PHILOSOPHICAL
TRANSACTIONS
OF THE
ROYAL SOCIETY OF LONDON.

SERIES A.
CONTAINING PAPERS OF A MATHEMATICAL OR PHYSICAL CHARACTER.

VOL. 207.

LONDON:
PRINTED BY HARRISON AND SONS, ST. MARTIN'S LANE, W.C.,
Printers in Ordinary to His Majesty.
FEBRUARY, 1908.
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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.

I. The Ionisation Produced by Hot Platinum in Different Gases.

By O. W. Richardson, M.A., D.Sc., Fellow of Trinity College and Clerk Maxwell Student, Cambridge University.

Communicated by Professor J. J. Thomson, F.R.S.

Received June 19,—Read June 28, 1906.

I.—§ 1. Introduction.

The principal objects of this investigation have been to examine the part played by the surrounding gas in the production of ions by hot metals and to discover, if possible, the mechanism by which the positive ions originate. In what follows, previous work on ionisation by hot metals will not be described, except in so far as it bears directly on the questions investigated, since the historical part of the subject has been fully treated in previous papers by the writer,* and others.

The present communication deals chiefly with the emission of positive ions from hot platinum, as earlier work has yielded much more information concerning the negative ionisation. In 1901 the writer† showed that a great number of facts in connection with the negative ionisation from hot metals could be explained by supposing that the electrons, of which the ions consist, were produced in the metal itself, from which they escaped by virtue of their kinetic energy. This theory makes the negative ionisation a function only of the metal surface and its temperature, and therefore independent of the nature and pressure of the surrounding gas, except in so far as this may have the effect of modifying the nature of the metallic surface. H. A. Wilson‡ has confirmed this part of the theory by showing that the negative leak, except when ionisation by collision occurs, has the same value in air, nitrogen, and water vapour over a wide range of pressures. Wilson also showed, however, that hydrogen greatly modifies the negative leak. The experiments in the present paper seem to show that the effect of hydrogen is due to some change it produces in the platinum surface; its abnormal behaviour is probably bound up with its electro-positive character.

* 'Jahrbuch der Radioaktivität u. Elektronik.'
† 'Camb. Phil. Proc.,' vol. 11, p. 286.
All the known evidence relating to the ionisation from hot solids goes to prove that the positive and negative ionisations are, in the majority of cases, entirely separate effects. It is true that, generally speaking, a hot metal produces ions of both signs simultaneously, but by suitably altering the conditions the ratio of the two ionisations can be made to change to almost any required extent, even at constant temperature, and the one can be made to vary greatly whilst the other remains practically constant, so that it is evident that the two ionisations are produced by the operation of at least two independent causes. The leak from hot solids is, therefore, essentially unipolar.

In the 'Philosophical Magazine' (6), vol. VI., p. 80, the writer showed that the current from a fresh positively-charged hot platinum wire fell off asymptotically with the time the wire was heated at constant temperature. An effect of this kind was first recorded by Elster and Geitel,* who noticed that an insulated plate near an incandescent platinum wire received a large positive charge when the wire was new, which gradually diminished, and ultimately changed sign with continued heating. This initial positive ionisation is presumably independent of the pressure, since it is very large in a good vacuum. Despite numerous experiments† its origin is still uncertain, but it is possibly due to some gas or volatile impurity present in the purest obtainable platinum.

By using a wire in which the initial positive leak had been reduced to a small value by heating in a good vacuum at a constant temperature at intervals extending over a long period of time, and subsequently letting in fresh air, the writer‡ succeeded in clearly showing that the leak, which was almost independent of the time, consisted of two parts, one proportional to, and the other independent of, the pressure of the air. So far as the writer is aware, this is the first experiment recorded which shows that any part of the positive leak from hot metals is a function of the pressure of the surrounding gas. The reasons which made such an effect difficult to detect are (1) the masking of the effect by the initial positive leak, if this has not been completely removed, and (2) irregularities and time effects in the part of the leak produced by the gas itself. These will be discussed at some length later in the paper.

In the present investigation a much more detailed study has been made of the ionisation in oxygen than in the other gases considered, for several reasons. In the first place, oxygen is a simple elementary gas which is easily prepared in a state of considerable purity. It has the additional advantage that small quantities of it produce a large increase in the positive ionisation which is readily measured. Finally, it acts as a self-purifying agent by oxidising, and so getting rid of, hydrogen—an impurity which it is of the utmost importance to avoid in experimenting on the ionisation produced by hot bodies.

† O. W. Richardson, 'C.R. Congrès Liège,' 1905, p. 50.
Besides oxygen, the present paper contains an account of measurements of the ionisation of both signs from hot platinum in air, nitrogen, helium, and hydrogen. There are also measurements of the ionisation from a platinum surface in air when a calculable quantity of hydrogen is diffusing out from the interior of the platinum. The last-named experiments shed a considerable amount of light on the mechanism of the processes by which the ions are produced.

It is necessary to say a word about the use of the term ionisation in this paper. By "the positive (or negative) ionisation" in a quantitative sense is meant the number of positive (or negative) ions liberated by 1 sq. centim. of the platinum surface per second under the conditions specified. The ionisations are, therefore, proportional to the respective saturation currents calculated per square centimetre of surface.

For convenience of reference the paper has been subdivided as follows:

I. § 1. Introduction.
II. § 2. Experimental arrangements.
III. The ionisation in oxygen:
   4. Hysteretic relations between current and E.M.F.
   5. Current and pressure.
   7. Uncontrollable variations.
   8. Comparison of different wires.
  10. Theory of the steady positive leak in oxygen.
IV. § 11. The ionisation in nitrogen.
V. § 12. The ionisation in air.
VI. § 13. The ionisation in helium.
VII. § 14. The ionisation in hydrogen.
VIII. § 15. Experiments with a platinum tube.
IX. § 16. Theoretical considerations.
X. § 17. Summary of principal results.

II. § 2. Experimental Arrangements.

Except where the contrary is distinctly stated, the arrangement of apparatus used was similar to that in the author's previous papers.* The platinum wires were supplied by Messrs. JOHNSON MATTHEY AND CO., and were of the purest material obtainable. They were 0.01 centim. in diameter and were in the form of a loop, the wire being about 7 centims. long. The ends of the loop were welded on to stouter platinum leads (A, fig. 1) which were sealed into one end of a glass tube about

8 centims. in length. The wire was heated electrically as before, and in measuring its temperature the same Wheatstone's bridge method was made use of to determine its resistance. This method is an exceedingly sensitive one, and there is no difficulty in keeping the resistance constant to one or two degrees at the highest temperatures. This is a matter of considerable importance in working with hot wires when the leak is a rapidly variable function of the temperature.

The whole of the apparatus, which was in electrical connection with the leads A, was insulated on paraffin blocks and could be charged to any potential between 0 and ±800 volts. Owing to the heating current through the platinum filament there was a fall of potential along the wire amounting to from about 2 to 6 volts according to the temperature, which had to be taken into account at low voltages. The current from the wire was measured by means of a Dolezalek electrometer with a suitable capacity attached to the quadrants. For insulating the plate B the dry glass inside the tube was found to be good enough, but outside it was protected by sealing wax surrounded by a guard ring.

In work of this kind the cleanliness and purity of the materials employed are of the utmost importance. In the apparatus shown in fig. 1 it will be noticed that all the parts are of platinum and glass. This enabled the tube to be cleaned with boiling nitric acid and distilled water before the experiments commenced. The ground-glass joint E enabled a further refinement to be effected by obviating the necessity of finally fusing the side tube on to the pump connections and thereby bringing the cleaned wire into contact with the gases from the blowpipe flame. The ground joint was lubricated with carefully purified graphite and was sealed with mercury externally.

The oxygen used was prepared in two ways. When small quantities only were required it was obtained by heating potassium permanganate in a tube sealed on to the apparatus. It was found advisable to have the tube containing the permanganate shut off from the rest of the apparatus by a mercury trap as it gave off a small quantity of gas or vapour even when the salt had been dried by heating to 120°C. for two hours before it was sealed up. The oxygen produced in this way is freed from dust by plugging up the front end of the permanganate tube with glass wool. When larger amounts of oxygen were required the above method was found to be inconvenient, and the electrolysis of concentrated caustic potash was substituted for it. The oxygen evolved underwent a preliminary drying by passing through a tube packed with solid potassium hydrate before being admitted, through a glass tap, to the main apparatus, where it was subjected to the further action of phosphorus
pentoxide. As thus prepared, the gas was liable to contain traces of hydrogen and hydrocarbons, but that these were not in sufficient amount to affect the results was proved by the fact that the oxygen prepared in this way gave the same results as that obtained from potassium permanganate, which must have been free from these impurities.

The resistance readings were reduced to platinum temperatures by the method described by Callendar.* The wire was standardised by determining the melting point of potassium sulphate by the method previously described.† For the parabolic correction, which is small at all the temperatures considered, Wilson's‡ value of the constant \( A = 151 \) was assumed. This assumption seems justifiable as the value referred to the same kind of platinum wire.

It has been pointed out above that it is necessary to get rid of the initial positive leak from hot platinum before experiments can be made on the part of the leak which is due to oxygen. The following figures give the actual magnitude of the two leaks for the wire which was employed in this investigation. The wire was cleaned by boiling with nitric acid and distilled water before commencing and the apparatus was pumped out to a pressure of 0.00005 millim. The initial positive leak under these conditions at a temperature of 804°C. was found to be equal to \( 1.62 \times 10^{-8} \) ampère. With the wire at a constant temperature this fell to half in about 10 minutes and, the rate of decay falling off with time, reached about one-tenth its original value after an hour's heating. Even after heating the wire for several hours a day for nearly a fortnight the part of the leak which was independent of the pressure could not be neglected in comparison with that which depended on the pressure, as the following numbers, which were obtained at a temperature of 721°C., testify:

<table>
<thead>
<tr>
<th>Pressure ( (\text{millim.}) )</th>
<th>Current ( (\text{ampère}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.045</td>
<td>( 1.8 \times 10^{-12} )</td>
</tr>
<tr>
<td>0.03</td>
<td>( 1.52 \times 10^{-12} )</td>
</tr>
<tr>
<td>0.016</td>
<td>( 1.4 \times 10^{-12} )</td>
</tr>
<tr>
<td>0.004</td>
<td>( 9.6 \times 10^{-15} )</td>
</tr>
<tr>
<td>0.0003</td>
<td>( 9.6 \times 10^{-15} )</td>
</tr>
</tbody>
</table>

These numbers show that increasing the pressure from 0 to 0.045 millim. increases the leak from \( 9.6 \times 10^{-13} \) to \( 1.8 \times 10^{-12} \). The part of the leak due to the gas, for very small pressures like the above, is very nearly proportional to the gas pressure. The residual initial leak \( (9.6 \times 10^{-13} \) ampère) exhibited by these results was about equal to the leak produced in oxygen at a pressure of 0.05 millim.; it was not permanent, however, but fell away till it could no longer be detected on the electrometer at this

* 'Phil. Mag.' [5], vol. 48, p. 519.
† 'Phil. Trans.,' A, vol. 201, p. 497.
temperature. In respect of falling away with time, the initial leak offers a very
marked contrast to the part of the leak which depends on the surrounding oxygen.
This was found to remain constant, except for a temporary variability, under the same
conditions during the whole of the time the experiments were being carried out.
The experiments on this particular wire lasted about three months and during that
time it was heated at various high temperatures for about 150 hours.

In the sequel it will be shown that as the pressure of the oxygen is increased the
current from the positively-charged wire asymptotically approaches a maximum
value. It is interesting to compare this value, which is independent of the pressure,
with the initial leak at the same temperature. The experiments show that at 804°C the
greatest positive leak from an old platinum wire of the above dimensions in
oxygen = 3·6 × 10⁻¹¹ ampère, and is therefore about one five-hundredth part of the
initial leak from a new wire.

Another source of trouble in these experiments arises from variations which take
place in the leak when all the controllable conditions are kept constant. These
variations, which will be considered more fully in the sequel, appear to fall into two
classes. The first are of a hysteretic nature and depend on the previous treatment
of the wire. For instance, if the gas pressure is suddenly lowered the leak does not
decrease immediately, but only gradually settles down to its final steady value.
Increasing the pressure gives rise to the converse effect. Sudden changes of
temperature, and in some cases of potential, will be shown to give rise to similar
hysteretic effects. These changes can be explained by supposing that the leak is due
not to the external gas, but to oxygen, which is held chemically or otherwise in the
superficial layers of the platinum, and that the amount necessary for equilibrium
takes time to adjust itself.

The second kind of variation seemed to be of a purely irregular nature, and
manifested itself by sudden jumps in the rate of movement of the electrometer spot
across the scale. This effect was specially marked at high pressures, and at low
pressures was not so noticeable. It may be due to the pressure of the contained
oxygen becoming great enough to force a way through the overlying layer of
platinum, and so giving rise to a sudden evolution of highly ionised gas.

To eliminate errors due to effects of the first kind, some time was always allowed
to elapse after each change had been made, and readings taken from time to time
until the leak became steady. At high pressures, where irregularities of the second
kind occurred in addition, it was more difficult to obtain the equilibrium value of the
leak; but by neglecting all readings where the movement of the spot was noticed to
be jerky, by always taking the smallest values of the leak, and by waiting till two or
more of these were identical, consistent results could always be obtained. This
procedure was rather tedious in some cases, but it seemed to be the only method, as
the irregularities concerned were not affected by any change in the controllable
conditions (except by diminishing the pressure).
III.—The Ionisation in Oxygen.

§ 3. Current and Electromotive Force.

In considering the results of experiments under this head it is important to remember that owing to the thinness of the wires used most of the fall of potential occurred near the surface of the wire. For this reason there was always a considerable electric intensity near the hot wire even when the potential difference between the electrodes was quite small. As a sufficient approximation for the experiments described in the next three sections we may take the electric intensity at the surface of the wire to be 40 V for the wires 0·1 millim. in diameter, and 20 V for the wires 0·2 millim. in diameter, where V is the applied potential difference in volts.

Except within certain limited ranges of pressure and voltage the positive leak from a hot wire in oxygen was found to be independent of the applied electromotive force. A saturation current therefore always exists, and it follows that, except in certain special cases, the number of positive ions produced per second by a hot platinum surface does not depend on the external electric field. For instance, an experiment at 700 millims. pressure and a temperature of 793° C. gave the following values of the current with different E.M.F.'s, the experiments being made in the order indicated:

<table>
<thead>
<tr>
<th>Volts</th>
<th>80</th>
<th>40</th>
<th>200</th>
<th>400</th>
<th>80</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>24·5</td>
<td>23</td>
<td>20</td>
</tr>
</tbody>
</table>

(1 = 1·19 x 10⁻¹² ampère)

The values of the current may be regarded as constant within the probable experimental error.

It is evident that at pressures near atmospheric, saturation is attained with a P.D. of less than 40 volts. As a matter of fact, in these cases, where all the ionisation is of one sign, there is, of course, no recombination and, provided the whole of the hot wire is at a positive potential great enough to overcome the tendency to diffuse back into the wire, all the ions produced reach the collecting electrode. A saturation current is thus obtained with a very small voltage. This is shown by some experiments made at a pressure of the same order of magnitude, 528 millims., as in the last experiment, and at a temperature of 706° C. The fall of potential along the filament, due to the heating current, was equal to 3·3 volts. The currents obtained with the various assigned mean voltages on the filament are as follows:

| Mean voltage | 0 1·75 38 1·75 3·7 1·75 5·8 18 1·75 38 0 |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Current     | 4   | 20  | 14·8| 18·5| 15·8| 19·5| 15·5| 15   | 20  | 14·8| 4·8 |

(1 = 6 x 10⁻¹⁵ ampère)
It will be seen that the maximum current is obtained with the potential at the middle point of the filament equal to +1.75 volts. Since there was a fall of potential of 3.3 volts along the filament due to the heating current, the more negative end would only be at a potential of +0.1 volt when saturation occurred; so that it is evident that the only competition the electrode experiences in collecting the ions is that due to the filament itself.

The mean potentials in cases where low voltages were used were determined by connecting a Weston voltmeter, one terminal of which was earthed, to each end of the filament in turn. The gradual decrease in the current as the potential rises from 1.75 to 38, which is very evident from the above numbers, will be dealt with later.

These current E.M.F. curves which show saturation at about 2 volts were only obtained at low temperatures. At higher temperatures the necessary voltage went up to about 40, as is shown by the following table:

<table>
<thead>
<tr>
<th>Mean voltage</th>
<th>+0</th>
<th>+4.1</th>
<th>+16</th>
<th>+42</th>
<th>+80</th>
<th>-40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>5</td>
<td>36</td>
<td>57</td>
<td>63</td>
<td>68</td>
<td>0.04</td>
</tr>
<tr>
<td>(I = 2.4 x 10^-11 ampère)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Temperature = 1180°C. Pressure = 89 millims.

The greater difficulty experienced in reaching saturation at high temperatures may possibly be due to the relatively greater magnitude of the negative ionisation which would make recombination a factor to be reckoned with.

The experiments show that a potential of +80 volts is sufficient to saturate the current from a platinum wire at all the temperatures used. This is of great importance in the sequel, where the leak with 80 volts is used to measure the total number of ions produced by a platinum wire under various conditions.

