44
	2	70 24	2a	91 15	77 46	
	3	70 17	3a	91 7	77 45	
Tl . . . . .	1	70 2	1a	90 37	77 49	77 50
	2	70 8	2a	90 42	77 50	
	3	70 5	3a	90 36	77 52	
Cd . . . . .	1	69 53	1a	90 21	77 50	77 52
	2	69 59	2a	90 26	77 52	
	3	69 55	3a	90 18	77 54	
F . . . . .	1	69 48	1a	90 13	77 52	77 54
	2	69 51	2a	90 12	77 54	
	3	69 45	3a	90 0	77 56	

The values obtained by TOPSØE and CHRISTIANSEN were for  $2E$   $142^\circ 50'$  and for  $2V_a$   $76^\circ 48'$ .

*Dispersion of the Median Lines.*—This is very small, and was determined with section-plate No. 3 immersed in monochlorbenzene, the refractive index of which

(1.5248 for Na-light) is very close to the mean refractive index of the crystals. The median lines are so dispersed in the symmetry plane that the first median line lies nearer to the inclined crystal-axis  $a$  by  $9'$  for red Li-light than for green Cd-light.

*Effect of Temperature on the Optic Axial Angle.*—Determinations with section-plate No. 2 at  $75^\circ$  C. showed that the apparent optic axial angle in air 2E diminished by  $11^\circ 24'$  on heating the plate to  $75^\circ$ , the angle being  $137^\circ 40'$  for Na-light at this temperature, whereas for  $15^\circ$  it was  $149^\circ 4'$ .

*Refractive Indices.*—Six  $60^\circ$ -prisms were ground, the two faces of each being symmetrical to ( $30^\circ$  from) a principal axial plane of the optical ellipsoid, and the refracting edge of each being parallel to a principal axis of the ellipsoid. Each prism thus yielded directly two of the three refractive indices  $\alpha$ ,  $\beta$ ,  $\gamma$ , and the combination of prisms was so arranged that  $\alpha$ ,  $\beta$ , and  $\gamma$  were each obtained four times in all. The four individual results for each index, for each of the seven wave-lengths employed, were remarkably close, and the final mean values of the four are given in the next table.

REFRACTIVE Indices of Ammonium Ferrous Selenate.

Light.	$\alpha$ .	$\beta$ .	$\gamma$ .
Li . . . . .	1.5177	1.5241	1.5343
C . . . . .	1.5182	1.5246	1.5348
Na . . . . .	1.5216	1.5280	1.5381
Tl . . . . .	1.5251	1.5314	1.5416
Cd . . . . .	1.5271	1.5334	1.5437
F. . . . .	1.5291	1.5354	1.5457
G. . . . .	1.5356	1.5422	1.5524

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.5292.

$\alpha$  = Vibration direction parallel to second median line,  $5^\circ 24'$  in front of vertical axis  $c$ .

$\beta$  = " " " " symmetry axis  $b$ .

$\gamma$  = " " " " first median line,  $10^\circ 45'$  above inclined axis  $a$ .

Double refraction,  $\text{Na}_{\gamma-\alpha} = 0.0165$ .

Only the  $\beta$ -indices were determined directly by TOPSØE and CHRISTIANSEN, for C, Na, and F-light, the values obtained being respectively 1.5226, 1.5260, and 1.5334.

General formula for  $\beta$ , for light of any wave-length  $\lambda$ , corrected to a vacuum (correction + 0.004) :—

$$\beta = 1.5076 + \frac{862\,174}{\lambda^2} - \frac{4\,865\,900\,000\,000}{\lambda^4} + \dots$$

The  $\alpha$  indices are equally well reproduced by the formula if the constant 1.5076 be diminished by 0.0064, and the  $\gamma$  indices if it be increased by 0.0102.

*Observations at  $65^\circ$  C.* indicated that the index  $\alpha$  diminishes by 0.0013 on heating to this temperature,  $\beta$  by 0.0016, and  $\gamma$  by 0.0018.

*Axial Ratios of the Optical Ellipsoid.*—The calculated values for the two types of ellipsoid are as under :—

Indicatrix . . . . .  $\alpha : \beta : \gamma = 0.9958 : 1 : 1.0066$ .  
 Optical Velocity Ellipsoid . . . . .  $a : b : c = 1.0042 : 1 : 0.9934$ .

*Molecular Optical Constants.*—These are given in the next table, calculated by both the formulas of LORENZ and of GLADSTONE and DALE.

	Axis of optical indicatrix . . .	$\alpha$ .	$\beta$ .	$\gamma$ .	
LORENZ	Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$ . . .	{ C	0.1384	0.1398	0.1420
		{ G	0.1422	0.1437	0.1459
,,	Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$ . . .	{ C	66.81	67.50	68.59
		{ G	68.68	69.38	70.46
,,	Specific dispersion, $n_G - n_C$ . . . . .	0.0038	0.0039	0.0039	
,,	Molecular dispersion, $m_G - m_C$ . . . . .	1.87	1.88	1.87	
GLADSTONE	Molecular refraction, $\frac{n - 1}{d} M$ . . . . . C	114.21	115.62	117.87	

Mean molecular refraction (GLADSTONE),  $\frac{1}{3}(\alpha + \beta + \gamma) = 115.90$ .