When the pressure of oxygen in the apparatus was of the order of one millimeter, the current ceased to be independent of the voltage at high voltages. A careful series of measurements was therefore made of the way in which the current varied with the voltage at different pressures. The results are given in the next table and are also exhibited graphically in fig. 2. The measurements at the lowest pressure (0.06 millim.) were made at a temperature of 822°C.; for all the other pressures the temperature was 808°C. To eliminate time changes, the leak with +80 volts was taken as a standard and was measured both before and after each observation with another voltage. This precaution was not really necessary, as the steady state had been reached before the measurements commenced, but it served as a useful check. On account of the method of taking the observations, and also because they do not all refer to the same temperature, the absolute values of the leaks have not been given, but for each pressure they are referred to the current with +80 volts as a standard.
which is put equal to unity. The absolute values at different pressures can be obtained from the results for the pressure variation which will be given in a later section.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Voltage</th>
<th>Voltage</th>
<th>Voltage</th>
<th>Voltage</th>
<th>Voltage</th>
<th>Voltage</th>
<th>Voltage</th>
<th>Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.46</td>
<td>1.1</td>
<td>1</td>
<td>0.94</td>
<td>1</td>
<td>0</td>
<td>0.96</td>
<td>2</td>
<td>1.69</td>
</tr>
<tr>
<td>1.05</td>
<td>1.03</td>
<td>1</td>
<td>0.96</td>
<td>1.17</td>
<td>0.27</td>
<td>1.22</td>
<td>1.97</td>
<td>1.70</td>
</tr>
<tr>
<td>0.58</td>
<td>1.06</td>
<td>1</td>
<td>1.24</td>
<td>1.29</td>
<td>1.43</td>
<td>1.70</td>
<td>2.72</td>
<td>3.55</td>
</tr>
<tr>
<td>0.186</td>
<td>1</td>
<td>1</td>
<td>1.19</td>
<td>1.38</td>
<td>1.65</td>
<td>1.87</td>
<td>2.27</td>
<td>3.8</td>
</tr>
<tr>
<td>0.06</td>
<td>0.81</td>
<td>1</td>
<td>1.01</td>
<td>1.40</td>
<td>1.68</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These results can readily be explained if we suppose that the wire produces at its surface a constant number of positive ions per second—which, however, depend, as will be seen later, on the pressure of the gas—and these ions are all collected unchanged by the electrode at low voltages. When the voltage increases to 200 or more, these positive ions produce others by collision and an increase in the current is obtained. The above increase in the current possesses all the features which are required by the view that it is due to ionisation by collision. The change produced by altering the P.D. from one to another assigned value increases as the pressure is diminished, reaches a maximum and ultimately disappears. Thus the ratio of the current under a given voltage to that under 80 volts reaches a maximum as the pressure is diminished.

The difference in the effect of the positive and negative ions from hot metals in VOL. CCVII.—A.
producing other ions by collisions is readily seen when the above curves are compared with similar ones given by H. A. Wilson* for the negative leak from hot platinum in air at different pressures. Wilson used wires of the same thickness and an apparatus of about the same dimensions as the author, so that the two sets of observations are quite comparable. It will be noticed that with the negative leak a given P.D. changes the current in a given ratio at a much higher pressure than with the positive leak. In addition, the pressures for the maximum current with a given voltage are much lower for the positive than the negative leak. For instance, when \( V = 340 \), the maximum current for the negative leak is somewhere between 12·1 and 0·81 millim., whereas for the positive leak it is at a pressure somewhere near 0·2 millim. Thus for corresponding effects the value of \( X/p \), where \( X \) is the electric intensity and \( p \) the pressure, has to be much greater when the positive ions are the active agents than when the negative ions are. The actual difference between the effects of the two kinds of ions is diminished owing to the fact that the negative ions which the original positive ions produce by collisions also act as ionising agents.

Curves resembling some of the above have been obtained previously by McClelland†, who also explained the increase in the current produced by the electromotive force as being due to the positive ions producing others by collisions.

The author has calculated the number of positive ions which reach a surrounding cylinder when a given number start from a wire of given radius at its centre and both the positive ions and the negative ions subsequently produced give rise to others by collision, in the hope that it might be applied to the further elucidation of the above experimental results. The expression obtained, however, is so complex that its manipulation, so as to fit the observations, did not seem likely to greatly advance our knowledge of the subject. There does not, however, so far as one can see, seem to be anything in these results contrary to the view that the positive ions from hot metals have about the same power as the positive ions produced by Röntgen rays in air of producing other ions by collisions, and that the other ions so produced consist, in any given case, of an ordinary positive ion together with a corpuscle.


The numbers given in Table 4, § 3, exemplify the curious fact that in some cases the current increased with diminishing potential difference. The case cited was not found to be an isolated instance, as the following numbers, obtained at a temperature of 826° C. and a pressure of 0·4 millim., testify:

† 'Camb. Phil. Proc.,' vol. 11, p. 300 (1902).
Similar results were obtained at a pressure of 0.0015 millim., so that this effect occurs at all pressures.

The numbers quoted do not give the value of the current immediately the potential was put on, but what it settled down to later. In all these cases it was found that on raising the potential the current was too big at first, and only settled down to its steady value after some minutes. Similarly, on changing to a low voltage the current was too small at first and subsequently increased somewhat. Effects of this kind were much more marked with wires which had not been heated very much, and will be considered more fully under § 13. They can obviously be explained if we assume that the electric field displaces the equilibrium condition in such a way as to reduce the number of ionising systems.

Effects of this kind could not be detected at higher temperatures, owing to the greater difficulty of attaining saturation already alluded to. In these cases it was found that, though no certain increase in the current could be detected on changing the potential from 40 to 80 volts, yet it increased by about 60 per cent. with a potential of 760 volts. This increase was approximately proportional to the voltage. When it occurred, 600 volts was used to measure the saturation current; it was not safe to go up to much higher voltages, owing to the possibility of ionisation by collisions occurring even at high pressures.


We come now to what has been regarded throughout as the main object of this investigation, namely, the relation between the ionisation produced by the wire and the pressure of the surrounding gas. In interpreting the results, it is important to remember (1) that the current was always saturated, and (2) that, at low temperatures at any rate, the negative leak in oxygen was always found to be small compared with the positive. These two results conjoined prove that volume ionisation of the gas round the wire is negligible, at any rate at low temperatures. Moreover, there is every reason to believe that the negative ionisation, which makes itself felt even in oxygen at higher temperatures, is the ordinary corpuscular emission from hot metals, so that everything points to the positive ionisation being due to an action which takes place at the surface of the metal.
In a previous paper, which has already been quoted, it was shown that the leak from a hot platinum wire in air at low pressures fell off as the pressure was reduced from about 0.1 millim. to 0 in such a way as to indicate that the leak consisted of two parts, one proportional to the pressure, and one independent of it. A similar experiment was now made with pure oxygen, except that observations were started at a higher pressure. The results of this experiment are given in the next table. The temperature was 816° C., and the potential on the filament +80 volts.

<table>
<thead>
<tr>
<th>Pressure in millims.</th>
<th>0·000008</th>
<th>0·00028</th>
<th>0·0183</th>
<th>0·116</th>
<th>0·207</th>
<th>0·374</th>
<th>0·675</th>
<th>1·26</th>
<th>2·18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (1 = 6 × 10⁻¹² ampère)</td>
<td>2·15</td>
<td>2·15</td>
<td>5·2</td>
<td>9·5</td>
<td>13</td>
<td>15·5</td>
<td>17</td>
<td>20</td>
<td>24</td>
</tr>
</tbody>
</table>

The pressure was varied by making one stroke of the pump and then making an observation, after waiting for everything to become steady, at the reduced pressure thus obtained. The order in which the observations were taken was thus that of diminishing pressure, so that any secular change which might be going on would go entirely in the one direction and might vitiate the results. In order to test whether an effect of this sort was coming in, fresh air was let into the apparatus the next day and observations again taken over a similar range. The results are exhibited along with the previous ones in fig. 3. The points marked thus × refer to the observations in Table IX., whilst those marked thus ○ refer to those taken on the following day. The experimental conditions were the same in both cases.

The lower curve may be compared with the numbers for air up to 0·11 millim. in the paper referred to above.* It will be seen that at these low pressures the part of the leak which depends on the gas is roughly proportional to the pressure, agreeing with what was previously found for air. The part of the leak which is independent of the pressure, which is clearly marked in fig. 3, is smaller relatively to the rest than in the previous experiments. It will not be noticed in the later curves, as it became too small to be noticable after a few days' more heating.

Although the results given in fig. 3 show that hysteretic effects had been largely

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eliminated from the experiments which they represent, still an inspection of the actual experimental numbers shows that such effects did occur. It was often observed, for instance, that if the wire had been heated for a time to a temperature higher than that at which observations were being taken, the value of the leak was too great for some time afterwards. For instance, in an experiment at 816° C., where the pressure was 1·4 millims. and the steady leak = 30, the unit being $6 \times 10^{-13}$ ampère, after heating for a few minutes to about 1100° C. the wire was found to give the following values of the leak at the times in minutes stated.

<table>
<thead>
<tr>
<th>Time . . . . . .</th>
<th>0</th>
<th>3</th>
<th>7</th>
<th>11</th>
<th>14</th>
<th>25</th>
<th>28</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current . . . .</td>
<td>90</td>
<td>70</td>
<td>56</td>
<td>44</td>
<td>40</td>
<td>30</td>
<td>31</td>
<td>30</td>
</tr>
</tbody>
</table>

It is evident from the above numbers that it took about 20 minutes for equilibrium to be established at this temperature, a fact which gives some indication of the prodigious labour required in taking the observations.

Another hysteretic effect, which is more likely to be a source of trouble in experiments on the effect of change of pressure, is a time lag of the change in the leak behind the change in the pressure. In testing for an effect of this kind it is evident, from the preceding paragraph, that it is necessary to keep the temperature constant while the pressure change is made. This is very difficult, since with a constant current through the wire its temperature is a function of the pressure of the surrounding gas, but by watching the galvanometer spot of the Wheatstone's bridge circuit, and manipulating the rheostats which control the heating current as quickly as possible, the temperature can be restrained from varying very much whilst the pressure change is being made. The following numbers represent the effect at 809° C. of suddenly reducing the pressure from 1·8 to 0·21 millim., the P.D. being +80 volts. The steady leak at 1·8 millims. had the value 18 ($1 = 1·9 \times 10^{-12}$ ampère); the leak at 0·21 millim. had the values given at the times stated.

<table>
<thead>
<tr>
<th>Time</th>
<th>12</th>
<th>12</th>
<th>12</th>
<th>12</th>
<th>12</th>
<th>12</th>
<th>1</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>minutes</td>
<td>35</td>
<td>38</td>
<td>41</td>
<td>46</td>
<td>51</td>
<td>56</td>
<td>4</td>
<td>7</td>
<td>42</td>
</tr>
<tr>
<td>Current</td>
<td>14·8</td>
<td>13·7</td>
<td>13</td>
<td>10</td>
<td>9·5</td>
<td>8·1</td>
<td>9</td>
<td>7·8</td>
<td>7·3</td>
</tr>
</tbody>
</table>

In a similar way, on increasing the pressure, keeping the temperature constant, it was found that the leak at the higher pressure was too small at first and only gradually rose to its final steady value.

It is evident from what has been said that the lag in the leak behind pressure
changes must have affected to some extent the results shown in fig. 3. The practically exact coincidence of the two curves might merely imply that the observations were taken at about the same rate in the two cases, so that the errors were about the same in each case. A check on this was, of course, afforded by the fact that values of the leak were only retained after they ceased to vary with the time; but partly owing to the great length of time required for equilibrium to be established, and partly owing to the invariable presence of irregularities of another kind, which will be considered later, it was very difficult to be sure that equilibrium had been attained in any specified case. For this reason it was thought desirable to have some further means of checking the extent to which these influences affected the measurements.

This was done by gradually increasing the oxygen pressure instead of diminishing it, as happened by taking readings after successive strokes of the pump. It is evident that under these conditions the pressure time lag will have the opposite effect to what it had when the pressure was being reduced, so that the lack of coincidence between the curves obtained with increasing and diminishing pressure will give a measure of the extent to which the lag effect has not been eliminated. What was required, then, was an arrangement which would deliver small adjustable quantities of oxygen into the main apparatus.

To do this, the apparatus shown in fig. 4 was devised. The principle of the method is to allow gas to flow into the apparatus through a very long narrow capillary tube under an adjustable difference of pressure for varying times. In the figure this part of the apparatus is shown together with the arrangement for furnishing the oxygen. The bulbous tube A contained pure dry potassium permanganate; by heating a small portion of it for variable lengths of time, any desired quantity of pure oxygen could be set free. Such a tube may be used time after time for long periods. B is a glass wool plug to stop the manganese dioxide dust which is produced when A is heated. C is a drawn-out glass tube which can be broken to let down the vacuum in this part of the apparatus if required. It is convenient to have the permanganate tube so that it can be shut off from the rest of the apparatus. This may be done by means of the mercury cut off D. At F is the fine capillary tube, bent as shown to economise space, through which the gas flowed into the main apparatus at H. This tube was about 140 centims. long, and was the narrowest
available in the laboratory. By means of the tube E, which, like D, was filled with mercury, both being connected to separate reservoirs, the volume above the mercury at E could be regulated, and so any desired variation could be made in the pressure driving the gas through the tube F. Finally the glass tap E allowed the time during which the flow took place to be varied in any desired manner. By suitably varying the two controlling factors it was found that the pressure in the main apparatus could be increased by any amount from 0·001 millim. to several centimetres at will. This apparatus works very well and will probably be found to be very convenient for work of this kind. It permits of a much greater range of variation of pressure than a regulator which it has been found convenient to employ in previous experiments, which is practically a tube like E sealed directly on to the apparatus. With this the pressure is regulated by the change of volume produced when the height of the mercury column is altered.

Using the apparatus just described, a series of measurements of the leak was now made, with the pressure of the oxygen gradually increasing. The temperature was 826° C. and the potential on the filament = +40 volts. The numbers obtained were as follows:

<table>
<thead>
<tr>
<th>Pressure in millims.</th>
<th>0·0107</th>
<th>0·029</th>
<th>0·055</th>
<th>0·12</th>
<th>0·294</th>
<th>0·474</th>
<th>1·09</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>2·9</td>
<td>4·4</td>
<td>6·6</td>
<td>11·1</td>
<td>19·4</td>
<td>23</td>
<td>35</td>
</tr>
<tr>
<td>(1 = 6 x 10^-13 ampère)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It will be observed that these numbers are very similar to those previously obtained with decreasing pressure, showing that the time effects do not play a very important part under the specified experimental conditions. In order to have a more exact test, two consecutive series of readings were taken, one with decreasing and the other with increasing pressure. The resulting observations are plotted in fig. 5. The temperature was 828° C. and the potential +38·2 volts. The points marked thus × were taken with the pressure decreasing, those marked thus ○ with the pressure increasing.

It will be seen that the two sets of points fall very nearly on the same curve, but that those with the pressure increasing tend to be lower than those with the pressure decreasing, in agreement with the time-lag effects previously described.

The experiments were now pushed to higher pressures, atmospheric pressure being
the upper limit. In doing so, great difficulty was experienced owing to the purely irregular effects mentioned on p. 6. These effects were characterised by sudden changes in the rate of leak of a purely temporary kind, and were quite different from the hysteretic effects previously described. Very often in the midst of a reading, when the electrometer spot was moving quietly across the scale at the usual rate, it would suddenly give a kick and dart right off without any warning or apparent cause. These kicks were much more marked at high than at low pressures. At pressures of about 1 millim. it was rare for a kick to increase the leak in 15 seconds by 25 per cent., whereas values of the leak equal to six times the minimum have been recorded at atmospheric pressure. The following numbers, obtained at a pressure of 366 millims. and a temperature of 80° C., furnish an excellent example of this kind of thing.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>h. m.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 31</td>
<td>31.7</td>
<td>steady</td>
</tr>
<tr>
<td>10 34</td>
<td>41</td>
<td>slight kick</td>
</tr>
<tr>
<td>10 37</td>
<td>33</td>
<td>steady</td>
</tr>
<tr>
<td>10 40</td>
<td>200</td>
<td>kick</td>
</tr>
<tr>
<td>10 43</td>
<td>31.5</td>
<td>steady</td>
</tr>
<tr>
<td>10 46</td>
<td>33</td>
<td>steady</td>
</tr>
</tbody>
</table>

The above represents the greatest value of the kick recorded. Generally speaking, the value of the leak only oscillated up to twice its minimum value. Further experiments on the source of these irregularities will be described later (§ 10). As no change in the arrangements has been found to eliminate them, they were avoided by always taking the minimum value of the leak, and readings were always taken until two consecutive minima agreed with one another. For instance, the true value of the current from the above observations was taken to be 32. This method was found to give consistent results.

The curves shown in fig. 6 represent the result of an experiment with the resistance of the wire maintained equal to that which it would have at a pressure of 1 millim. and a temperature of 816° C., the potential on the filament being +40 volts. The unit of current is \(6 \times 10^{-18}\) ampère. All the observations except two were taken with the pressure decreasing. The lower curve represents the same observations as the upper, but the pressure scale is magnified ten-fold. The two observations marked thus \(\mathcal{O}\) are on the scale of the upper curve. They were made with the pressure increasing after the other series were finished, and were taken very rapidly, so that equilibrium was not fully established. They both fall well below the rest, owing to the time-lag effect described above. The other points fall very nearly on the curves drawn.
The independence of pressure exhibited by the leak at high pressures seemed at first sight a very surprising result and led the author to enquire whether there might not be something wrong with the temperature measurements at high pressures. As has been explained, the criterion employed to obtain a constant temperature so far has been a constant resistance of the wire. Now the resistance measures the average temperature of the wire across its section, whereas what is required in these measurements is a constant surface temperature, so that any change which alters the temperature gradient from the centre of the wire to the circumference will alter the surface temperature at constant resistance. Increasing the gas pressure facilitates the flow of heat from the surface of the wire and must therefore increase the internal radial temperature gradient. It is evident, then, that increasing the gas pressure lowers the surface temperature when the resistance is kept constant. It might be thought that this effect would be small in the thin wires used (0.01 centim. diameter), but the leak is a very rapidly varying function of the temperature, so a small temperature error produces a big change in the leak.