*Comparison of Results.*

The successful completion of the investigation of the potassium salt of this ferrous iron group enables a full comparison to be made of the crystals of all the four salts of this group, on exactly the same lines as the four salts of each of the three groups (zinc, magnesium, and nickel) of double selenates already described have been compared. The fact that crystals of potassium ferrous selenate only form at temperatures very near to 0° C., and spontaneously decompose into an opaque porcelain-like substance, in less than half a day in moderately cold weather and almost immediately at the temperature of a warm day, together with the fact that the crystals of caesium ferrous selenate are magnificently transparent and relatively permanent, capable of preservation in closed vessels for years, afford striking proof of the *progression in stability* with the rise of atomic weight and atomic number of the alkali metal.

*Habit.*—The progression in habit which has been observed in the other groups of both double selenates and double sulphates is very clearly exhibited by the ferrous iron group of double selenates. An inspection of figs. 1 and 2 (potassium salt), 4 (rubidium salt), and 6 (caesium salt) will make clear the progressive diminution in the relative development of the faces of  $c \{001\}$ , and the relative growth of the faces of  $q \{011\}$  from very small and subordinate in the potassium salt to predominatingly large in the caesium salt, through the intermediate stage of a moderate size in the rubidium salt. The importance of the faces of  $p \{110\}$  similarly diminishes more or

less regularly from the potassium to the caesium salt, through the rubidium salt. The ammonium salt, shown in figs. 8 and 9, forms crystals of all types of development, but a great majority are of the intermediate type exhibited in fig. 8. Fig. 9 illustrates a crystal showing faces of  $c\{001\}$  and  $g\{011\}$  very like those of a potassium salt of the series. In all four salts of the iron group there is a marked tendency for a larger development of the faces of  $r'\{201\}$  than in the other groups of double selenates studied. A similar fact was observed with respect to the ferrous iron group of double sulphates.

*Crystal Elements and Angles.*—The axial angles and axial ratios are compared in the following table.

COMPARISON of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	$\beta$ .	$a : b : c$
Potassium ferrous selenate . .	$103^{\circ} 50'$	$0.7490 : 1 : 0.5044$
Rubidium „ „ . .	$104^{\circ} 57'$	$0.7424 : 1 : 0.5000$
Ammonium „ „ . .	$106^{\circ} 9'$	$0.7433 : 1 : 0.5019$
Cæsium „ „ . .	$106^{\circ} 2'$	$0.7308 : 1 : 0.4979$

The differences between the morphological axial angles of the three alkali metallic salts are  $1^{\circ} 7'$  between the potassium and rubidium salts,  $1^{\circ} 5'$  between the rubidium and caesium salts, and  $2^{\circ} 12'$  between the potassium and caesium salts. Obviously, therefore, the axial angle  $\beta$  increases in direct proportion to the increase of the atomic weight and atomic number of the alkali metal. As the values of the two latter constants will be constantly required in the course of these comparisons, they are given below for reference.

	K.	Rb - K.	Rb.	Cs - Rb.	Cs.	Cs - K.
Atomic weights . .	38.85	46	84.9	47	131.9	$93 = 2 \times 46.5$
Atomic numbers . .	19	18	37	18	55	$36 = 2 \times 18$

As rubidium stands precisely half-way between potassium and caesium as regards atomic weight and atomic number, so does the crystallographic (monoclinic) axial angle  $\beta$  stand half-way in the case of the rubidium salt.

The axial angle of ammonium ferrous selenate is very nearly identical with ( $7'$  larger than) that of the caesium salt.

The morphological axial ratios of the rubidium salt are intermediate between those for the potassium and caesium salts. Those of the ammonium salt are close to those of the rubidium salt, and thus partake of an intermediate character in the group. This fact is in complete harmony with the supposition of true isomorphism of the ammonium salt with the three alkali metallic salts of the group.

The following table institutes a complete comparison of the crystal angles of the four salts. A careful analysis of these results has been made, by tabulating all the differences between analogous angles of the four salts, and the results of the analysis are concentrated in the short table which follows that of the angles.

COMPARISON of the Interfacial Angles.

Angle.	KFe selenate.	RbFe selenate.	CsFe selenate.	AmFe selenate.
$\left\{ \begin{array}{l} ac = (100) : (001) \\ as = (100) : (101) \\ sc = (101) : (001) \\ cr' = (001) : (\bar{2}01) \\ cs' = (001) : (\bar{1}01) \\ s'r' = (\bar{1}01) : (\bar{2}01) \\ r'a = (\bar{2}01) : (\bar{1}00) \end{array} \right.$	$\begin{array}{l} 76 \ 10 \\ 46 \ 46 \\ 29 \ 24 \\ 62 \ 38 \\ 37 \ 58 \\ 24 \ 40 \\ 41 \ 12 \end{array}$	$\begin{array}{l} 75 \ 3 \\ 46 \ 2 \\ 29 \ 1 \\ 63 \ 24 \\ 38 \ 15 \\ 25 \ 9 \\ 41 \ 33 \end{array}$	$\begin{array}{l} 73 \ 58 \\ 45 \ 9 \\ 28 \ 49 \\ 64 \ 29 \\ 38 \ 51 \\ 25 \ 38 \\ 41 \ 33 \end{array}$	$\begin{array}{l} 73 \ 51 \\ 45 \ 13 \\ 28 \ 38 \\ 64 \ 17 \\ 38 \ 36 \\ 25 \ 41 \\ 41 \ 52 \end{array}$
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp' = (110) : (120) \\ p'b = (120) : (010) \\ pb = (110) : (010) \\ pp''' = (110) : (130) \\ p''b = (130) : (010) \end{array} \right.$	$\begin{array}{l} 36 \ 1 \\ 19 \ 28 \\ 34 \ 31 \\ 53 \ 59 \\ 29 \ 21 \\ 24 \ 38 \end{array}$	$\begin{array}{l} 35 \ 39 \\ 19 \ 28 \\ 34 \ 53 \\ 54 \ 21 \\ 29 \ 25 \\ 24 \ 56 \end{array}$	$\begin{array}{l} 35 \ 7 \\ 19 \ 28 \\ 35 \ 25 \\ 54 \ 53 \\ 29 \ 31 \\ 25 \ 22 \end{array}$	$\begin{array}{l} 35 \ 30 \\ 19 \ 28 \\ 35 \ 2 \\ 54 \ 30 \\ 29 \ 27 \\ 25 \ 3 \end{array}$
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qb = (011) : (010) \end{array} \right.$	$\begin{array}{l} 26 \ 6 \\ 63 \ 54 \end{array}$	$\begin{array}{l} 25 \ 47 \\ 64 \ 13 \end{array}$	$\begin{array}{l} 25 \ 34 \\ 64 \ 26 \end{array}$	$\begin{array}{l} 25 \ 44 \\ 64 \ 16 \end{array}$
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \\ aq = (100) : (011) \\ qo' = (011) : (\bar{1}11) \\ o'a = (\bar{1}11) : (\bar{1}00) \end{array} \right.$	$\begin{array}{l} 49 \ 59 \\ 27 \ 37 \\ 77 \ 36 \\ 34 \ 12 \\ 68 \ 12 \end{array}$	$\begin{array}{l} 49 \ 13 \\ 27 \ 21 \\ 76 \ 34 \\ 34 \ 28 \\ 68 \ 58 \end{array}$	$\begin{array}{l} 48 \ 19 \\ 27 \ 16 \\ 75 \ 35 \\ 35 \ 3 \\ 69 \ 22 \end{array}$	$\begin{array}{l} 48 \ 25 \\ 27 \ 5 \\ 75 \ 30 \\ 34 \ 48 \\ 69 \ 42 \end{array}$
$\left\{ \begin{array}{l} co = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \\ po' = (110) : (11\bar{1}) \\ o'c = (11\bar{1}) : (00\bar{1}) \end{array} \right.$	$\begin{array}{l} 35 \ 9 \\ 43 \ 42 \\ 78 \ 51 \\ 56 \ 54 \\ 44 \ 15 \end{array}$	$\begin{array}{l} 34 \ 38 \\ 43 \ 16 \\ 77 \ 54 \\ 57 \ 39 \\ 44 \ 27 \end{array}$	$\begin{array}{l} 34 \ 18 \\ 42 \ 39 \\ 76 \ 57 \\ 58 \ 7 \\ 44 \ 56 \end{array}$	$\begin{array}{l} 34 \ 14 \\ 42 \ 41 \\ 76 \ 55 \\ 58 \ 13 \\ 44 \ 52 \end{array}$
$\left\{ \begin{array}{l} bo = (010) : (111) \\ os = (111) : (101) \end{array} \right.$	$\begin{array}{l} 69 \ 49 \\ 20 \ 11 \end{array}$	$\begin{array}{l} 70 \ 12 \\ 19 \ 48 \end{array}$	$\begin{array}{l} 70 \ 34 \\ 19 \ 26 \end{array}$	$\begin{array}{l} 70 \ 24 \\ 19 \ 36 \end{array}$
$\left\{ \begin{array}{l} bo' = (010) : (\bar{1}11) \\ o's' = (\bar{1}11) : (\bar{1}01) \end{array} \right.$	$\begin{array}{l} 65 \ 17 \\ 24 \ 43 \end{array}$	$\begin{array}{l} 65 \ 20 \\ 24 \ 40 \end{array}$	$\begin{array}{l} 65 \ 21 \\ 24 \ 39 \end{array}$	$\begin{array}{l} 65 \ 7 \\ 24 \ 53 \end{array}$
$\left\{ \begin{array}{l} sq = (101) : (011) \\ qp = (011) : (\bar{1}10) \\ ps = (\bar{1}10) : (\bar{1}0\bar{1}) \end{array} \right.$	$\begin{array}{l} 38 \ 31 \\ 85 \ 8 \\ 56 \ 21 \end{array}$	$\begin{array}{l} 38 \ 3 \\ 86 \ 17 \\ 55 \ 40 \end{array}$	$\begin{array}{l} 37 \ 47 \\ 87 \ 27 \\ 54 \ 46 \end{array}$	$\begin{array}{l} 37 \ 45 \\ 87 \ 15 \\ 55 \ 0 \end{array}$
$\left\{ \begin{array}{l} s'q = (\bar{1}01) : (011) \\ qp = (011) : (110) \\ ps' = (110) : (10\bar{1}) \end{array} \right.$	$\begin{array}{l} 44 \ 55 \\ 64 \ 23 \\ 70 \ 42 \end{array}$	$\begin{array}{l} 45 \ 0 \\ 63 \ 45 \\ 71 \ 15 \end{array}$	$\begin{array}{l} 45 \ 22 \\ 63 \ 8 \\ 71 \ 30 \end{array}$	$\begin{array}{l} 45 \ 15 \\ 62 \ 52 \\ 71 \ 53 \end{array}$
$\left\{ \begin{array}{l} r'o' = (\bar{2}01) : (\bar{1}11) \\ o'p = (\bar{1}11) : (110) \\ pr' = (110) : (\bar{2}0\bar{1}) \end{array} \right.$	$\begin{array}{l} 34 \ 22 \\ 93 \ 7 \\ 52 \ 31 \end{array}$	$\begin{array}{l} 34 \ 39 \\ 92 \ 48 \\ 52 \ 33 \end{array}$	$\begin{array}{l} 34 \ 59 \\ 92 \ 46 \\ 52 \ 15 \end{array}$	$\begin{array}{l} 35 \ 9 \\ 92 \ 10 \\ 52 \ 41 \end{array}$