To eliminate this error, which only enters into the experiments on the pressure variation, and then is only important at somewhat high pressures, a method was devised by which the surface temperature was kept constant. A tube similar to that shown in fig. 1 was constructed, exhausted, and sealed up. The wire in it was then heated to a standard temperature by means of a constant current. A portion of this filament was then compared with a similarly situated portion of that from which the leak was being measured, and the heating current through the latter was adjusted until the two appeared to be of the same brightness. Both hot wire tubes were shut up in a black-lined box, and by looking into this through a tube furnished with paper slits the field of view could be limited to those portions of the filaments which it was desired to compare.
This method was rather rough and very tedious to use. Great care was necessary to get reliable results with it, and the strain this involved, added to the natural difficulties of the experiments, rendered the method almost impracticable. However, a number of series of observations were taken by this method of direct comparison. The results of one of them are given in the following table:

<table>
<thead>
<tr>
<th>Pressure in millims.</th>
<th>0.96</th>
<th>3.8</th>
<th>14</th>
<th>58</th>
<th>135</th>
<th>252</th>
<th>537</th>
<th>747</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>8.0</td>
<td>9.8</td>
<td>10.7</td>
<td>15</td>
<td>17</td>
<td>19.5</td>
<td>24</td>
<td>22</td>
</tr>
<tr>
<td>(1 = 1.19 x 10^-12 ampère)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The temperature was about 800° C. and the voltage +200. Roughly speaking, these numbers serve to confirm those which were obtained by the resistance method; they show that the leak varies very little with the pressure at high pressures. On the other hand, there is a more rapid variation than that previously found, indicating that the resistance method did make the temperatures too low at the higher pressures.

It was found that a better way to make use of this optical method of obtaining a constant temperature was to determine the change of resistance required to keep the filaments equally bright when the pressure was varied, and to use the results thus got to correct the readings for the leak at constant resistance to what they would be at constant temperature according to the optical criterion. This procedure may appear pointless at first sight, but it is not. The advantage of it lies in the fact that it separates the difficulties of the optical regulation process from those which are due to the vagaries of the leak itself. The leak then was measured with the wire heated so that its resistance remained constant; this is done by the purely mechanical process of keeping a galvanometer spot at the middle of a scale, so that all the attention of the observer could be devoted to the actual measurement of the leak itself. Similarly, in finding the way the resistance changed for the same brightness, all the attention could be devoted to seeing when the two wires were equally bright. It was far easier to carry out both these operations separately and combine the results than to do both things at once, and the results obtained were far more consistent.

Working in this way a curve was obtained giving the resistance at various pressures corresponding to a constant temperature. A curve was also plotted, from experiments which will be described later, showing the relation between the leak at constant pressure and the resistance. On combining these two curves so as to eliminate the resistance, a third curve was obtained which gave the factor by which the leak at any pressure had to be multiplied to bring it to the value it would have at the temperature which the wire was at when the pressure was 1 millim.
Treated in this way the numbers plotted in fig. 6 yield those exhibited in fig. 7. As before, the temperature is $816^\circ$ C., the voltage +40, and the unit of current $6 \times 10^{-18}$ ampère, the pressure being expressed in millimetres.

It will be seen that despite the temperature correction which has been made the leak varies very little with the pressure at high pressures and is probably asymptotic to a line somewhere about $y = 56$.

The preceding observations show that the positive ionisation produced by a hot platinum wire in oxygen at temperatures below $900^\circ$ C. is approximately proportional to the square root of the pressure at low pressures. As the pressure is raised, the rate of increase of leak with pressure gradually diminishes so that the leak tends to approach a steady value asymptotically at high pressures. A similar result was found to hold at higher temperatures, with the difference that the rate of increase was greater at low pressures. At $1180^\circ$ C. the leak was nearly proportional to the pressure below 2 millims., and the rate of increase at higher pressures fell off as before. The numbers supporting this conclusion will be found below in Part IV.

Before leaving this part of the subject it is necessary to consider another source of error to which the experiments were liable. This was due to the walls of the tube getting heated. During the course of the experiments the author tried the effect of heating the tube in which the measurements were being made by means of a Bunsen burner placed outside it. This was found to produce an enormous increase in the leak. In one instance, where the pressure before heating the tube was 0.0005 millim., heating for a few minutes with a Bunsen burner increased the leak from $2.2 \times 10^{-13}$ ampère to $5 \times 10^{-9}$ ampère, i.e., in a ratio of 1 to 20,000. At the same time the gas evolved from the walls only sent up the pressure to 0.001 millim. This curious and interesting effect, which is being further investigated, does not appear to depend on the state of cleanliness of the tube, as it showed itself with apparently undiminished vigour after the tube had been taken down and boiled out three times with pure nitric acid and subsequently rinsed out seven times with boiling distilled water. The effect was also obtained in air at atmospheric pressure and in a vacuum produced by liquid air and charcoal, where it was impossible for the wire to come in contact with mercury vapour or vapours given out by phosphorus pentoxide.

Whatever the cause of this effect may turn out to be, it is clear that it might have completely vitiated the present measurements of the leak in oxygen and other gases. In fact, the following considerations will show that a small trace of the above effect might easily simulate the effects investigated. When the gas pressure is very low,
very little heat is carried from the hot wire to the surrounding electrode and the walls of the tube, which consequently remain quite cold. As soon, however, as the pressure of the gas is increased the temperature of the walls increases too, and if the above effect were coming into play, the increase in the leak due to the heating of the walls might easily appear to be a steady function of the pressure of the gas in the tube.

It was considered advisable to settle this question definitely by examining the leak in a vessel in which the only thing which could possibly get hot was the platinum wire itself. This was done by means of the apparatus shown in fig. 8. The metal tube A served as the electrode to which the leak was measured and thus replaced both the glass tube and the platinum electrode in the previous apparatus. This outer tube was kept cold by means of water placed in the inverted wide-mouthed bottle B. A heavy brass tube C, permanently connected to earth and insulated from A by a clean rubber stopper D, served as a guard ring to prevent leakage from the high potential wire E across the supports to the testing electrode system AB. The guard tube C had a heavy flange G soldered to it which formed a base for the apparatus and rested on the bottom of an earthed biscuit tin F. The lower end of the tube C projected through a hole in the tin. The hot platinum wire was bound to the thick copper leads H by means of fine copper wire, and the leads were supported and insulated from the guard tube C by means of the rubber stopper K. Both the hot wire leads and the guard tube were kept cold by a stream of water flowing through the composition spiral PLMQ. The part of this which was laced round the leads H was insulated from them by thin rubber tube. This was found to conduct heat well enough to keep the leads cold.
This apparatus, in which effects due to heating of the walls were prevented, was found to give exactly the same kind of results as the earlier experiments. For instance, the saturation current in oxygen at different pressures was found to have the following values:

<table>
<thead>
<tr>
<th>Pressure in millims.</th>
<th>2</th>
<th>0.043</th>
<th>0.07</th>
<th>0.014</th>
<th>124</th>
<th>56</th>
<th>12</th>
<th>2.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>64</td>
<td>38</td>
<td>22</td>
<td>13</td>
<td>228</td>
<td>180</td>
<td>156</td>
<td>99</td>
</tr>
</tbody>
</table>

The temperature in this experiment was 976° C. and the unit of current $7 \times 10^{-13}$ ampère. The observations were taken in the order of the numbers in the table.

Several other points were tested with this apparatus, one of which was to see whether the lag in the leak behind changes the pressure still held. The wire was giving a minimum leak of 36 divisions under a pressure of 0.64 millim. when the oxygen was pumped out as rapidly as possible to a pressure of 0.004 millim. The temperature was then adjusted to its former value, and the following minimum values of the leak were observed at the times stated, the time being reckoned from the point at which the temperature first became steady.

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>5</th>
<th>10</th>
<th>14</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>24</td>
<td>20</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

Evidently the wire requires time to adjust itself to the changed conditions, so that this effect cannot be attributed to anything given off owing to the walls becoming heated.

The irregular changes in the leak previously noticed seemed to occur in this vessel to about the same extent as in the others, so they also cannot be ascribed to anything from the walls of the tube.

Some puzzling effects which have been observed may, however, probably be assigned to this cause, and it seems advisable to mention them for the benefit of other workers in this subject. The writer has several times obtained a large increase of the leak with the pressure at high pressures, especially with the wire at a high temperature. This effect has, however, only been found to occur when the whole tube became very hot and it could be reduced to a small value by simply blowing cold air on to the outside of the tube. Another effect which probably arises in the same way is an increase in the leak at a given temperature produced by heating the wire for a short time to a considerably higher temperature (see p. 13). Both these effects appear to be really due to the walls of the tube becoming heated.
Experiments were also made to see if the negative ionisation in oxygen varied with the pressure of the gas. The temperature was 1100°C, and the saturation currents with the wire charged positively and negatively respectively at the different pressures were those shown in the accompanying table.

<table>
<thead>
<tr>
<th>Pressure in millims.</th>
<th>0.64</th>
<th>0.15</th>
<th>0.12</th>
<th>0.026</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ve current</td>
<td>87</td>
<td>27</td>
<td>21</td>
<td>9</td>
</tr>
<tr>
<td>-ve current</td>
<td>19</td>
<td>22.5</td>
<td>21</td>
<td>21.5</td>
</tr>
</tbody>
</table>

The potentials used were +40 and −7.5 volts respectively. These were tested and found to produce saturation. With the potentials employed there was no possibility of the measurements being vitiated by ionisation by collisions. The results show that, whilst the oxygen increases the positive leak ten-fold, the negative remains unchanged within the limits of experimental error. The independence of negative ionisation and gas pressure, which had been previously observed by McClelland and H. A. Wilson, will be found to be of considerable importance later in interpreting the results on the positive ionisation.


The last section forms a fairly complete investigation of the way in which the positive ionisation from hot platinum in oxygen varies with the pressure, when the temperature is kept constant, for a considerable range of temperatures. The phenomenon was next investigated by measuring the ionisation at constant pressure when the temperature of the wire was varied.

The measurements were made with the glass tube apparatus previously described. Rough experiments were made at several pressures, but only those at pressures of 1 to 3 millims. have been retained. At very low pressures irregular results were got, doubtless owing to changes in the composition of the small quantity of gas present in the apparatus, whilst at pressures comparable with atmospheric it was feared that an error might creep in owing to the walls of the tube becoming heated. At pressures of about 2 millims., however, several wires were tried and found to give consistent results over a range from about 700°C. to 1250°C. It was found convenient to measure the negative current at each temperature along with the positive. The results therefore enable us to compare the positive and negative ionisations from wires under identical conditions. The ionisation would, no doubt, be proportional to the area of the hot metal surface if the surface were uniformly heated. As, however, the wires are colder at the ends owing to the heat being conducted away through the leads, the effects from wires of different lengths and thicknesses will not be strictly
comparable with their superficial areas. To allow for this, 0·5 centim. was subtracted in every case from the length of the wire. The area thus reduced will be referred to as the effective area of the surface of the wire.

A wire 0·1 millim. in diameter, which had been heated in oxygen for a period of about three months (usually for several hours a day), was found to give the following values of the positive and negative saturation currents at the temperatures stated:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>+ Current (ampère)</th>
<th>− Current (ampère)</th>
</tr>
</thead>
<tbody>
<tr>
<td>708</td>
<td>$1.6 \times 10^{-12}$</td>
<td>—</td>
</tr>
<tr>
<td>770</td>
<td>$6.7 \times 10^{-12}$</td>
<td>—</td>
</tr>
<tr>
<td>826</td>
<td>$1.5 \times 10^{-11}$</td>
<td>$1.1 \times 10^{-14}$</td>
</tr>
<tr>
<td>885</td>
<td>$3.2 \times 10^{-11}$</td>
<td>$6.7 \times 10^{-14}$</td>
</tr>
<tr>
<td>940</td>
<td>$5.8 \times 10^{-11}$</td>
<td>$8.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>999</td>
<td>$1.1 \times 10^{-10}$</td>
<td>$6.2 \times 10^{-12}$</td>
</tr>
<tr>
<td>1058</td>
<td>$3.8 \times 10^{-10}$</td>
<td>$3.2 \times 10^{-11}$</td>
</tr>
<tr>
<td>1119</td>
<td>$6.4 \times 10^{-10}$</td>
<td>$3.3 \times 10^{-10}$</td>
</tr>
<tr>
<td>1181</td>
<td>$1.1 \times 10^{-9}$</td>
<td>$1.6 \times 10^{-9}$</td>
</tr>
<tr>
<td>1227</td>
<td>$1.7 \times 10^{-9}$</td>
<td>—</td>
</tr>
</tbody>
</table>

The pressure of the oxygen in the above experiment was 1·47 millims., and the effective superficial area of the wire was 0·223 sq. centim. In this experiment the negative ionisation was measured with 40 volts P.D. This would probably give rise to ionisation by collisions at the pressure during the experiment, so that the values for the negative ionisation in the table are probably somewhat greater than the true saturation values.

In proceeding from a low to a high temperature it was usually found that the leak at the high temperature was too big at first and subsequently fell to a smaller value. This effect did not, however, occur in a wire which had been heated in oxygen for a very long time—for instance, it was not noticed in the above series of observations—and is probably due to the wire not really having reached a state of equilibrium.

It will be noticed that the value of the positive ionisation increases very rapidly with the temperature of the wire, though not so rapidly as the negative corpuscular radiation. The relationship between the two is brought out more clearly when the results are exhibited graphically as in fig. 9. The continuous curves with points thus $\times$ represent the positive, and the dotted curves with points thus $\circ$ the negative, ionisation. The scale of current is different for the different curves. For curves (1) and (4) the unit is $10^{-12}$ ampère, for (2) and (5) $1 = 10^{-11}$ ampère, and for (3) and (6) $1 = 10^{-10}$ ampère. The two leaks become equal at about 1230° C., though the positive is far bigger than the negative at low temperatures.

Although the negative ionisation increases far more rapidly than the positive, both depend on the temperature in the same general kind of way; in fact, the positive ionisation, so far as its temperature relations are concerned, obeys the law originally
deduced by the author for the negative ionisation, and can be expressed by means of the formula $A\theta^b e^{-b\theta}$, where $A$ and $b$ are constants and $\theta$ is the absolute temperature. The constant $b$ which measures the work done in setting free an ion is, in general, much smaller in the case of the positive than the negative ionisation. This may be tested, as the writer has explained in previous papers, by taking logarithms, when, if $L$ is the current and $A'$ a new constant,

$$\log_{10} L/\theta^b = A' - b/(2\cdot30\theta).$$

The value of the logarithm should therefore be a linear function of $1/\theta$. Values of $\log_{10} L/\theta^b$, where $L$ is the current per unit area of surface for two wires of different lengths and diameters, have been plotted against $1/\theta$ in the accompanying diagram.

The extent to which the points fall on two straight lines furnishes a test both of the applicability of the above formula and also of the nature of the agreement between different wires. The data for the wires tested are (1) diameter = 0.01 centim., effective superficial area = 0.223 sq. centim., positive ionisation-points thus $\times$; (2) diameter = 0.02 centim., effective area = 0.66 sq. centim., positive ionisation-points thus $\diamond$, negative ionisation-points thus $\ast$.

It will be observed that the points for the positive leak, and also for the negative leak, fall very nearly on the same straight line for the two wires. This shows not only that the leak may be expressed by a formula of the above type, but also that the constants $A$ and $b$ which enter into the formula are the same for both wires. The tangent of the angle the above lines make with the axis of $1/\theta$ is a measure of the work done in setting free an ion. This quantity is evidently much less for the positive than for the negative ions. The value of this work is conveniently expressed in calories per gramme molecule of ions, a gramme molecule of ions being the amount which would occupy 22.4 litres if in the state of gas at 0° C. and 760 millims.
Expressed in this way, the numbers can at once be compared with the heats of various purely chemical reactions. The best series of experiments in oxygen (at 1.5 millims. pressure) gave for the work required to set free a corpuscle $\omega_+ = 13.55 \times 10^4$ calories. This is in good agreement with Wilson's value $13.11 \times 10^4$ for the negative leak from hot platinum in air at a low pressure.* The value of the work required to set free a positive ion was found to be $\omega_+ = 3.04 \times 10^4$ calories. The heats of the most intense chemical actions involving only one valency range around $5 \times 10^4$ calories, so that the energy required to liberate a positive ion is somewhat smaller, and that required to set free a negative ion considerably bigger, than the greatest amount of energy set free in any known chemical reaction.


We have seen (p. 16) that the positive leak in oxygen, particularly at high pressures, continually varies in an erratic manner, even when all the controllable

conditions are apparently kept constant. The following numbers, which refer to a temperature of about 900° C., illustrate the kind of thing that occurs. The wire, which was 0·2 millim. in diameter, was maintained at a potential of +40 volts, the pressure of the oxygen being atmospheric. All the conditions were kept constant; the unavoidable variation in the temperature of the wire was continuously registered by the galvanometer spot, and was not sufficient to cause a variation of 5 per cent. in the value of the leak. Nevertheless, readings at 2-minute intervals gave the following values for the current:—146, 180, 178, 228, 158, 170, 150, 246, 166, 324, 198, 174, 198.

Naturally the existence of a variability of this kind makes it very difficult to find out what is the real effect of changing the controllable conditions, and the author has spent a great deal of time in trying to get rid of it. In this he has been unsuccessful. It looks, in fact, as though this variability is in some way or another an inherent part of the phenomena. In some respects it seems to follow definite laws. It is more marked at high than at low pressures, and at low than at high temperatures. The positive leak at temperatures above 1200° C. seemed to show very little variability. It is not due to trivial variations in the state of the gas in the tube, as the negative leak, measured under the same conditions as the positive, did not show it. For the same reason it cannot be due to discharges from points which might form on the surface of the platinum.

It was found to be present whatever the voltage on the filament. Boiling out the tube with nitric acid and distilled water left it unaffected. Slightly heating the walls of the tube with a Bunsen burner did not affect it, although heating the walls more strongly was found to give the big leak mentioned on p. 19. The big leak thus produced, on the contrary, was steady and did not vary capriciously with the time. The variability was not due to vapour given off intermittently from the heated walls of the tube, as it occurred in undiminished intensity in the tube whose walls, &c., were cooled with water. It might have been ascribed to the intermittent escape of occluded hydrogen, were it not that a wire which had recently been heated in hydrogen did not show the effect to a greater extent than a wire which had been heated in an atmosphere of oxygen over a period of about three months.

There seems to be no escape from the conclusion that this effect is caused by some periodic change in the state of the platinum surface. If the metal was continually undergoing recrystallisation accompanied by the emission of absorbed gas, equilibrium might possibly be incapable of ever being attained, and the results might simulate those which have been observed. It does not seem advisable to speculate further on this point. The real question from the point of view of this investigation is whether the selection of the minimum values in the case of the measurements at high pressures is legitimate or not. They certainly seemed far more definite than the maximum or the average values, but apart from this and the apparently remote possibility that the “jumps” are really due to the escape of some substance foreign
to the platinum there is no reason for taking one set of values rather than the other. On these grounds the results at low pressures may be considered more reliable than those at high ones.

§ 8. **Comparison of Different Wires.**

After the last section it is refreshing to find that the ionisation from hot wires is capable in some ways of exhibiting a certain amount of constancy. The results given on pp. 24 and 25 show that two wires at any rate gave approximately the same amount of ionisation, both positive and negative, per unit area with the same pressure of oxygen at all temperatures from 700° C. to 1250° C. In the course of the investigation the positive ionisation in oxygen, under similar conditions of pressure and temperature, was measured for four different wires having different linear dimensions. It is interesting to compare the leaks from these per unit area of surface when reduced, by means of the results which have been obtained, to some standard pressure and temperature. The pressure selected is 1.5 millims., and the leaks at this pressure are given for two temperatures, viz., 770° C. and 880° C. The data will be found in the following table (see next page).

The wires numbered (1), (2), and (4) were each 0.1 millim. in diameter, while No. (3) was 0.2 millim. in diameter. It will be noticed that, although the area of the wires varied in the ratio of nearly one to four, and the different wires had been very differently treated, yet the values of the leak per unit area, as shown by the last two columns, are very nearly the same in every case. The values furnished by the first wire on May 5 and July 14 are especially interesting, since they show that, once the steady condition is attained, there is no further falling off due to continued heating in oxygen at a red heat. This wire was heated for several hours on most days between the two dates to a temperature varying between 750° C. and 1100° C. As the observations recorded with wire No. 3 near the temperatures of 770° C. and 880° C. were a little irregular, the values were selected by drawing a curve like fig. 9 and finding the values of the leak at these temperatures from the curve. In regard to this wire it is only fair to say that it was subsequently heated strongly in hydrogen, and after that treatment was found to give a much smaller leak (about one-third to one-fourth) than before. It seems probable, however, that this is due to a permanent change produced by the hydrogen in the texture of the metal surface. It has often been observed that the surface of platinum which has been heated in hydrogen develops a roughened crystalline appearance. This change does not appear to be produced by heating in oxygen, at any rate at temperatures below 1100° C. The alteration could not be due to an error in the temperature brought about by a change in the temperature coefficient of the resistance, as the negative leak was not reduced in as great a ratio as the positive. The figures for the last wire are of interest, as they were obtained in the tube with water-cooled walls and were therefore free from any effect from the walls.
<table>
<thead>
<tr>
<th>Date</th>
<th>Pressure (millins)</th>
<th>Temperature (°C)</th>
<th>No. of wires</th>
<th>Effective area (sq. centim.)</th>
<th>Observed current (ampere)</th>
<th>Leakage per unit area at 1.5 millins and θ = 880° C.</th>
<th>Total leak at P = 1.5 millins and θ = 770° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 5, 1905</td>
<td>1.15</td>
<td>771</td>
<td>(1)</td>
<td>0.223</td>
<td>7.1 × 10^{-12}</td>
<td>7.5 × 10^{-12}</td>
<td>7.5 × 10^{-12}</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>885</td>
<td>(1)</td>
<td>0.223</td>
<td>28.1 × 10^{-12}</td>
<td>6.8 × 10^{-12}</td>
<td>6.8 × 10^{-12}</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>709</td>
<td>(1)</td>
<td>0.223</td>
<td>6.6 × 10^{-12}</td>
<td>30.5 × 10^{-12}</td>
<td>30.5 × 10^{-12}</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>828</td>
<td>(2)</td>
<td>0.223</td>
<td>4.93 × 10^{-12}</td>
<td>23.0 × 10^{-12}</td>
<td>23.0 × 10^{-12}</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>799</td>
<td>(2)</td>
<td>0.214</td>
<td>21.0 × 10^{-12}</td>
<td>31.8 × 10^{-12}</td>
<td>31.8 × 10^{-12}</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>878</td>
<td>(3)</td>
<td>0.214</td>
<td>4.7 × 10^{-12}</td>
<td>85.0 × 10^{-12}</td>
<td>85.0 × 10^{-12}</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>943</td>
<td>(4)</td>
<td>0.170</td>
<td>69.0 × 10^{-12}</td>
<td>129.8 × 10^{-12}</td>
<td>129.8 × 10^{-12}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>July 14, 1905</td>
<td>1.44</td>
<td>709</td>
<td>(1)</td>
<td>0.223</td>
<td>7.8 × 10^{-12}</td>
<td>23.0 × 10^{-12}</td>
<td>23.0 × 10^{-12}</td>
</tr>
<tr>
<td></td>
<td>1.44</td>
<td>828</td>
<td>(1)</td>
<td>0.223</td>
<td>25.6 × 10^{-12}</td>
<td>4.7 × 10^{-12}</td>
<td>4.7 × 10^{-12}</td>
</tr>
<tr>
<td></td>
<td>1.44</td>
<td>799</td>
<td>(2)</td>
<td>0.214</td>
<td>878</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.44</td>
<td>943</td>
<td>(4)</td>
<td>0.170</td>
<td>69.0 × 10^{-12}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>July 20, 1905</td>
<td>2.08</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>2.08</td>
<td>943</td>
<td>(4)</td>
<td>0.170</td>
<td>69.0 × 10^{-12}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>February 26, 1906</td>
<td>2.00</td>
<td>709</td>
<td>(2)</td>
<td>0.214</td>
<td>878</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>943</td>
<td>(4)</td>
<td>0.170</td>
<td>69.0 × 10^{-12}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>March 16, 1906</td>
<td>2.45</td>
<td>943</td>
<td>(4)</td>
<td>0.170</td>
<td>69.0 × 10^{-12}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The writer* has shown that a new platinum wire, even when well cleaned with boiling nitric acid and distilled water, gives rise to an abnormally high positive ionisation when heated in a vacuum. This initial ionisation gradually falls off to a small value, but it is found that a wire which has lost most of this initial effect still exhibits peculiar properties when the leak from it in an atmosphere of oxygen or air is examined. These effects, which only seem to disappear after continued heating at a low pressure, are characterised by great variation of current with electromotive force together with time changes in the current under constant voltage.

It has been shown that an old wire exhibits little variation of the current with electromotive force with voltages above 40. Changing the voltage from +40 to +760 never more than doubled the current in the case of an old wire at atmospheric pressure. In the case of a new wire, however, a change in the voltage generally altered the current in the ratio of the applied voltage. The current did not, however, remain steady at the new value. If the voltage had been increased it gradually fell to a value much nearer that which it had at the lower voltage. The steady value which the current seemed to be approaching was greater the higher the voltage, and what may be called the steady increase with voltage was generally greater the newer the wire. The converse increase in the current subsequent to lowering the voltage was also sometimes observed, but was much smaller.

The following numbers, which were obtained in air at atmospheric pressure at a temperature of about 900° C., with a wire which was not very new and therefore did not show the effect in its most exaggerated form, will illustrate the kind of thing that occurred. The wire under +40 volts was giving a leak which oscillated from 33 to 44 divisions, the minimum value of 33 divisions being, however, fairly constant. The voltage was changed to +360, when readings every successive 3 minutes gave for the values of the leak 117, 97, 79, 68, 70, 73. On changing the voltage back to +40, the leaks at 3-minute intervals were 21, 25, 22, 23.

The above experiments were carried out in the glass tube apparatus first described. This apparatus relies for its insulation inside the tube solely on the surface of the glass. It seemed possible that queer effects like the above might be obtained on changing the voltage if the surface of the glass were getting charged up. This might be especially likely to happen after a new wire had been sealed into the tube, owing to the surface retaining a film of moisture, since it was necessary to introduce moisture to clean out the tube.

For these reasons it seemed advisable to test the question with a form of apparatus which was not liable to these objections. The apparatus used was really designed for some experiments on the leak from a platinum tube which will be described later (see fig. 16, p. 54). The hot wire was insulated along the axis of three equal cylindrical

* 'Phil. Mag.' [6], vol. 6, p. 80.
tubes of aluminium. The two outside tubes acted as a guard ring, so that the leak was only measured from the uniformly heated central part of the wire to the surrounding middle cylinder. In addition to this, all the insulation was surrounded by earthed tubes, so that there was no possibility of it becoming charged up by strong ionisation. The effects previously observed were fully confirmed with this apparatus.

A new wire, not specially cleaned, placed in this apparatus gave with +40 volts a leak of 100 divisions which remained constant for 1 hour 40 minutes. On raising the potential to +760 volts the following values of the current were obtained at the times stated:

<table>
<thead>
<tr>
<th>Time</th>
<th>2</th>
<th>2</th>
<th>2</th>
<th>2</th>
<th>3</th>
<th>3</th>
<th>3</th>
<th>3</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>hours</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>minutes</td>
<td>44</td>
<td>47</td>
<td>50</td>
<td>58</td>
<td>4</td>
<td>9</td>
<td>20</td>
<td>31</td>
<td>38</td>
<td>44</td>
</tr>
<tr>
<td>Current</td>
<td>3570</td>
<td>1930</td>
<td>950</td>
<td>760</td>
<td>570</td>
<td>485</td>
<td>475</td>
<td>190</td>
<td>115</td>
<td>112</td>
</tr>
</tbody>
</table>

On returning to +40 volts, the leaks at successive six-minute intervals were 80, 84, 90, 94. The temperature in this experiment was 925° C. A similar experiment with a hot platinum tube 2 millims. in external diameter showed the same kind of effect, and also an increase in the positive leak, when the tube had been left negatively charged.

The obvious conclusion from these experiments is that part of the leak from a new wire is emitted by something which is itself positively charged, and is therefore removed when the wire is positive, but not when it is negative. Dust given off by the platinum might be expected to become positively electrified by virtue of point discharge action in the strong field in the neighbourhood of the hot wire whatever the sign of its electrification when it left the wire. It would thus be retained by a negatively, but not by a positively-charged wire. On the other hand, there appears to be no obvious reason either why dust should produce the observed effects or why a new wire should give off more dust than an old one. Blowing a current of air past the wire had no marked effect on the positive leak under a high voltage. The general complexity of these initial phenomena would seem, however, to indicate that there is more in them than the above simple explanation demands.

What the process of ageing a wire for the purpose of this investigation consists in is not quite clear. Mere heating alone will not do it. A new wire, which was heated for about a week in the air of the laboratory before being tested, was found to behave like a new wire when the leak was tested. The above experiments would seem to indicate that the presence of a big positive charge on the wire is instrumental in facilitating the decay of the initial leak, whilst, other things being equal, the rate of decay is greater at low than at high pressures. It looks as though the initial leak
from a new wire was due to the presence of some gas which was positively charged when emitted by the wire.* Such a gas might be expected to diffuse away from the wire more readily at a low than a high pressure and under a high than a low field.


The view which the author has been led to as the result of the foregoing experiments is that the positive, as well as the negative, ions are produced in the first instance inside the metal, or, at any rate, so far within the surface that their rate of production is in general uninfluenced by the external field. The experiments, in addition, afford strong support to the view that the positive ions are furnished not by the platinum itself, but by the oxygen absorbed or dissolved in the transition layer between the metal and the surrounding gas. That the positive ions do not arise in the space outside the free metal surface appears to be distinctly indicated by the following considerations.

We have seen that the positive and negative ionisations from hot platinum vary with the temperature according to the same kind of law, but quite independently of one another. This is exemplified by the fact that at a pressure of 1·5 millims. of oxygen the two leaks are equal to one another at about 1230° C., whereas at 700° C. the saturation current with the wire negative is about $10^{-7}$ of its value with the wire positive. The disparity between the two leaks points strongly to the view that they are the result of separate actions; it proves, in addition, that there is no considerable amount of volume ionisation, but it does not prove that the ions are not formed outside the wire. For instance, an oxygen molecule might attack a positively-charged platinum atom, with the result that of the two oxygen atoms present in the molecule the one carrying the negative charge combined with the platinum, whilst the other one was set free, forming a positive ion. Of course, the negative ion would in a sense be free while the interaction was taking place, but it would always be within a distance from the attracting positive ion comparable with the radius of the sphere of molecular action, and the interionic attraction would probably be enormous compared with the greatest external field of force (about $10^8$ volts per centimetre) which could be applied.

There are two main objections to the foregoing view, which otherwise has the advantage of simplicity to recommend it. One of these is the way in which the leak lags behind change of pressure. It will be noticed that the above theory would make the leak proportional to the rate of reaction between the $O_2$ and the free platinum. In order to explain the variation of the leak with pressure under steady pressures, it is necessary to assume, what is otherwise probable, that the proportion of uncombined

* This conclusion receives strong support from previous experiments by the writer, in which he showed that the ionising power of a new wire could be transferred to a second wire, previously rendered inactive by heating, if this were negatively charged. 'Phil. Mag.,' [6], vol. 6, p. 86.
platinum is smaller at high than at low pressures. Hence, if the pressure were suddenly changed from a high to a low value, the leak at constant temperature should be small at first and then gradually rise to a steady value, while suddenly increasing the pressure should give rise to the converse effect. As a matter of fact, the opposite of this is what has been observed in both cases, indicating that the ionisation is proportional to the "combined" rather than to the "free" platinum, if it is permissible to use these words in a rather wider sense than that usually understood by the term chemical combination.

The other objection depends on the way in which the steady leak varies with the pressure at low pressures. The preceding view would make the leak directly proportional to the pressure at low pressures at all temperatures, whereas the experiments show that at low temperatures and pressures the leak varies as the square root of the pressure. This result is also readily explained if we suppose the ionisation to be proportional to the amount of combined or absorbed oxygen rather than to the rate of chemical action between the oxygen and the platinum.

For the reasons stated, it seems necessary to seek the cause of the ionisation within the surface layer of the metal. On the molecular theory a metal, and in fact any solid, will possess a surface layer in which the molecules are more loosely held together than in the interior. On account of the well-known tenacity with which films of gas adhere to solid bodies, it seems reasonable to suppose that this layer will be capable of being penetrated by the surrounding gas, and that when equilibrium is established the absorbed gas will have a density which is very great compared with that of the free gas outside. This comes to assuming that a gas molecule loses potential energy when it enters the surface layer. To explain the results it is necessary to assume, in addition, that, for reasons connected with the structure of the metal, only dissociated oxygen atoms and not the ordinary molecules are capable of entering the surface layer. This assumption receives some support from the fact that the hydrogen which diffuses through hot platinum has been shown to be in the atomic form.* In order to make the problem definite we shall suppose the surface layer to be only a few atoms thick, and that each platinum atom is capable of retaining one oxygen atom in its immediate neighbourhood. The problem, then, reduces to what is virtually the determination of the condition of chemical equilibrium. Let the maximum concentration of the free platinum, i.e., the concentration when no gas is present, reckoned as so much per unit area, be \(a\), and let the concentration of the platinum which is used up by retaining its sufficient quontum of gas at time \(t = x\). Then the concentration of the free platinum at time \(t = a-x\). Let the external gas pressure = \(P\), then the pressure of the dissociated oxygen = \(p\), where \(p\) is given by the quadratic

\[
p^2 = k (P-p) \quad \ldots \ldots \ldots \ldots \ldots \ldots (1)
\]

* Cf. Winkelmann, 'Drude's Ann.' vol. 8, p. 388; and Richardson, Nicol and Parnell, 'Phil. Mag.' [6], vol. 8, p. 1.
$k$ being the dissociation constant of free oxygen. The rate of formation of the Pt, O systems is evidently proportional to $p(a-x)$, whilst their rate of decomposition is proportional to $x$. The total rate of increase is therefore

$$\frac{dx}{dt} = Ap(a-x)-Br,$$

$A$ and $B$ being constants. In the steady state $dx/dt = 0$, and

$$x = \frac{Apa}{B+Ap} = \frac{af(P)}{b+f(P)} \ldots \ldots \ldots \ldots \ldots \ldots (2),$$

if we write $b = B/A$ and $p = f(P)$. Assuming that the positive ionisation is proportional to the amount of adsorbed oxygen, its variation with the pressure will be given by the above expression.