## ANGULAR Changes for Double Selenates containing Ferrous Iron.

Replacement.	Average change.	Maximum change.
K by Rb . . . . .	27	69 = 1 9
K by Cs . . . . .	55	139 = 2 19
K by NH <sub>4</sub> . . . . .	54	139 = 2 19

In 37 of the 38 angles compared the value for the rubidium salt is intermediate between the values for the potassium and caesium salts. In the case of the single exception the change is very small.

The average and maximum changes of angle are exactly twice as large when potassium is replaced by caesium as when potassium is replaced by rubidium, corresponding precisely to the change in atomic weight ( $K \sim Cs = 93$  and  $K \sim Rb = 46$ ), or atomic number ( $K \sim Cs = 36$  and  $K \sim Rb = 18$ ). Thus the average change of angle, and also the maximum amount of angular alteration observed, are directly proportional to the change in the atomic weight or number.

As regards the position of the ammonium salt, in 35 of the 38 compared angles the changes for the K by NH<sub>4</sub> replacement are in the same direction as for the metallic replacements K by Rb and K by Cs, and the other three are cases where the changes are very minute.

In 34 of these 35 cases the changes for the K by NH<sub>4</sub> replacement are greater than when potassium is replaced by rubidium, and in 15 of them the changes are somewhat greater than those which occur when potassium is replaced by caesium. When all the K by NH<sub>4</sub> changes are added together (as regards amounts, irrespective of sign), and the mean taken, in the same manner as was done for the metallic replacements, this average change for the ammonium replacement of potassium is found to be practically identical with the average change which occurs when potassium is replaced by caesium; the maximum amount of change observed (for K by NH<sub>4</sub>) is also identical with that which occurs for the K by Cs replacement. Thus the angular effect of replacing potassium by ammonium is of the same order as that of the weightier metallic interchange, a fact in full keeping with the supposition of the isomorphism.

*Volume Constants.*—The densities, molecular volumes and topic axial ratios are compared in the next table.



## VOLUME Constants of the Iron Group of Double Selenates.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
KFe selenate . .	524.72	2.494	210.39	$\chi$ : $\psi$ : $\omega$ 6.2230 : 8.3085 : 4.1908
RbFe „ . .	616.82	2.800	220.29	6.3109 : 8.5006 : 4.2503
CsFe „ . .	710.82	3.048	233.21	6.3847 : 8.7366 : 4.3499
NH <sub>4</sub> Fe „ . .	482.88	2.191	220.39	6.3212 : 8.5043 : 4.2684

The *density* increases with the atomic weight of the alkali metal, and is greater by 6 to 5 for the K by Rb replacement than for the Rb by Cs interchange. The ammonium salt is the lightest member of the group, corresponding to the low molecular weight of the radicle NH<sub>4</sub>.