The assumption that the ionisation is proportional to the amount of adsorbed oxygen does not commit us to the view that the ions are liberated by the decomposition of an oxide of platinum, though it is not inconsistent with that view. The phenomena of electrolysis show that, when molecular disruption is accompanied by electrical separation, the metal tends to receive a positive, and the non-metallic element a negative, charge. We might therefore expect the oxygen to be liberated from hot metals in the form of negative ions, whereas it is found that the oxygen receives a positive charge. This seems to indicate that the positive ions are not charged oxygen atoms when they are expelled from the system platinum-oxygen, which possibly becomes unstable owing to continued corpuscular bombardment. However, since we know so little of the material constitution of the positive ions, it seems unprofitable to dwell any longer on the question of their precise origin.

Returning to the consideration of the formula that has been obtained for the leak in equation (2), we see that when the amount of dissociation is small $p = k^1P^1$. This will be the case at low temperatures if the pressure is not too small, so that under these circumstances the ionisation will vary with the pressure as $\alpha P^1/(\beta + P^1)$, $\alpha$ and $\beta$ being constants. This expression is evidently of the right form, for when $P$ is small it varies as $P^1$, whilst when $P$ is great it becomes independent of $P$, and this is the kind of variation with pressure that was found experimentally. The numbers in the following table, which refer to an experiment at $730^\circ$ C., furnish a means of examining the agreement with the formula in more detail. The unit of current is $10^{-12}$ ampère. The constants in the formula are $\alpha = 12$, $\beta = 3\cdot9$, the pressures being reckoned in millimetres of mercury.

The agreement between the observed and calculated values of the ionisation is as close as the experimental results warrant. In general, the observed leak tends to be smaller than the calculated at the very lowest pressures, owing to the concentration of the dissociated oxygen beginning to vary with the pressure more rapidly than as
the square root. The above numbers yield, for the maximum current the above wire was capable of furnishing, at 730°C, the value $12 \times 10^{-12}$ ampère, or, per square centimetre of surface, $54 \times 10^{-12}$ ampère.

The following series refer to a somewhat higher temperature (820°C) and furnish a more complete test of the way the formula works at higher pressures. In this case $\alpha$ was taken $= 56 \times 10^{-12}$ ampère and $\beta = 4.0$ (millims. of mercury).

<table>
<thead>
<tr>
<th>Pressure in millims. of Hg.</th>
<th>$P_i$</th>
<th>Calculated leak, $x = x P_i/(\beta + P_i)$</th>
<th>Observed leak</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006</td>
<td>0.078</td>
<td>0.23</td>
<td>0.17</td>
</tr>
<tr>
<td>0.025</td>
<td>0.158</td>
<td>0.465</td>
<td>0.46</td>
</tr>
<tr>
<td>0.045</td>
<td>0.212</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>0.077</td>
<td>0.278</td>
<td>0.80</td>
<td>0.795</td>
</tr>
<tr>
<td>0.085</td>
<td>0.292</td>
<td>0.84</td>
<td>0.84</td>
</tr>
<tr>
<td>0.102</td>
<td>0.32</td>
<td>0.91</td>
<td>0.94</td>
</tr>
<tr>
<td>0.143</td>
<td>0.378</td>
<td>1.06</td>
<td>1.23</td>
</tr>
<tr>
<td>0.26</td>
<td>0.51</td>
<td>1.39</td>
<td>1.58</td>
</tr>
<tr>
<td>0.454</td>
<td>0.674</td>
<td>1.77</td>
<td>1.84</td>
</tr>
<tr>
<td>0.95</td>
<td>0.97</td>
<td>2.48</td>
<td>2.5</td>
</tr>
<tr>
<td>4.3</td>
<td>2.08</td>
<td>4.2</td>
<td>4.5</td>
</tr>
<tr>
<td>17.0</td>
<td>4.13</td>
<td>6.18</td>
<td>6.0</td>
</tr>
<tr>
<td>66.0</td>
<td>8.1</td>
<td>8.1</td>
<td>8.7</td>
</tr>
</tbody>
</table>

The maximum value of the positive ionisation in oxygen at 820°C appears from these numbers to be $= 2.5 \times 10^{-10}$ ampère per square centimetre. The values of the above leaks at the lowest pressures are probably somewhat high, as it was found to be impracticable to wait long enough to be certain that equilibrium had become fully established.

We have seen that the assumption that the denominator in the expression for the positive ionisation is of the form $\beta + P_i$ is an approximation which will only hold at
low temperatures. The numbers given below show that at 1170° C. the leak is very closely represented by an expression of the form \( \alpha P/(\beta + P) \), which would be the value given by the theory if most of the gas outside the wire were dissociated. This is likely enough to be the case at pressures of the order of 1 millim., and at higher pressures the exact form of \( f(P) \) has very little influence on the result. No doubt a better agreement could have been obtained by putting in the theoretical value for \( P \), viz., \( \sqrt{kP + \frac{1}{4}P^2 - \frac{1}{2}k} \), but this involves introducing a new constant \( k \) into the expression for the ionisation, a refinement which is not warranted by the exactitude of the experimental results. It appeared to be impossible to test the theory more fully by pushing the experiments to a higher order of accuracy, on account of the irregularities which have already been described.

The experimental values of the ionisation at 1170° C. and those calculated from the formula \( \alpha P/(\beta + P) \) are given in the following table. \( \alpha \) was taken = 38\( \times 10^{-10} \) amperé, and \( \beta = 4.8 \) millims. of mercury:

<table>
<thead>
<tr>
<th>Pressure in millims. of Hg.</th>
<th>Calculated leak, ( x = \alpha P/(\beta + P) )</th>
<th>Observed leak.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14</td>
<td>0.96</td>
<td>1.08</td>
</tr>
<tr>
<td>0.30</td>
<td>2.0</td>
<td>2.24</td>
</tr>
<tr>
<td>0.39</td>
<td>2.56</td>
<td>2.85</td>
</tr>
<tr>
<td>0.62</td>
<td>3.9</td>
<td>4.35</td>
</tr>
<tr>
<td>1.27</td>
<td>7.2</td>
<td>7.9</td>
</tr>
<tr>
<td>2.06</td>
<td>10.4</td>
<td>11.3</td>
</tr>
<tr>
<td>5.3</td>
<td>18.8</td>
<td>19.9</td>
</tr>
<tr>
<td>23.5</td>
<td>30.8</td>
<td>31.5</td>
</tr>
<tr>
<td>89</td>
<td>36.0</td>
<td>35.9</td>
</tr>
</tbody>
</table>

The greatest value of the positive leak in oxygen at 1170° C. works out at 1.7\( \times 10^{-8} \) amperé per square centimetre of platinum surface. The smaller amount of variation with temperature exhibited by the constant \( \beta \) is a surprising result. At the two lower temperatures \( \beta = Bk^{-1}A^{-1} \) in the notation previously employed, and its constancy with temperature implies that the heat of formation of the platinum-oxygen systems from atomic oxygen is nearly equal to the heat of formation of an oxygen molecule from two atoms. At the higher temperature \( \beta \) is equal to \( B/A \), and its value in conjunction with the preceding result implies that \( B/A \) is small compared with 4.8 at the lower temperatures.

According to the present theory, the energy change associated with the action which gives rise to a positive ion is given exactly by the temperature variation of the maximum value of the leak and not by the temperature variation of the leak under a pressure of 1.47 millims. as was assumed on p. 25. The preceding results enable us to correct for this, but as the effect of the correction is smaller than the probable experimental error it has not been proceeded with.

\[ \text{E 2} \]
IV.—§ 11. The Ionisation in Nitrogen.

The nitrogen used in the experiments was prepared from air and therefore contained the inert gases in the proportion in which they occur to nitrogen in the atmosphere. So far as was possible without using very elaborate refinements, care was taken to free it from oxygen, hydrogen, carbon dioxide, dust and organic impurities. The air of the laboratory was allowed to bubble very slowly through a wash bottle containing alkaline pyrogallate and then passed over (1) a red-hot tube about 60 centims. long containing copper and copper oxide, (2) a long tube packed with cotton wool, and (3) a tube 30 centims. long packed with fused potash and plugged with glass wool, before it was admitted into the apparatus. Inside the apparatus it was finally dried over \( \text{P}_2\text{O}_5 \) and further purified (1) at low pressures by exposure to sodium amalgam from a cathode of which a discharge could be passed from time to time, (2) at high pressures by heating a copper spiral red hot in it. The copper spiral had previously been heated in a vacuum to drive off occluded hydrogen. With regard to the discharge from the sodium amalgam cathode it was found advisable not to pass it too frequently, as it absorbs nitrogen rather quickly, but not so quickly as it absorbs oxygen. All the purifying arrangements were placed close to the testing bulb and between it and the rest of the apparatus so as to be as efficient as possible. After the nitrogen had been prepared, the copper in the hot tube was always found to be quite bright except at the front end.

The positive ionisation in nitrogen is small compared with that in oxygen, especially at low pressures. As we have seen, a small quantity of oxygen has a very big effect on the positive leak, and it might therefore be supposed that the leaks observed in nitrogen were due to traces of oxygen which had not been removed by the purifying processes. This, however, is rendered improbable by the fact that the ionisation in nitrogen differs in character in certain important respects from that in oxygen. The current requires a greater electromotive force to saturate it under similar conditions, and it also showed time changes, after altering the applied E.M.F., similar to those observed in a new wire. These changes were never observed in a wire which had been heated in oxygen for a long time.

On letting in fresh nitrogen the leak was always found to have a much bigger value than that at which it finally settled down. The rate of decay was very big at first, but after a time became extremely slow, so that there still seemed to be a slow decrease after several hours' heating at \( 900^\circ \text{C} \). This decrease may have been due to the gradual absorption of oxygen. No decrease in pressure could be observed, but this does not prove anything, as the decrease in the pressure required to account for the observed effects, supposing them due to oxygen, would fall within the probable experimental error. The measurements of the relation between the current and the applied E.M.F., &c., refer to the state in which the leak was varying very slowly, if at all, with the time.
The relation between current and E.M.F. at 2·8 millims. pressure and 905° C. is given by the following numbers:

<table>
<thead>
<tr>
<th>Volts</th>
<th>+0·3</th>
<th>+2·2</th>
<th>+7</th>
<th>+11</th>
<th>+40</th>
<th>+80</th>
<th>+160</th>
<th>+240</th>
<th>+360</th>
<th>+40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>0·19</td>
<td>0·52</td>
<td>0·66</td>
<td>0·77</td>
<td>1·0</td>
<td>1·1</td>
<td>1·3</td>
<td>1·33</td>
<td>1·58</td>
<td>0·53</td>
</tr>
</tbody>
</table>

$(1 = 3·9 \times 10^{-12}$ ampère per sq. centim.)

At 760 millims. and 920° C. the values found were:

<table>
<thead>
<tr>
<th>Volts</th>
<th>+40</th>
<th>+120</th>
<th>+200</th>
<th>+360</th>
<th>+560</th>
<th>+760</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>9</td>
<td>26</td>
<td>32</td>
<td>40</td>
<td>41</td>
<td>42</td>
</tr>
</tbody>
</table>

$(1 = 5·3 \times 10^{-12}$ ampère per sq. centim.)

Compared with oxygen under similar conditions, these numbers, which are shown graphically in fig. 11, show that the ionisation in nitrogen requires a greater applied E.M.F. to produce saturation. With the above wire, which was 0·02 centim. in diameter, the current in oxygen showed very little increase with voltage after 40 volts. The increase with 360 volts at 2·8 millims. is due to the occurrence of ionisation by collisions.

The variation with temperature of the leak in nitrogen at a pressure of 2·8 millims. was also examined. On raising the temperature the leak was too big at first and usually required about 20 minutes to fall to its minimum value. The numbers obtained for the positive and negative ionisation are given in the accompanying table:

![Fig. 11.](image-url)
These numbers were found to obey the formula $A_0^i e^{-\alpha t}$. The values of the energy changes associated with the liberation of a gram-molecule of positive and negative ions respectively are found to be $\omega_+ = 7 \times 10^4$ calories and $\omega_- = 11 \times 2 \times 10^4$ calories. Thus the work required to liberate a positive ion from platinum in an atmosphere of nitrogen is more than twice the value of the corresponding quantity in oxygen.

At low pressures the positive saturation current in nitrogen was found at 905°C to consist of two parts, one independent of the pressure and the other nearly proportional to it. This is shown by the following numbers:

<table>
<thead>
<tr>
<th>Pressure in millims.</th>
<th>0.067</th>
<th>0.14</th>
<th>0.3</th>
<th>0.6</th>
<th>1.3</th>
<th>2.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>2.6</td>
<td>2.6</td>
<td>2.2</td>
<td>3.0</td>
<td>4.3</td>
<td>6.6</td>
</tr>
<tr>
<td>($1 = 3.3 \times 10^{-10}$ ampère per sq. centim.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The current did not continue increasing with the pressure at the above rate up to atmospheric pressure, but at slightly higher pressures than the above the current curve began to bend round towards the pressure axis. It did not, however, tend to become independent of the pressure as in the case of oxygen, but it increased at a rate proportional to the pressure at high pressures. The variation of saturation current with pressure up to atmospheric pressure is shown in the lower curve in fig. 11. The unit of current = 1.05 $\times 10^{-12}$ ampère per square centimetre. The temperature was 920°C.

The nitrogen used in the last experiment was allowed to remain all night in the apparatus, whilst both the platinum wire and the copper spiral were heated in it. During this time the leak with +40 volts decreased considerably, as is shown by the following numbers:

Oxygen was certainly absorbed during the above heating by the copper spiral, for it was afterwards found to be blackened. It is therefore difficult to be certain that the final value of the ionisation was really due to nitrogen rather than to a small trace of oxygen which the copper spiral was incapable of removing. Assuming that
PRODUCED BY HOT PLATINUM IN DIFFERENT GASES.

<table>
<thead>
<tr>
<th>Time</th>
<th>P.M. 5.43</th>
<th>P.M. 6.01</th>
<th>P.M. 6.40</th>
<th>P.M. 7.11</th>
<th>P.M. 9.12</th>
<th>A.M. 10.06</th>
<th>A.M. 10.30</th>
<th>P.M. 3.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>48</td>
<td>39</td>
<td>34</td>
<td>28</td>
<td>24</td>
<td>14.5</td>
<td>10.5</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>(1 = 7 \times 10^{-13}) ampère per sq. centim.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Oxygen and nitrogen act quite independently of each other in producing the positive ionisation—reasons will be adduced later for showing that this is improbable—the proportion of oxygen to nitrogen required to account for the whole of the leak in nitrogen at atmospheric pressure would be about 1 to 10,000. Against this it is necessary to set the following facts:—

1. The ions in nitrogen appear to be considerably bigger than those in oxygen, as shown by the current E.M.F. curves.

2. The experiments on air indicate that nitrogen does not simply act as a diluent to oxygen, but exerts a marked retarding effect on its power of producing positive ionisation, so that a trace of oxygen present would exert a much smaller effect than that obtained on the basis of the above calculation.

3. The positive ionisation in nitrogen varies more rapidly with temperature than that in oxygen. The numbers indicate that the energy necessary to liberate a positive ion from hot platinum in nitrogen is rather more than twice the value for oxygen.

On the whole, the balance of evidence seems to be in favour of the view that nitrogen produces a genuine positive ionisation which is considerably smaller than that in oxygen at about 900°C.

V.—§ 12. THE IONISATION IN AIR.

The air used in these experiments was purified by passing slowly through two tubes, one packed with cotton wool and the other with fused caustic potash. It was subsequently dried over phosphorus pentoxide inside the apparatus. The general characters of the results in air are similar to those in oxygen, but the current was found to be more difficult to saturate under otherwise like conditions.

The relation between the current and the electromotive force at atmospheric pressure is given by the lower curve in fig. 12. The observations to which both the curves in fig. 12 refer were made with the water-cooled apparatus already described. The temperature was 976°C., the effective area of the wire 0.170 sq. centims., and the unit of current \(7 \times 10^{-13}\) ampère. The upper curve gives the value of the saturation current at different pressures. In this curve the leak at the four highest pressures was measured with +704 volts, the next with +512 volts, and the two lowest with +120 volts. This method of gradually decreasing the voltage as the pressure was lowered, so as to ensure approximate saturation and at the same time
avoid the occurrence of ionisation by collision, was frequently adopted in this investigation.

![Graph](image)

The temperature variation of the approximately saturated leak in air at atmospheric pressure was also examined with the wire 0.2 millim. diameter in the glass tube apparatus. The numbers obtained are given in the following table. The effective area of this wire was 0.66 sq. centim.:—

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Current $V = +560$</th>
<th>Current $V = -40$</th>
</tr>
</thead>
<tbody>
<tr>
<td>618</td>
<td>$9.3 \times 10^{-12}$</td>
<td>$3.3 \times 10^{-14}$</td>
</tr>
<tr>
<td>893</td>
<td>$2.2 \times 10^{-11}$</td>
<td>$5.3 \times 10^{-14}$</td>
</tr>
<tr>
<td>900</td>
<td>$5.2 \times 10^{-11}$</td>
<td>$3.2 \times 10^{-13}$</td>
</tr>
<tr>
<td>978</td>
<td>$3.3 \times 10^{-10}$</td>
<td>$4.2 \times 10^{-12}$</td>
</tr>
<tr>
<td>1064</td>
<td>$8.0 \times 10^{-10}$</td>
<td>$3.8 \times 10^{-11}$</td>
</tr>
<tr>
<td>1150</td>
<td>$2.0 \times 10^{-9}$</td>
<td>$2.6 \times 10^{-10}$</td>
</tr>
<tr>
<td>1236</td>
<td>$6.7 \times 10^{-9}$</td>
<td>—</td>
</tr>
</tbody>
</table>

These numbers may be compared with the values for the leak in oxygen at different temperatures given on p. 23. In doing this it is necessary to multiply the latter by a factor of about 3.3, which varies slightly with the temperature, to bring the positive leak to its value at atmospheric pressure. Both sets of numbers have also to be divided by the effective areas of the respective wires. When this is done, it will be seen that the maximum leak in oxygen is greater than that in air at all temperatures, though the latter increases more rapidly with the temperature. Both the positive and negative leaks in air obey the formula $A \theta e^{-w\theta}$; the values of the constants which determine the energy change associated with the formation of one
gram equivalent of each kind of ions being respectively \( \omega_+ = 4.92 \times 10^4 \) and \( \omega_- = 8.97 \times 10^4 \) calories. The value of \( \omega_- \) for oxygen was \( 13.5 \times 10^4 \) calories; the lower value obtained in air is possibly due to \(-40\) volts not being sufficient to produce saturation. Experiments were not made to test this at the time, but some results obtained by H. A. Wilson\(^*\) indicate that this might have been the case. The value of \( 4.92 \times 10^4 \) for \( \omega_+ \) is intermediate between the values \( 3.04 \times 10^4 \) and \( 7.12 \times 10^4 \) found for oxygen and nitrogen respectively.

Referring to the above table, we find for the maximum current in air the values \( 2.2 \times 10^{-11} \) and \( 5.2 \times 10^{-11} \) ampère at \( 893^\circ \) C. and \( 900^\circ \) C. respectively. Taking the mean of these, \( 3.7 \times 10^{-11} \) ampère, to be the true value at \( 897^\circ \) C., and dividing by \( 0.66 \) to reduce to unit area, we find for the maximum current at \( 897^\circ \) C. the value \( 5.5 \times 10^{-11} \) ampère per square centimetre. The corresponding quantity in oxygen deduced from fig. 9 (here we have to multiply by \( 3.3 \) on account of the low pressure) is \( 5.8 \times 10^{-10} \) ampère per square centimetre, or ten times the corresponding quantity in air. Again, referring to fig. 12, we see that the maximum leak in air at \( 976^\circ \) C. is \( 4.5 \times 10^{-10} \) ampère per square centimetre, a number which agrees satisfactorily with the value \( 4.95 \times 10^{-10} \) ampère per square centimetre given by the table on p. 40. The maximum leak in oxygen deduced from fig. 10 is \( 1.2 \times 10^{-10} \) ampère per square centimetre, nearly three times the value for air. It is interesting to compare with these numbers what the values for air would be if the nitrogen had no effect. Since air contains \( 21 \) per cent. of oxygen by volume, on this basis the leak in air at \( 760 \) millims. would be the same as that in oxygen at \( 160 \) millims. Referring to fig. 7, we see that this should be equal to \( 0.775 \) of the value in oxygen at \( 760 \) millims. This would give \( 44 \times 10^{-11} \) and \( 9.5 \times 10^{-10} \) ampère per square centimetre at the two temperatures instead of the values \( 5.5 \times 10^{-11} \) and \( 4.5 \times 10^{-10} \) actually found.

This result, that the positive ionisation in air was smaller than if the nitrogen had been removed, seemed at first sight very surprising, and further experiments were made to test the question directly. This was done by letting air and oxygen into the apparatus immediately after each other and measuring the leak at atmospheric pressure. The experiments were carried out at \( 895^\circ \) C. The values obtained are given in the subjoined table, that in nitrogen being added for comparison. The experiments were carried out in the order of the table, proceeding from above downwards. The unit of current is \( 7 \times 10^{-13} \) ampère.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Saturation current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>29</td>
</tr>
<tr>
<td>Air</td>
<td>70</td>
</tr>
<tr>
<td>Oxygen</td>
<td>336</td>
</tr>
<tr>
<td>Air</td>
<td>70</td>
</tr>
<tr>
<td>Oxygen</td>
<td>244</td>
</tr>
</tbody>
</table>

* 'Phil. Trans.,' A, vol. 202, p. 256, fig. 5.

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The oxygen in the first experiment was prepared by electrolyzing caustic potash, in the second by heating potassium permanganate. The difference in the values for oxygen is probably "accidental."

The disparity between the two leaks is considerably smaller than that calculated from the table, but it shows that nitrogen has a distinct inhibiting effect on the positive ionisation produced by oxygen. It may do this by combining with the free oxygen ions and so reducing their concentration, or by associating with the platinum and so reducing the amount available for combination with oxygen. The latter view would give a satisfactory quantitative explanation of the results.

VI.—§ 13. The Ionisation in Helium.

A few experiments were made in this gas chiefly with the object of finding out if hot platinum would liberate positive ions in an atmosphere in which the possibility of chemical action in the ordinary sense was excluded. The helium used was obtained from Messrs. Tyrer and Co., Sterling Chemical Works, Stratford, E. After admitting it into the apparatus it was dried over phosphorus pentoxide and purified by means of a discharge from a cathode of sodium potassium alloy. The tube used for this purpose is shown in fig. 13. After the apparatus had been completely exhausted, the liquid alloy was admitted through the stop-cock A. Care has to be exercised in doing this, as the alloy is liable to stick in the tube, and, when it begins to move again, to do so with such violence that it is projected into other parts of the apparatus. The electrical connection to the cathode was made by the platinum wire B sealed into the glass. The anode C was of aluminium. The side tubes D, E led to the pentoxide bulb and testing vessel and to the pump and McLeod gauge respectively.

Mey* has shown that the discharge from a cathode of sodium potassium alloy given by an induction coil rapidly absorbs all gases except the inert ones. The discharge used was found to run down 3 millims. of air to a pressure comparable with that due to the residual argon in about 20 minutes. The discharge was allowed to pass for several hours before measurements of the leak were made. The helium must have been very pure to start with, as no decrease in pressure was observed with the McLeod gauge. The spectrum was also examined from time to time, and no lines belonging to any gas other than helium were noticed.

There is every reason to believe that the helium used in these experiments attained a very high degree of purity, and that the leak observed is really due to helium and not to traces of some other gas present. The leak resembled that

* 'Drude's Ann.,' vol. 11, p. 138.
in nitrogen in showing too big a value after the wire had been allowed to remain cold and only gradually settling down to a steady value. It is very difficult to explain this effect as being due to the absorption of impurities, as it appeared to be much the same whether the discharge had been run before the leak was tested or not. It seems far more likely to be due to a change taking place in the platinum. The following measurements at $907^\circ$ C. of the leak at 2.4 millims. pressure with +11 volts on the filament show the way it varied with time:

<table>
<thead>
<tr>
<th>Time</th>
<th>A.M. 10.46</th>
<th>A.M. 10.48</th>
<th>A.M. 11.10</th>
<th>A.M. 11.25</th>
<th>A.M. 11.50</th>
<th>P.M. 12.09</th>
<th>P.M. 12.26</th>
<th>P.M. 2.21</th>
<th>P.M. 2.41</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>314</td>
<td>294</td>
<td>194</td>
<td>156</td>
<td>134</td>
<td>148</td>
<td>124</td>
<td>134</td>
<td>130</td>
</tr>
<tr>
<td>$(1 = 3 \cdot 3 \times 10^{-14}$ ampère per sq. centim.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The values of the steady leak under +11 volts at the same temperature and different pressures are as follows:

<table>
<thead>
<tr>
<th>Pressure in millims. of Hg</th>
<th>0.07</th>
<th>0.32</th>
<th>2.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>18</td>
<td>54</td>
<td>130</td>
</tr>
<tr>
<td>$(1 = 3 \cdot 3 \times 10^{-14}$ ampère per sq. centim.)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The positive ionisation in helium at 2 millims. pressure and $907^\circ$ C. appears to be, roughly speaking, about three times that in nitrogen and one-fortieth that in oxygen under like conditions.

The above experiments are not complete enough to enable us to deduce the law according to which the leak in helium varies with the pressure. The experiments were not pushed up to high pressures owing to the difficulty of ensuring the purity of the gas. They are chiefly of interest as showing that hot metals can produce ionisation in the inert gases when chemical action is out of the question.

VII.—§ 14. THE IONISATION IN HYDROGEN.

A large number of experiments have been made with this gas, but the phenomena are very complicated, so that it is difficult to be quite certain of the interpretation of the results. This is largely owing to our ignorance of the absorption and diffusion of hydrogen in platinum at low pressures. Some of the effects observed seem to be of considerable interest and importance, and they will be described in order to give greater completeness to this account of the subject. Discussion of the theoretical bearing of the results will be avoided except in so far as it is necessary to render the purpose of the experiments intelligible, and generally speaking the writer is of opinion that this part of the work ought to be regarded as a preliminary exploration.
of a very complex question. So far as the negative leak is concerned, the ground has been previously examined, and valuable results obtained by H. A. Wilson.*

The hydrogen used in the experiments was prepared for the most part by the action of pure zinc on pure hydrochloric acid with a little ferric chloride added to make the action go. It was passed over solid potash and cotton wool before being admitted into the apparatus. In some cases, when only a little hydrogen was required, it was admitted into the apparatus by diffusion through the walls of a platinum tube heated in a spirit-lamp flame. This method is a very convenient one for obtaining a small quantity of hydrogen in a high degree of purity. As is well known, the negative ionisation produced by hot platinum in an atmosphere of hydrogen is very big, and it was found impossible to use the electrometer in the ordinary way, with a condenser attached to the quadrants, in order to measure the currents obtained. These currents, which amounted to as much as $10^{-4}$ ampère in some cases, were measured by taking the steady deflection when the electrometer quadrants were connected by a high resistance which could be varied from one to one million ohms. This was a very convenient arrangement, as it enabled the same instrument, by simply changing a few plugs, to be used for measuring any current from $10^{-1}$ to $10^{-14}$ ampère.

Interesting effects are observed when a wire, which has previously been heated in oxygen only is first heated in hydrogen. Such a wire gives rise to an abnormally high positive ionisation which gradually decays with time, whilst the negative ionisation increases simultaneously. The kind of thing that occurs is typified by the numbers in the subjoined table. The wire, which was 0.1 millim. in diameter and had an effective area of 0.214 sq. centim., had previously been heated in oxygen at 2 millims. pressure at a temperature of 800° C. Under these conditions it was giving about $8.5 \times 10^{-12}$ ampère positive leak, the negative leak being small compared with this value. The wire was then allowed to cool, the oxygen pumped out, and hydrogen let in to a pressure of 27.5 millims. The currents, with potentials of −40 volts on the filament, were then measured at different times at a constant temperature of 800° C., with the result shown by the table.

<table>
<thead>
<tr>
<th>Time (hours . . .)</th>
<th>3</th>
<th>3</th>
<th>3</th>
<th>3</th>
<th>3</th>
<th>3</th>
<th>4</th>
<th>4</th>
<th>4</th>
<th>4</th>
<th>4</th>
<th>5</th>
<th>5</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>32</td>
<td>36</td>
<td>42</td>
<td>44</td>
<td>47</td>
<td>52</td>
<td>56</td>
<td>58</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>15</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>Current, + . . . .</td>
<td>54</td>
<td>47.5</td>
<td>30.5</td>
<td>24</td>
<td>20</td>
<td>14</td>
<td>---</td>
<td>---</td>
<td>15.5</td>
<td>10</td>
<td>7.5</td>
<td>7.1</td>
<td>---</td>
<td>10</td>
</tr>
<tr>
<td>(1 = 10^{-12} ampère)</td>
<td>4</td>
<td>7.8</td>
<td>2.6</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>8</td>
<td>8.4</td>
<td>---</td>
<td>---</td>
<td>75</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Current, − . . . .</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>3.96</td>
<td>3.4</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>(1 = 10^{-8} ampère)</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>---</td>
<td>---</td>
<td>8</td>
<td>8.4</td>
<td>---</td>
<td>---</td>
<td>75</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

It will be noticed that after the wire had been charged negatively, the positive leak was abnormally high. This may be a spurious effect due to the insulation

PRODUCED BY HOT PLATINUM IN DIFFERENT GASES.

becoming charged by the copious negative ionisation. It was impossible to test the question with the apparatus used.

A second wire, 0.2 millim. in diameter, was tested and found to give results almost identical with the above when it was heated in hydrogen for the first time at 860°C. This wire was afterwards heated in hydrogen and later in oxygen for several days, mostly at a temperature of about 1100°C. A long time after the wire had again got into a steady condition in regard to the ionisation in oxygen the oxygen was pumped out and hydrogen re-admitted. The wire was now heated in hydrogen at 26 millims. pressure at a temperature of 900°C, when it was found that the above slow time changes had almost disappeared. The negative leak when first measured about 10 minutes after first heating the wire was 6.72 x 10^{-5} ampère, whilst the positive was 4.5 x 10^{-12} ampère. They subsequently rose and fell to 8 x 10^{-5} ampère and 6.7 x 10^{-12} ampère respectively. The difference between the two cases seems to indicate that heating in hydrogen produces a permanent change in the constitution of the platinum. There are two other facts which support this contention. One is the permanent reduction of the value of the steady positive leak in oxygen produced by continued heating in hydrogen, which was mentioned on p. 27. The other is that the surface of a wire which has been heated for a long time in hydrogen becomes visibly pitted and cracked. This change does not appear to be produced by heating, to moderate temperatures at any rate, in oxygen.

Observations were also recorded of the variation in the ionisation when the gas in which the wire was heated was changed from hydrogen to oxygen. The change from one gas to the other was carried out in the same way as in the previous case. Oxygen was admitted to a pressure of 1.067 millims. and the wire maintained at 900°C. Under these circumstances the negative leak was found to fall at once to the small value previously obtained in oxygen. The negative leak when first measured registered 2 x 10^{-13} ampère per square centimetre, and it was found to possess the same value 20 minutes later. The positive leak, on the contrary, fell gradually during 3 hours from 4.8 x 10^{-11} to 8.9 x 10^{-12} ampère, more than half the fall occurring in the first half hour. This decrease in the ionisation was accompanied by a slight decrease in the pressure of the oxygen, which fell to 1.026 millims., indicating that hydrogen had been evolved by the wire, had combined with the oxygen, and that the water formed had been absorbed by the phosphorus pentoxide. This experiment indicates that hydrogen diffusing out of a hot platinum wire increases the positive leak in oxygen, but is without effect on the negative leak. This conclusion will be more fully established by experiments to be described later.

The last experiment shows that although a considerable amount of hydrogen may remain in the wire, the addition of a small quantity of oxygen at once reduces the negative ionisation to a small value. This indicates that the great negative ionisation produced by hydrogen in platinum is due to some change of a very superficial character. On the other hand, a wire which has previously only been heated in
oxygen only appears to attain to the high value of the leak in hydrogen with extreme slowness when heated in that gas. It seems very difficult to reconcile these statements if the only time effect occurring is the diffusion of hydrogen into and out of the wire.

The relation between the negative leak in hydrogen and the applied electromotive force was next examined. It was found that the normal curve, exhibiting saturation and a definite relation between current and electromotive force, could only be obtained under very restricted conditions. The normal relation referred to is that exhibited by fig. 14. This experiment was made with the wire 0·2 millim. in diameter and 0·66 sq. centim. effective area; the pressure of hydrogen was 3·8 millims. and the temperature 900° C.

The heating current caused a fall of potential of about 5 volts along the filament; the potentials given are the potentials of the middle point of the filament. The unit of current is $1\times10^{-8}$ ampère. The increase in the current with voltages greater than 20 indicates that ionisation by collisions was beginning to come in.

On pushing these experiments to higher potentials, it was found that the current ceased to be a definite function of the applied E.M.F. and varied in a curious way with the time. The mystery was cleared up when considerably higher potentials were applied. The experiments were carried out at 1084° C. with a wire 0·1 millim. in diameter and an effective area of 0·214 sq. centim. The pressure was 1·77 millims.; the unit of current to which the following numbers refer is $10^{-8}$ ampère. It was found that under a high voltage the steady current was smaller than under a low one. For instance, under 19 volts the wire had been giving a steady negative leak of about 147 divisions. At a certain instant the voltage was changed to 286, when the following values of the current were obtained after the intervals of time stated:

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>10</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>62</td>
<td>44</td>
<td>37</td>
<td>33</td>
<td>28·5</td>
<td>26</td>
</tr>
<tr>
<td>$(1 = 10^{-8}$ ampère)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(V = -286)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The voltage was now reduced to 80, when the current was found to remain almost steady for some time at 7 divisions. It did not, however, stay at this value, but after a time began to increase, slowly at first, then more rapidly, then more slowly again, until it finally became steady at about 220 divisions. This great reduction of the leak by applying a big voltage and subsequent slow increase under a low voltage
was observed time after time with two different wires under varied conditions of temperature and pressure. On the other hand, the absolute values of the leaks finally obtained seemed very capricious. The general character of these time changes is exhibited by fig. 15.

In order to make the experiments comparable, the wire was maintained at a potential of -286 volts for 120 seconds before the readings under any assigned voltage were commenced. For obvious reasons the voltage on the filament during any one set of readings was never changed.

The reduction in the negative leak by applying a big voltage does not occur under the following conditions:—(1) At very low pressures (< 0.1 millim.), (2) at high pressures (200 millims.), (3) when the wire is positively charged. The subsequent increase in the ionisation occurs if the wire is either uncharged or charged positively as well as under a low negative potential. The time required for the establishment of the final equilibrium appears to decrease fairly rapidly as the temperature increases. The voltages employed in the previous experiments were never great enough to produce a luminous discharge, though the effect does occur if a luminous discharge passes. The reduction in the ionisation is greater if the wire is made the cathode than if it is made the anode.
All the above facts point to the view that the reduction of the negative leak in hydrogen produced by the application of a high potential is due to a change in the surface caused by the bombardment of the surface by the positive ions produced in the gas by ionising collisions. This view is supported by the fact that after the high potential had been applied a greater heating current was always required to maintain the wire at its original temperature. This shows that the amount of heat radiated from the surface at a given temperature was greater than before, so that the nature of the surface must have become changed in some way.