The *molecular volumes* of the three alkali metallic salts progress at an accelerating rate with the rise in atomic weight or atomic number of the alkali metal. When potassium is replaced by rubidium the increase is to the extent of 9.9 units, but when rubidium is replaced by caesium the increase amounts to 12.92 units. The interchange of caesium for potassium is accompanied by an increase of 22.82 units. The molecular volume of ammonium ferrous selenate is almost exactly identical with that of rubidium ferrous selenate, being 0.1 unit higher, the replacement of potassium by ammonium being accompanied by an increase of exactly 10 units.

The *topic axial ratios* follow similar rules, being the directional expression of the volume along the directions of the crystallographic axes, and proportionately to the lengths of those axes. The values of corresponding ratios are always intermediate in the case of the rubidium salt, between the values for the potassium and caesium salts; a regular extension of the edges of the unit cell of the structural space-lattice thus occurs as potassium is replaced by rubidium and the latter in turn by caesium. The lengths of the cell edges for the ammonium salt are almost the same as, very slightly greater than, those for rubidium ferrous selenate.

This striking fact of the congruency of the ammonium and rubidium salts—which is in keeping with all the author's previous results for the other groups of double selenates yet investigated, for the whole of the groups of double sulphates of this monoclinic series, and for the two rhombic groups of simple alkali sulphates and selenates—affords yet another confirmation of those former results, and further substantiates the important conclusions which were drawn therefrom in a memoir\* read to the Royal Society in November, 1916.

*Cleavage.*—All four salts exhibit the development of cleavage parallel to  $r'\{\bar{2}01\}$ , the cleavage common to the whole series. Some of the ammonium salts of the series

\* 'Roy. Soc. Proc.,' A, vol. 93, p. 72 (1917).

have in addition shown cleavage parallel to the symmetry plane,  $b \{010\}$ , but this has not been observed in the case of ammonium ferrous selenate.

*Orientation of the Optical Ellipsoid.*—The optical ellipsoid (either the indicatrix or the optical velocity ellipsoid) rotates on the symmetry axis  $b$  of the crystal—which is identical with the intermediate axis of the ellipsoid ( $\beta$  of the indicatrix or  $\mathfrak{b}$  of the velocity ellipsoid) and is the only one of the three axes which is fixed, in accordance with monoclinic symmetry—when one of the alkali bases is replaced by another. The best mode of comparing its position is to state the inclination of the  $\alpha$  axis of the indicatrix or  $\mathfrak{a}$  axis of the velocity ellipsoid to the vertical crystal-axis  $c$ , as is done in the next table.

*Inclinations of  $\alpha$ -Extinctions of the Fe Double Selenates in front of Axis  $c$ .*  
(2M.L. in all four salts.)

AmFe selenate	$5^{\circ} 24'$	RbFe selenate	$13^{\circ} 37'$ ,
KFe	„ $10^{\circ} 27'$	CsFe	„ $21^{\circ} 4'$ .

The table is also expressed graphically in fig. 11, which further shows the positions of the other perpendicular axis  $\gamma$  also lying in the symmetry plane, which is that of

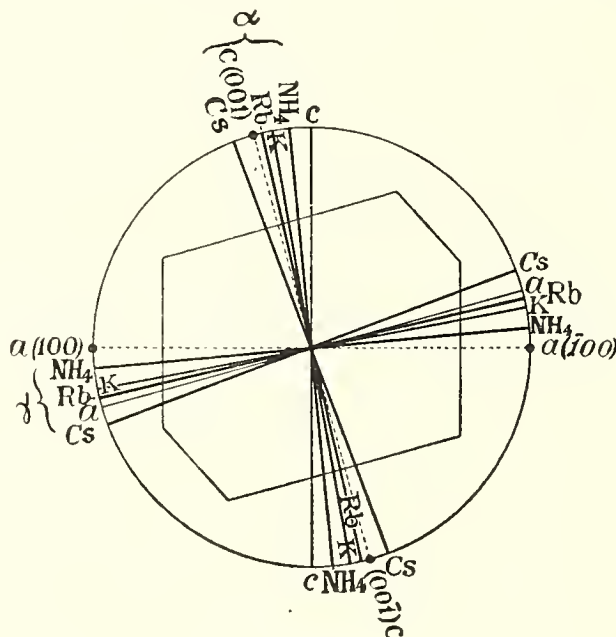


Fig. 11.

the paper. The  $\alpha$  axis is the second median line (obtuse bisectrix of optic axial angle) in all four salts, the  $\gamma$  axis being the direction of the first median line (acute bisectrix of optic axial angle).

The position of the ellipsoid is seen to be such that its axis lies close in front of (only  $5^{\circ} 24'$  from) the vertical axis  $c$ , in the case of the ammonium salt; it rotates so that its  $\alpha$  axis is  $10^{\circ} 27'$  from axis  $c$  for the potassium salt; further, till the axis is  $13^{\circ} 37'$  inclined for the rubidium salt, and still further to  $21^{\circ} 4'$  for the caesium salt.