Two views which are not mutually exclusive may be taken as to the nature of the action by which the bombardment of the positive ions, which are really weak canal rays, reduces the negative leak. They may act either by destroying a layer of positively-charged hydrogen which helps the corpuscles out of the metal, or they may merely allow the absorbed hydrogen to escape from the wire. The last suggestion receives strong support from the recent experiments of SKINNER on the evolution of hydrogen from metallic cathodes under the influence of the luminous discharge.* On the other hand, it is difficult to conceive how bombardment by positive ions for two minutes can allow so much hydrogen to escape from a wire that it takes several hours for it to diffuse back again. On the whole, the evidence, though inconclusive, is in favour of the double layer theory.

The writer has examined the effect of changing the temperature on the value of the steady negative ionisation in hydrogen, and has confirmed WILSON’s† result that increasing the temperature gives a leak which is too big initially, whilst decreasing the temperature has the converse effect. The curve showing the recovery with time, after heating to a high temperature, is similar in form to that obtained after exposure to a high potential, although the ratio of final to initial value of the leak was smaller in the cases examined.

So far little has been said about the steady positive ionisation in hydrogen. We saw on p. 44 that a wire when first heated in hydrogen gives a considerable positive leak which gradually decays with time. It is an interesting question whether this decay would go on indefinitely, or if the positive leak has a minimum value depending in pressure, temperature, &c. The following experiments show that the steady positive leak due to hydrogen at 3·8 millims. pressure and a temperature of 900° C. is very small, even if it exists.

The wire (diameter = 0·2 millim. and effective area 0·67 sq. centim.) was maintained at a constant temperature of 900° C. in a hydrogen vacuum for about 3½ hours. By pumping from time to time, the steady pressure was kept below 0·001 millim., though hydrogen was being given off by the wire. The values of the leak with + 40 volts at various times were as follows:—

The rate of evolution of hydrogen from the wire decreased considerably during the above experiment. During the first half hour the pressure in the apparatus rose by 0.0033 millim., and during the last half hour by 0.00016 millim. The volume of the apparatus was about 2000 cub. centims., that of the wire being 0.0033 cub. centim. The amount of hydrogen left in the wire would probably be comparable with that given out in the last half hour, so that the pressure of the hydrogen inside the wire would, according to the above numbers, still be considerable. The current $2 \times 10^{-13}$ ampère at the end of the experiment might be due to the residual gas left in the wire, so that these experiments are not contrary to the view that the positive leak in hydrogen, such as it is, is due to absorbed gas.

The effect of letting in hydrogen to a pressure of 3.8 millims. was now tried, and the leak at 900° C. measured at various times, with the results shown.

The big leak obtained on letting in the fresh gas is a somewhat surprising result, but might possibly be due to impurities which are gradually destroyed or removed. The point which seems most important is the small value, $5.2 \times 10^{-12}$ ampère, of the steady leak at this pressure. This was only two and a-half times the value of the positive leak obtained after the wire had been heated for 3½ hours in a good vacuum. The value of the positive leak in oxygen at this pressure and temperature would have been about $10^{-10}$ ampère, or nearly twenty times the above number.

Owing to the smallness of the positive leak in hydrogen, together with other difficulties which arose, few other satisfactory measurements were made on it.

Measurements of the variation with pressure of the negative ionisation from hot platinum in hydrogen have been made by H. A. Wilson.* Wilson's method consisted in measuring the leak when hydrogen at successively increasing pressures

had been admitted to a wire previously oxidised in nitric acid. At a temperature of 1350°C, the ionisation increased rather less rapidly than if it were proportional to the pressure up to 0.014 millim. The writer* has made experiments to see if the same kind of results could be obtained by decreasing the pressure from a high initial value. The first experiments were made at 900°C, and indicated that the leak with −40 volts consisted of two parts, one proportional to, and the other independent of, the pressure. The part proportional to the pressure could be accounted for as being due to ionisation by collisions, so that the nett result was a leak independent of the pressure. This leak remained constant when the wire was left hot for 2.4 hours, although some gas was given off by the wire, the pressure rising from 0.00033 to 0.0017 millim. This result might be reconciled with Wilson's by supposing that the gas was retained by the platinum with extreme tenacity, and that the amount evolved during the 2.4 hours' heating was merely an insignificant fraction of what remained in the wire.

To test this supposition, an experiment was carried out at a much higher temperature (1390°C.), and an attempt was made to estimate the rate of evolution of hydrogen by the wire from time to time from the increase in the pressure of the McLeod gauge. Before commencing the experiment the wire had been heated for some time in hydrogen at a pressure of 1.35 millims., so presumably equilibrium at this pressure would have been approximately established. The amount of hydrogen still retained under these conditions appears to be very large. The rate of increase of pressure per hour after heatings for the time in hours stated is given by the following numbers:

<table>
<thead>
<tr>
<th>Increase of pressure (millims.) per hour</th>
<th>0.0064</th>
<th>0.0055</th>
<th>0.0052</th>
<th>0.0050</th>
<th>0.0033</th>
<th>0.0014</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean time (hours)</td>
<td>0</td>
<td>2</td>
<td>2.2</td>
<td>3</td>
<td>5.5</td>
<td>11</td>
</tr>
</tbody>
</table>

The numbers are only approximate, as the McLeod gauge was not well adapted for measuring small pressures accurately. The volume of the apparatus (pump, McLeod gauge, &c.) was of the order 2000 cub. centims., that of the wire being 0.0033 cub. centim. On the assumption that all the increase of pressure is due to hydrogen evolved by the wire, the concentration of hydrogen in a platinum wire at 1350°C. in equilibrium with hydrogen outside at a pressure not greater than 1 millim. (it may have been considerably less than this) must be of the order of that corresponding to a pressure of $2 \times 10^4$ millims. of mercury. It seems probable that most of the increase of pressure is really due to hydrogen evolved from the wire and not from the walls of

* It is only fair to state that Wilson describes experiments on the effect of reducing the pressure of the hydrogen, which gave a much greater diminution in the leak than that observed by the writer (vide H. A. Wilson, loc. cit., p. 266).
the vessel, since this protracted increasing of the pressure in a vacuum was not observed after a wire had been heated in other gases. Even if the above large amount of gas has to be got rid of the rate of escape seems very slow; in fact, the numbers show that the law for the rate of diffusion of hydrogen through hot platinum obtained by Richardson, Nicol and Parnell* at pressures greater than 1 millim. does not hold at low pressures. It is probable that at these pressures it is necessary to take external dissociation into account (vide loc. cit.).

Whilst the preceding measurements of the rate of evolution of hydrogen were being recorded, readings of the current with 13 volts on the filament were taken simultaneously. This value of the potential was used in order to ensure saturation (see fig. 15) and at the same time to avoid the occurrence of ionisation by collisions as far as possible. The readings were commenced at a pressure of 0.3 millim., and the current was found to decrease by about 40 per cent. of its value on reducing the pressure to 0.002 millim. This additional part of the current, which is nearly proportional to the pressure, may be accounted for by supposing it to be due to ionisation by collisions. The wire was then heated for 16$\frac{1}{2}$ hours at a low pressure, during which time gas was given off at the rates indicated by the numbers in the last table. The values of the leak (1 = 10$^{-6}$ ampère) and the times, reckoned from the instant at which the apparatus was first pumped down to 0.002 millim. pressure, at which they were recorded are given in the next table:

<table>
<thead>
<tr>
<th>Time</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>hours minutes</td>
<td>0 0 2 2 3 3 5 6 16 16</td>
</tr>
</tbody>
</table>

At a first glance these numbers indicate a continual falling off in the value of the leak at constant temperature as the gas escapes from the wire. The criterion for constant temperature was the resistance of the wire, and it was found that, owing to the sputtering of metal which takes place at high temperatures, the resistance of the wire at 0° C. had increased considerably during the course of the above experiment. When this was allowed for it was found that the average temperature of the wire at the close of the above experiment was 1280° C. instead of 1370° C., its value when the experiment started. The leak at 1280° C. should have been about three divisions instead of twelve, so that pumping out the gas had apparently increased the leak. This paradoxical result is probably caused by the fact that the above method of reckoning over-corrects for the effect of loss by sputtering. A calculation from the numbers in the last table but one shows that the wire had lost

* 'Phil. Mag.,' vol. 8, p. 1.
about nine-tenths of the hydrogen originally present in it at the end of the experiment, so that the experiment appears to warrant the conclusion that the amount of the negative ionisation depends very little on the amount of hydrogen in the wire. In fact, the hydrogen appears to act by altering the condition of the surface of the wire, and once this change has taken place it is very little affected by changes in the amount of hydrogen either outside or inside. The most reasonable view appears to be to suppose that the positively charged hydrogen atoms form an electrical double layer, which helps the corpuscles out of the metal.

A few measurements of the variations of the ionisation, both positive and negative, with the temperature were made in hydrogen. Experiments at pressures of the order of 1 millim. were found to be particularly difficult to carry out on account of the length of time required for equilibrium to be established and the difficulty of being certain that it was established. The following values, with a pressure of 1.90 millims. represent the best series of measurements at this kind of pressure.

<table>
<thead>
<tr>
<th>Temperature, °C. . . . . . .</th>
<th>860</th>
<th>1017</th>
<th>1181</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current . . . . . . .</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ampères per sq. centim.) (V = + 40)</td>
<td>2·5 × 10⁻¹¹</td>
<td>13 × 10⁻¹¹</td>
<td>112 × 10⁻¹¹</td>
</tr>
<tr>
<td>Current . . . . . . .</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ampères per sq. centim.) (V = - 40)</td>
<td>4·7 × 10⁻¹⁰</td>
<td>—</td>
<td>11 × 10⁻⁶</td>
</tr>
</tbody>
</table>

These numbers for the positive ionisation will be seen to be considerably greater when the difference of temperature is allowed for than the minimum value given on p. 49. This indicates that the steady condition had not really been attained when the measurements were made, although the final reading was never recorded until the leak appeared to be varying very slowly, if at all, with the time. [Another possibility, which must be kept in view, is that these inconsistencies are due to some other undiscovered factor, which is not taken account of.] If we calculate from the above numbers the energy change associated with the liberation of a gramme molecule of ions of each sign we find \( w_+ = 3·58 \times 10^4 \) calories and \( w_- = 12·0 \times 10^4 \) calories.

A series of measurements was also made at a much higher pressure (226 millims.). The numbers obtained are given in the table following.

No regular change could be detected in the value of the positive ionisation at the lowest temperature over a space of half-an-hour. This tends to confirm the conclusion from the experiments on p. 49 that there is a positive leak in hydrogen which is a function of the pressure. At low pressures this is much smaller than the positive leak in oxygen, but it increases more rapidly with the pressure. It also
appears to increase more rapidly with the temperature. The values of the negative leak are bigger than those obtained at the lower pressures for the same temperature, the difference being greatest at the lower temperatures. This would seem to indicate that the small increase in the negative leak with pressure obtained at the lowest pressure, and which it was suggested might be due to ionisation by collisions, is really a genuine direct effect of the gas and becomes greatly magnified at high pressures.

The values of the energy change associated with the liberation of one gramme molecule of each kind of ions at this pressure are $w_+ = 5.7 \times 10^4$ calories and $w_- = 5.56 \times 10^4$ calories. Thus increasing the pressure of the hydrogen appears to increase the work required for a positive ion to escape from the metal, whereas it decreases it in the case of the negative ion. This result so far as it refers to the negative ionisation has previously been obtained by H. A. Wilson.*

VIII.—§ 15. Experiments with a Platinum Tube.

The writer has also made experiments on the change produced in the ionisation at the outside surface of a platinum tube in air when hydrogen was allowed to diffuse from the inside of the tube. A brief abstract of the results obtained has already been published†; the present section gives a more detailed account of the experiments. These platinum tube experiments, in the opinion of the writer, settle decisively a number of questions which have been, or might be, raised with regard to the origin of the ionisation produced by hot platinum. For instance, H. A. Wilson‡ has suggested that the negative ionisation produced by hot platinum in air is due to traces of occluded hydrogen which are retained by the wire in a very persistent manner. If this were the case, the small negative leak in air would be enormously increased by allowing any considerable quantity of hydrogen to diffuse out of the wire from inside. As a matter of fact, when hydrogen was allowed to diffuse out of the walls of the tube at a rate corresponding to 2 cub. centims. at

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>860</th>
<th>1017</th>
<th>1097</th>
<th>1181</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ampères per sq. centim.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(V = +560)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ampères per sq. centim.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(V = −40)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

‡ 'Phil. Trans.,' vol. 202, p. 243.
atmospheric pressure per square centimetre of surface per minute, not the slightest change could be detected in the value of the negative leak. This proves indubitably that the negative ionisation produced by hot platinum in air is not due to traces of absorbed hydrogen.

The apparatus used in this part of the investigation is shown in fig. 16. The platinum tube ABA' was about 15 centims. long, and its internal and external diameters were 0·05 and 0·10 centim. respectively. It was clamped at each end by the metal supports E, E', and heated by means of a current let in at D, D'. The current of hydrogen or air inside the tube was let through by means of the glass tubes A, A' sealed on at each end of the platinum tube. The temperature of the tube was measured by means of the thermocouple C, C' of platinum and rhodioplatinum welded on to the middle point B. The wire was surrounded by three aluminium cylinders, F, G, and F', to the middle one of which the leak was measured. The outer cylinders acted as guard rings and maintained a uniform field near the central uniformly heated part of the tube B. The dimensions of the middle cylinder were: length = 3 centims., diameter = 3·2 centims. The various supports E, I, I', E', could slide in holes cut in a slab of vulcanised fibre LL', which was used because ebonite was found to buckle with the heat. When they had been adjusted in position they could be clamped by means of screws. The vulcanised fibre was not found to be sufficiently good insulating material, so the support L to the testing electrode was protected by
an earth-connected tube J in which it was held by an ebonite cylinder K. The whole of this part of the apparatus was fixed in a wooden box covered with lead foil connected to earth.

In reducing the thermocouple readings to temperatures, the platinum temperature was first calculated by making use of the reading corresponding to the melting-point of potassium sulphate. This point was determined experimentally in the way already described. The platinum temperatures were then reduced to centigrade by means of the correction curve given by CALLendar.* The legitimacy of this process was tested by making an independent determination of the melting-point of sodium sulphate. The value found was 885° C., and is within 2° of that (883° C.) given by HEYCOCK and NEVILLE for this constant.

Sealed on to A' were a mercury manometer, a glass bulb of about 300 cub. centims. capacity, and a glass tap. The last named was connected to the apparatus for delivering and purifying the hydrogen which was prepared, as described previously, by the action of pure zinc on hydrochloric acid. From experiments on the diffusion of the hydrogen through the walls of the platinum tube it is believed to have been exceptionally pure. The tube A was also sealed on to a three-way tap so that the hydrogen or air could be either sucked by means of a water pump or allowed to bubble through water. These arrangements made it easy (1) to test if the hydrogen was diffusing through the tube properly, (2) to replace the stream of hydrogen by air and vice versa, and (3) to change the pressure inside the apparatus which regulated the rate of diffusion of the hydrogen through the walls of the tube.

It is convenient to consider first the effect of the hydrogen on the negative ionisation in air. Preliminary experiments showed that the current could not be saturated by the voltages at the writer's disposal, so the current with -80 volts was measured instead of the saturation current. This makes the absolute values of the currents considerably smaller than those previously obtained, more especially as the latter are probably greater than the normal on account of ionisation by collisions (see p. 23). The first test was made at 1200° C. After the tube had been heated for a long time with air both inside and outside, the current with -80 volts was found to be $21 \times 10^{-14}$ ampère per square centimetre of surface. The tube was then allowed to cool, the air replaced by hydrogen inside, and the leak again measured. With hydrogen inside at a pressure of 115 millins, the leak under the same conditions was $26 \times 10^{-14}$ ampère per square centimetre, and with hydrogen at atmospheric pressure $24 \times 10^{-14}$ ampère per square centimetre. These numbers are all equal within the probable accuracy of the temperature regulation.

Another experiment was made at 1380° C. The current with -80 volts with hydrogen inside the apparatus at atmospheric pressure was found to be $3.7 \times 10^{-11}$ ampère per square centimetre, and with the hydrogen at 65 millins, the current was $3.6 \times 10^{-11}$ ampère per square centimetre. In the latter case the amount of hydrogen

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* 'Phil. Mag.' [5], vol. 48, p. 519.
diffusing through the wire would have been rather less than one-third of what it was in the former. A calculation based on the results of Richardson, Nicol, and Parnell* showed that the amount of hydrogen diffusing through each square centimetre of surface of the platinum per minute must have been equal to about 2 cub. centims. at $0^\circ$ C. and 760 millims.

Since the platinum tube in these experiments was giving the small negative ionisations normally produced in air before the hydrogen was allowed to diffuse through, the above experiments prove indisputably that the negative ionisation produced by hot platinum in air and other gases is not due to residual traces of absorbed hydrogen. It appears to be possible to go further than this and to say that the effect, on the leak, of hydrogen inside the metal is not due to its direct action as hydrogen, but to some change it produces in the properties of the metal surface. This change appears to be inhibited when the metal is heated in an atmosphere of air or oxygen.