The position of the ellipsoid for the rubidium salt is thus intermediate between its positions for the potassium and cæsium salts, and the amount of rotation is an accelerating one as the atomic weight and number of the alkali metal rises.

*Optic Axial Angles.*—These can be directly compared, as the double refraction is positive and the first median line is analogously disposed, subject to the rotation just described, in all four salts. The values are set out in the next table.

OPTIC AXIAL ANGLES  $2V_a$  OF THE IRON GROUP OF DOUBLE SELENATES.

	KFe selenate.	RbFe selenate.	AmFe selenate.	CsFe selenate.
Li . . . . .	64 11	73 35	77 36	82 58
C . . . . .	64 12	73 34	77 37	82 56
Na . . . . .	64 18	73 32	77 44	82 47
Tl . . . . .	64 25	73 30	77 50	82 33
Cd . . . . .	64 30	73 28	77 52	82 25
F . . . . .	64 36	73 26	77 54	82 20

It will be apparent that the optic axial angle increases as the atomic weight and number of the alkali metal rises, and the value for the rubidium salt is about midway between the values for the potassium and cæsium salts. The optic axial angle of ammonium ferrous selenate is slightly larger than that of rubidium ferrous selenate.

*Refractive Indices.*—The refractive indices are compared in the table on next page, together with the mean refractive index for sodium light and the magnitude of the double refraction.

It will be observed that the mean refractive index for the rubidium salt is intermediate between the values for the potassium and cæsium salts, although the advance of this specific refractive constant in the case of the rubidium salt is not much beyond that of the potassium salt. The double refraction (difference between  $\alpha$  and  $\gamma$  indices) progressively diminishes (with acceleration) as the atomic weight and number of the alkali metal rises, and the result of this is curious on the  $\gamma$  indices, these indices for the rubidium salt being brought lower than those for the potassium salt. Although the increasingly progressive diminution of the double refraction tends also to reduce the  $\gamma$  indices of the cæsium salt, the rapidly accelerating progressive growth of refracting power causes even these indices of the cæsium salt, like the  $\alpha$  and  $\beta$  indices, to show a clear advance in the refractive indices of this salt. The real progression in the refractive power is shown, however, by the molecular refraction, which will presently be dealt with.

The refractive indices of ammonium ferrous selenate are intermediate between those of rubidium and cæsium ferrous selenates.

## COMPARISON of the Refractive Indices.

Index.	Light.	KFe selenate.	RbFe selenate.	NH <sub>4</sub> Fe selenate.	CsFe selenate.
$\alpha$ . . . . .	Li. . . . .	1.5059	1.5099	1.5177	1.5269
	C . . . . .	1.5064	1.5104	1.5182	1.5274
	Na . . . . .	1.5095	1.5133	1.5216	1.5306
	Tl. . . . .	1.5127	1.5165	1.5251	1.5339
	Cd . . . . .	1.5145	1.5184	1.5271	1.5359
	F . . . . .	1.5164	1.5202	1.5291	1.5379
	G . . . . .	1.5224	1.5264	1.5356	1.5442
$\beta$ . . . . .	Li. . . . .	1.5144	1.5165	1.5241	1.5317
	C . . . . .	1.5149	1.5170	1.5246	1.5322
	Na . . . . .	1.5182	1.5200	1.5280	1.5352
	Tl. . . . .	1.5215	1.5233	1.5314	1.5385
	Cd . . . . .	1.5234	1.5252	1.5334	1.5405
	F . . . . .	1.5253	1.5272	1.5354	1.5425
	G . . . . .	1.5314	1.5334	1.5422	1.5488
$\gamma$ . . . . .	Li. . . . .	1.5306	1.5290	1.5343	1.5379
	C . . . . .	1.5311	1.5295	1.5348	1.5384
	Na . . . . .	1.5345	1.5328	1.5381	1.5414
	Tl. . . . .	1.5379	1.5363	1.5416	1.5450
	Cd . . . . .	1.5399	1.5382	1.5437	1.5470
	F . . . . .	1.5421	1.5404	1.5457	1.5491
	G . . . . .	1.5483	1.5467	1.5524	1.5555
Mean refractive index $\frac{1}{3}(\alpha + \beta + \gamma)$ for Na light		1.5207	1.5220	1.5292	1.5357
Double refraction, $\text{Na}_{\gamma-\alpha}$ . . . . .		0.0250	0.0195	0.0165	0.0108

*Double Refraction.*—This property has been shown to diminish at a rate accelerating with the rise of the atomic weight of the alkali metal. The total diminution between potassium and caesium ferrous selenates is 0.0142. For the two analogous salts of the nickel group last studied\* it was found to be 0.0152; while for the zinc and magnesium groups previously studied it was less and still less, 0.0128 and 0.0112. This smaller change in the double refraction in the two last-mentioned groups was only just adequate to reverse the progression of the  $\gamma$  indices in RbZn and RbMg selenates, these indices being lower than those of KZn and KMg selenates by 0.0004 only.

## AXIAL Ratios of the Optical Indicatrix.

	$\alpha$ : $\beta$ : $\gamma$	$\alpha$ : $\beta$ : $\gamma$
KFe selenate . . . . .	0.9943 : 1 : 1.0107	0.9943 : 1 : 1.0107
RbFe „ . . . . .	0.9956 : 1 : 1.0084	0.9968 : 1.0012 : 1.0096
NH <sub>4</sub> Fe „ . . . . .	0.9958 : 1 : 1.0066	1.0022 : 1.0064 : 1.0131
CsFe „ . . . . .	0.9970 : 1 : 1.0040	1.0082 : 1.0112 : 1.0153

\* 'Phil. Trans.,' A, vol. 217, p. 229 (1917).

## AXIAL Ratios of the Optical Velocity Ellipsoid.

	a	:	b	:	c	a	:	b	:	c
KFe selenate . . .	1.0058	:	1	:	0.9894	1.0058	:	1	:	0.9894
RbFe „ . . .	1.0044	:	1	:	0.9916	1.0032	:	0.9988	:	0.9905
NH <sub>4</sub> Fe „ . . .	1.0042	:	1	:	0.9934	0.9978	:	0.9936	:	0.9871
CsFe „ . . .	1.0030	:	1	:	0.9960	0.9919	:	0.9889	:	0.9849

*Axial Ratios of the Optical Ellipsoid.*—The values of these ratios are given in the two preceding tables. Besides the ratios calculated with the  $\beta$  value for each salt as unity, a second set is given (as in the cases of the previous groups studied) in which the  $\beta$  value for the potassium salt is taken as unity for all the four salts of the group, thus enabling the progress of the axial directional change in the dimensions of the optical ellipsoid to be followed on the passage from one salt to another. The left-hand series show a regular progression with the atomic weight and number of the alkali metal. The right-hand series emphasise the accelerating nature of the change, modified by the effect of the diminution of double refraction in causing the set-back of the  $\gamma$  values, which is apparent in the case of rubidium ferrous selenate.

The position of the ammonium salt is seen to be intermediate between the rubidium and caesium salts, as regards both series of ratios, which may be considered as yet another confirmation that ammonium ferrous sulphate is correctly regarded as truly isomorphous with potassium, rubidium, and caesium ferrous selenates.

*Molecular Optical Constants.*—These constants are as valuable with regard to the optics of the group as were the molecular volumes and topic axial ratios in indicating the true relations of the salts in regard to their morphology. They are given in the next three tables. The conclusions derivable from them are the following.

The whole of the molecular optical constants of the rubidium salt are intermediate between those of the potassium and caesium salts of the group. The important molecular refraction, whether calculated by the formula of LORENZ or by that of GLADSTONE and DALE, increases with increase of atomic weight and atomic number of the interchangeable alkali metals, and at an accelerating rate, the replacements respectively of potassium by rubidium and rubidium by caesium being accompanied by increases in mean molecular refraction of 5.46 and 9.89 Gladstone units, which are in the proportion of 3 : 5. The result is unaffected by temperature change, as the effect of the latter is similar on both the density and refractive power, both diminishing on raising the temperature.

The molecular refraction of the ammonium salt is very close indeed to that of the rubidium salt, being very slightly higher to the extent of one Lorenz or two Gladstone units; the mean molecular refraction by GLADSTONE'S formula is 1.57 higher. This result is analogous to that regarding the structural dimensions, the ammonium salt being shown to be practically isostructural with the rubidium salt.

TABLE of Specific Refraction and Dispersion (LORENZ).

Salt.	Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$ .						Specific dispersion. $n_G - n_C$ .		
	For ray C (Hz).			For ray H $\gamma$ near G.			$\alpha$ .	$\beta$ .	$\gamma$ .
	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .			
AmFe selenate	0.1384	0.1398	0.1420	0.1422	0.1437	0.1459	0.0038	0.0039	0.0039
KFe „	0.1192	0.1209	0.1241	0.1224	0.1241	0.1274	0.0032	0.0032	0.0033
RbFe „	0.1069	0.1080	0.1102	0.1097	0.1109	0.1132	0.0028	0.0029	0.0030
CsFe „	0.1009	0.1017	0.1027	0.1036	0.1043	0.1054	0.0027	0.0026	0.0027

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$ .						Molecular dispersion. $m_G - m_C$ .		
	For ray C (Hz).			For ray H $\gamma$ near G.			$\alpha$ .	$\beta$ .	$\gamma$ .
	$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .			
KFe selenate	62.55	63.43	65.10	64.21	65.13	66.85	1.66	1.70	1.75
RbFe „	65.93	66.65	68.00	67.66	68.41	69.83	1.73	1.76	1.83
AmFe „	66.81	67.50	68.59	68.68	69.38	70.46	1.87	1.88	1.87
CsFe „	71.74	72.29	72.99	73.64	74.16	74.91	1.90	1.87	1.92

MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n - 1}{d} M$ for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha + \beta + \gamma)$ .
	$\alpha$ .	$\beta$ .	$\gamma$ .	
KFe selenate . . . . .	106.54	108.33	111.74	108.87
RbFe „ . . . . .	112.44	113.89	116.65	114.33
AmFe „ . . . . .	114.21	115.62	117.87	115.90
CsFe „ . . . . .	122.99	124.11	125.56	124.22

On comparing the results for the molecular refraction of the iron group of double selenates with the similar ones for the iron group of double sulphates,\* in order to

\* 'Roy. Soc. Proc.,' A, vol. 88, p. 382 (1913).

arrive at the effect of replacing sulphur by selenium, it is found that the selenate values are higher by 6.94 to 8.06 Lorenz units or 12.76 to 14.23 Gladstone units. As there are two atoms present of the sulphur or selenium, this affords as the increase per atom on replacing sulphur by selenium 3.47 to 4.03 Lorenz units or 6.38 to 7.12 Gladstone units. The following, therefore, is the table for the effect of the replacement of sulphur by selenium in the monoclinic hexahydrated double salt series brought up to date as regards the groups of double selenates now completely investigated.

It will be remembered that the double sulphate series has been quite completed, as regards all the eight known groups.

INCREASE of Molecular Refraction on Replacing S by Se.

Salt group.	Lorenz units.	Gladstone units.
Iron . . . . .	3.5-4.0	6.4-7.1
Nickel . . . . .	3.5-4.0	6.3-7.2
Magnesium . . . . .	3.4-3.6	6.3-6.7
Zinc . . . . .	3.5-3.7	6.5-6.9
Simple salts . . . . .	3.4-3.8	6.2-7.2

The table also includes the effect of replacing sulphur in the simple alkali sulphates by selenium, and the result is seen to be almost (and in the mean exactly) identically the same. The effect of replacing sulphur by selenium as regards molecular refraction, is thus found to be on the average 3.6 or 6.7 units, according as the formula of LORENZ or that of GLADSTONE and DALE is employed.

*Summary of Main Conclusions.*

The outstanding result of this investigation of the iron group of double selenates of this grand series of isomorphous salts  $R_2M \left( \begin{smallmatrix} S \\ Se \\ O_4 \end{smallmatrix} \right)_2 \cdot 6H_2O$ , is to add further evidence of the truth of the general law of progression of the crystallographic, structural, and optical properties with the atomic weight and atomic number of the interchangeable alkali metals (represented by R) potassium, rubidium, and caesium. The change in the principal interfacial and axial angle, the monoclinic angle  $\beta$ , the mean change of all the 38 different interfacial angles, and the maximum change of angle, when one alkali metal is replaced by another, are all directly proportional to the change in the atomic weight or number, to a degree of precision which is surprising. The change in the dimensions of the structural unit cell of the space-lattice, as indicated by the molecular volumes and the topic axial ratios, and the corresponding optical change as indicated by the molecular refraction, are instances and expressions of the accelerating progressive effect of the increase of the atomic weight or number of the alkali metal.

The mystery as to why this should be so, formerly surrounding the similar results derived from the three groups of double selenates and eight groups of double sulphates previously described by the author, has now been completely lifted, as shown in the addendum of February 7, 1917, to the author's last communication,\* by the brilliant discovery of MOSELEY, that the atomic sequence number is a fundamental constant governing the structure and complexity of the chemical atom. For as the atomic number is itself a measure of the positive charge on the atomic nucleus, and therefore correspondingly governs the number of negative electrons clustered around it, it must of necessity follow that a family group of chemical elements so vigorous as that of the monovalent alkali metals, each differing from the next by two whole rows (series) of elements in the periodic classification, must bring about by their successive replacement of each other a progressive change, corresponding to the increased atomic complexity, in the properties of the crystals of the salts in which they replace one another as dominating elements. As the atomic weight varies similarly to the atomic number, the differences between potassium and rubidium on the one hand and rubidium and caesium on the other being similarly related (equal) with respect to both constants, the law of progression may be stated with respect to either constant with like validity. To state it with respect to the atomic number is the better and more logical way, however, as the reason for the law is then at once apparent.

One other important result is the further confirmation afforded, by the results for this iron group of double selenates, of the isostructural relationship of the ammonium and rubidium salts of any group of the series. The interesting application of this conclusion as a test for the Pope-Barlow theory of valency volume to which special reference was made in a former communication,† is still further justified by the results now presented, which are clearly incompatible with that theory.

In concluding this description of the ferrous double selenates satisfaction may, perhaps, be legitimately expressed that it has, after attempts lasting over several years, been at last found possible to isolate and investigate completely crystals so difficult to prepare, and so extremely fugitive when prepared, as those of potassium ferrous selenate.

\* 'Phil. Trans.,' A, vol. 217, p. 234 (1917).

† 'Roy. Soc. Proc.,' A, vol. 93, p. 72 (1917).

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