To substantiate this conclusion it is necessary to prove that there was enough hydrogen inside the outer surface of the wire during the experiment to have appreciably altered the value of the negative leak if it were exerting its full effect. This may be done by finding a minimum value of the external hydrogen pressure which would just stop the diffusion outwards for an instant. If the velocities of the escaped hydrogen molecules were suddenly reversed, the diffusion would stop momentarily, and the external pressure then occurring would give the minimum external pressure which would keep the hydrogen inside the surface layer in equilibrium. The equilibrium pressure might be greater than this, but could not be less. In the experiment the mass of hydrogen diffusing through 1 sq. centim. per second at $1380^\circ$ C. = $2.65 \times 10^{-7}$ gramme. In free hydrogen at 1 centim. pressure the mass which is carried across an area of 1 sq. centim. per second = $2.3 \times 10^{-2}$ gramme at $1380^\circ$ C. Hence the minimum value of the external pressure with which the hydrogen instantaneously present inside the surface layer could be in equilibrium is $1.15 \times 10^{-4}$ millim. It is necessary to show that a pressure of this amount of hydrogen would have produced an appreciable increase in the value of the leak. According to one table given by H. A. Wilson (loc. cit., p. 265), at $1350^\circ$ C. hydrogen at $6 \times 10^{-4}$ millim. pressure increases the negative leak by a factor of 2500. The writer, however, is inclined to think that a more accurate comparison with the present experiments can be got by comparing the tables on pp. 260 and 269 of Wilson's paper. These show that hydrogen at a pressure of $13 \times 10^{-4}$ millim. increases the leak at $1375^\circ$ C. by a factor of 8, so that $1.15 \times 10^{-4}$ millim. would cause an increase by a factor of not less than 1.6. The experiments recorded in the present paper (p. 52) also indicate an increase in the leak of about 100-fold at $1340^\circ$ C. due to hydrogen at a pressure certainly less than $10^{-2}$ millim. On the assumption that the negative ionisation is nearly proportional to the pressure, this would give about the

* 'Phil. Mag.' [5], vol. 8, p. 1.
same increase due to $10^{-4}$ millim. as that obtained above. Reasons have been adduced earlier in this paper (p. 52) for believing that the assumption that the negative ionisation is nearly proportional to the pressure of the hydrogen is incorrect. It has been retained in the present argument because it is the assumption which is most unfavourable to the view advocated. On the most unfavourable view, then, the hydrogen diffusing through the wire should have produced an increase of at least 60 per cent. in the leak. Allowing an experimental uncertainty of 20 per cent., no change could be detected in the leak due to the diffusion of hydrogen through the wire. This strongly supports the view, which also seems required on other grounds, that the hydrogen does not act *per se*, but produces some change in the platinum surface, and this change is prevented from taking place if the platinum is heated in air.*

In contrast to the negative ionisation, the positive ionisation produced by the hot platinum tube was found to be altered when hydrogen was allowed to diffuse through from inside. In fact, at constant temperature an additional amount of ionisation is caused thereby which is proportional to the amount of hydrogen diffusing through the tube.

At high temperatures the positive ionisation was found to be readily saturated. Thus at $1200^\circ$ C, the leak with +80 volts was equal to 64 divisions, and with +400 volts 75 divisions with air inside the tube; with hydrogen diffusing through, the values under these voltages were 88 and 95 divisions respectively. These proportions were much the same, so the leak was generally measured with +80 volts, as higher voltages were not always available. On changing from a low to a high voltage, a big leak was often noticed at first, but this always fell away in a few minutes, until, approximately, the above ratio was obtained. Effects of this kind have already been described in detail (see §9). At low temperatures the positive ionisation obtained with this apparatus seemed to be different in character, for it was

[* Note added September 7, 1906.—It seems advisable to indicate the exact bearing of this argument more precisely. It is intended to confirm the conclusion, which has been drawn from direct experiment on page 52, that the high value of the negative ionisation in a vacuum containing traces of hydrogen is due to the fact that the hydrogen keeps the surface of the wire in a certain state, rather than that the wire contains a certain amount of hydrogen. The writer does not wish to create the impression that hydrogen never exerts a direct influence on the magnitude of the negative leak. The numbers on p. 53 show that the value of the ionisation, at constant temperature, increases with the pressure of the hydrogen at high pressures; so that it is probable that at high pressures there is a negative leak which is a definite function of the pressure of the hydrogen. This is also demanded by the fact that the constant $\omega$, which enters into the temperature formula, is dependent on the pressure.

A comparison of the table at the top of page 53 with that on page 52 would seem to indicate that the ionisation in hydrogen at 1.9 millims. pressure is much greater than in a hydrogen vacuum. The writer considers, however, that these experiments are not comparable with one another, owing to the wires having been differently treated before the two experiments. The *direct tests* made on pp. 50 and 51 showed that decreasing the pressure from about 1 millim. to 0.001 millim. only reduced the ionisation in hydrogen by about 40 per cent. of its value.]
impossible to saturate it. This is shown by the following numbers for the positive current under different voltages at 809° C.:

<table>
<thead>
<tr>
<th>Volts, +</th>
<th>0</th>
<th>4</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>80</th>
<th>400</th>
<th>960</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>0</td>
<td>2.6</td>
<td>10</td>
<td>22</td>
<td>32</td>
<td>64</td>
<td>225</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>($1 = 1.8 \times 10^{-12}$ ampere per sq. centim.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A number of experiments were made to find the cause of this anomalous behaviour at low temperature, but no satisfactory conclusion was arrived at. Fortunately, this does not matter much as far as the present investigation is concerned, for the experiments described below were all carried out at much higher temperatures, when saturation was very nearly attained with 80 volts.

Experiments on the variation of the positive ionisation with the rate at which hydrogen was diffusing through the walls of the tube were made at 1200° C. approximately. The rate of diffusion was varied by varying the pressure of the hydrogen inside the apparatus, since the quantity diffusing in a given time has been shown* to vary very nearly as the square root of the pressure inside. The way in which the saturation current varied with the pressure $P$ of the hydrogen inside the tube is shown by the following numbers:

<table>
<thead>
<tr>
<th>$P$</th>
<th>Current.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($1 = 1.8 \times 10^{-11}$ ampères per sq. centim.)</td>
</tr>
<tr>
<td>Found.</td>
<td>Calculated.</td>
</tr>
<tr>
<td>millims.</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>30</td>
<td>51</td>
</tr>
<tr>
<td>60</td>
<td>56.3</td>
</tr>
<tr>
<td>172</td>
<td>64</td>
</tr>
<tr>
<td>780</td>
<td>90</td>
</tr>
</tbody>
</table>

The numbers in the last column were calculated by assuming that the current was equal to $a + bP^2$, $a$ and $b$ being constants. The agreement of the results shows that the leak consists of two parts, one independent of, and the other proportional to, the square root of the pressure of the hydrogen inside the tube. The effect of the hydrogen diffusing out of the platinum, therefore, is to produce an additional number of positive ions proportional to the amount of hydrogen diffusing out.

These results tend to indicate that the hydrogen inside the metal, which is known from other considerations to be in the atomic state, is positively charged. Only a small fraction (about $10^{-7}$) of the hydrogen comes out in the ionic form, but on

* Richardson, Nicol, and Parnell, loc. cit.
account of the electrostatic attraction the charged atoms might be expected to have greater difficulty in escaping from the metal. This would especially be the case at low temperatures, and may account for the hydrogen set free from palladium not being ionised. These considerations are also in agreement with the fact that electrolytic hydrogen, which is positively charged, is capable of diffusing into some metals—for instance iron—at ordinary temperatures.

Experiments were also made to see how the positive ionisation in air varied with the temperature, (1) when the tube had been heated for a long time in air and there was no hydrogen inside the tube, (2) with a constant pressure (atmospheric) of hydrogen inside. The results, which extend from 973° C. to 1331° C., are exhibited in fig. 17; the numbers in brackets denote the order in which the observations were taken. The upper curve represents the ionisation with hydrogen inside the tube, the lower one that without. The difference between corresponding ordinates represents the part of the ionisation which is due to the hydrogen diffusing through at any temperature. The values of the hydrogen part of the current \(1 = 1.8 \times 10^{-12} \text{ ampère per square centimetre}\) at various temperatures are given in the following table:

<table>
<thead>
<tr>
<th>Temperature, ° C</th>
<th>973</th>
<th>1052</th>
<th>1129</th>
<th>1200</th>
<th>1262</th>
<th>1331</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>6</td>
<td>17</td>
<td>13</td>
<td>80</td>
<td>172</td>
<td>340</td>
</tr>
</tbody>
</table>

These numbers increase much more rapidly with the temperature than the quantities of hydrogen diffusing as given by Richardson, Nicol, and Parnell's experiments. Hence the efficiency for producing positive ionisation of a given amount of hydrogen diffusing out of platinum increases rapidly with increasing temperature.
The fact that hydrogen diffusing out of a platinum wire produces a positive ionisation proportional to the amount of gas diffusing, taken in conjunction with the fact that the additional ionisation so produced, even when the amount of gas diffusing per minute is equal to 1 cub. centim. at 0° C. and 760 millims. per square centimetre, is only about equal to the positive leak, when no hydrogen is apparently present, proves that the positive ionisation in oxygen and other gases as well as the negative is not due to residual traces of absorbed hydrogen. This position has already been shown to be highly probable by other considerations, the chief of which are:—(1) The constancy of the positive ionisation in oxygen with long-continued heating, (2) the agreement between different wires, (3) the fact that heating a wire in hydrogen seemed to produce a permanent decrease, and not an increase, when the steady ionisation it produced in oxygen was measured subsequently.

IX.—§ 16. Some Theoretical Considerations.

The above experiments show that the steady positive ionisation produced by hot platinum in different gases, so far as its variation with temperature is concerned, obeys a formula first deduced by the writer† and shown to represent the negative corpuscular ionisation from hot platinum. That this would be the case was rendered highly probable by the fact established by the writer‡ some time ago that the temperature relations of the positive ionisation, when it is changing with time, were adequately expressed by the formula \( C = A \theta e^{-Q} \), \( A \) and \( Q \) being constants. The only theoretical conclusion which this temperature relation seems to warrant is that the liberation of an ion occurs when the dynamical system from which it is produced acquires a certain amount of energy, which is furnished, it may be indirectly, by the energy of thermal agitation of surrounding systems. It does not really afford any evidence as to whether the production of ions is, or is not, accompanied by chemical action.

It is interesting to compare the values of \( Q \), which represent, on the assumption that equilibrium is possible, the amount of energy in calories associated with the production of 1 gramme equivalent of ions. The numbers which were obtained are given in the following table:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pressure</th>
<th>( Q_+ )</th>
<th>( Q_- )</th>
<th>( N_+ )</th>
<th>( N_- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>2</td>
<td>3.04 ( \times 10^4 )</td>
<td>13.55 ( \times 10^4 )</td>
<td>5 ( \times 10^{19} )</td>
<td>3 ( \times 10^{28} )</td>
</tr>
<tr>
<td>Air</td>
<td>760</td>
<td>4.92 ( \times 10^4 )</td>
<td>8.97 ( \times 10^4 )</td>
<td>5 ( \times 10^{19} )</td>
<td>10^{15}</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.8</td>
<td>7.12 ( \times 10^4 )</td>
<td>11.2 ( \times 10^4 )</td>
<td>3 ( \times 10^{19} )</td>
<td>2 ( \times 10^{21} )</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.9</td>
<td>3.58 ( \times 10^4 )</td>
<td>12.0 ( \times 10^4 )</td>
<td>10^{11}</td>
<td>10^{26}</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>226</td>
<td>5.7 ( \times 10^4 )</td>
<td>5.56 ( \times 10^4 )</td>
<td>10^{15}</td>
<td>2 ( \times 10^{14} )</td>
</tr>
</tbody>
</table>

† 'B.A. Reports, Cambridge,' 1904, p. 472.
The only general conclusion which these numbers point to is that the work required to liberate a positive ion tends to be smaller than that required to liberate a negative ion. This is probably due to the fact that the negative ions are corpuscles, whereas the positive ions are associated with a certain amount of matter.

Throughout this paper, the view has been maintained with regard to the negative ionisation that it is due to the escape of corpuscles which are present in a more or less free condition inside the metal, the variations in the amount of negative ionisation caused by different gases being due to the effect the gases have on the amount of work necessary for a corpuscle to get through the surface. The positive ionisation, on the other hand, has been supposed to be caused entirely by traces of gas absorbed by the metal. There is, however, another view of the origin of the positive ionisation which cannot be lightly dismissed. This is that it is due to the escape of positive ions which are moving freely inside the metal in much the same way as the negative corpuscles have been supposed to be, and that the effects of different gases are simply due to the changes they produce in the surface. There are a number of considerations which make this hypothesis plausible at first sight. It would give an obvious explanation of why the positive obeyed the same temperature law as the negative ionisation, and would also account for the work necessary for a positive ion to escape being in general smaller than that for a negative ion. For since the particles at the surface of the metal are all at the same temperature, the energy of a moving ion will tend to become equalised with the average value for the metal at each collision, so that, to take an exaggerated case, an ion which had found its velocity reduced to nothing, owing to the work it had done in getting through a certain fraction of the surface, would get a fresh start if it made a collision. Thus the work function in question will be equal to the average amount of work to be done between the last collision inside the metal and a point outside; it will thus be greater for an ion with a long free path, such as a corpuscle, than for one with a short free path. On this view, the effects of different gases are to be explained by the changes they produce in the work required for an ion to escape from the surface layer. This might occur by the formation of an electrical double layer, or simply by a change in the physical properties of the bounding region, or by both. The former would act differentially on the positive and negative ionisations, whilst the latter might be expected to act in the same way, though not necessarily to the same extent, on both. A combination of the two could obviously be made to account for any observed simultaneous change in the two leaks. If we calculate the number of ions per cubic centimetre inside the metal from the ionisation in different gases according to the formula previously given by the author, we get the numbers given in the columns $N_+$ and $N_-$ in the last table. These numbers do not mean much, owing to the ignorance of other data which really enter into the calculation, but on the view at present discussed they should range

around the true value for the number of free ions per cubic centimetre. This would give for the positive ions $10^{13}$ and for the negative $10^{23}$; thus the number of free positive ions would be insignificant compared with the number of free negative ions, and the theory would at once account for this small value for the amount of one metal transported into another by the electric current.*

To test this theory, which has both simplicity and elegance to recommend it, both the positive and negative ionisations were measured simultaneously in oxygen at low pressures. The very great increase in the positive ionisation, produced by small quantities of oxygen as compared with other gases, would indicate, if we accept the above view, that the effect was probably specific and caused by the formation of an electrical double layer. In this case, increasing the positive should decrease the negative leak. The results of this experiment, which are given on p. 22, show that although the oxygen altered the positive leak in a ratio of 10 to 1, the negative leak was not changed by 20 per cent. As it is very unlikely that some other effect of the oxygen would compensate so well as this, the writer considers that this experiment renders the above view very improbable. It is chiefly on account of this experiment that the view, that the positive ionisation is due to the absorbed gas, and only indirectly to the metal, has been adopted in describing the results obtained in this investigation.

X.—§ 17. Summary of the Principal Results.

The positive ionisation, i.e., the number of positive ions produced by 1 sq. centim. of platinum surface per second, possesses a minimum value, which depends on temperature and pressure, in most gases. The positive ionisation in oxygen at a low pressure (< 1 millim.) is much greater than in the other gases tried. In oxygen at low pressures, and temperatures below 1000° C., the ionisation varies as the square root of the pressure; at higher temperatures and low pressures it varies nearly directly as the pressure, whilst at higher pressures at all temperatures the variation with pressure is slower, so that at pressures approaching atmospheric the ionisation becomes practically independent of the pressure.

The variation with pressure in air is similar to that in oxygen. In nitrogen and hydrogen the ionisation appeared to increase more rapidly with the pressure at high pressures than in oxygen. In very pure helium at low pressures there was a positive ionisation which was a function of the pressure.

The experiments on ionisation by collisions indicate that the positive ions liberated by hot platinum in oxygen are of the same order of magnitude as those produced by the collisions. They are not great masses approximating to dust particles.

The positive leak in oxygen always oscillated round a certain value under specified

* This view can easily be made to give a reasonable quantitative explanation of the change in the positive ionisation produced by oxygen at different pressures.
conditions. It was, therefore, never steady, so the minimum values were taken. This kind of effect was much less marked, if it occurred at all, in the other gases.

The minimum value of the positive ionisation was found to remain practically constant with a wire heated during three months at various times, for 150 hours altogether, in oxygen at 900°C to 1000°C. Moreover, four different wires of different dimensions, after continued heating in oxygen, gave nearly the same value for the ionisations at the same temperatures and pressures.

The positive ionisation in air at constant temperature is smaller than that which would be obtained if the nitrogen were withdrawn, so as to leave only oxygen at a low pressure. The nitrogen, therefore, exerts an inhibiting effect on the oxygen.

The minimum value of the positive ionisation at a definite pressure in all gases appears to be connected with the temperature by the relation first deduced by the author for the negative ionisation. This relation may be written \( i = A \theta e^{-Q/\theta} \), where \( i \) is the ionisation, \( \theta \) is the absolute temperature, and \( A \) and \( Q \) are constants. The value of the constant \( Q \), which is a measure of the energy associated with the liberation of an ion, is in most cases smaller for the positive than for the negative ionisation.

These results refer to wires which have been heated in a vacuum and subsequently in the gas in question for a long time. New wires exhibit peculiar properties, especially in regard to their behaviour under different electromotive forces. Old wires also exhibit hysteretic effects with change of pressure and temperature.

The view is developed that the positive ionisation is caused by the gas adsorbed by the metal and the consequence examined of supposing the ionisation to be proportional to the amount of the adsorbed gas present. In the case of oxygen, by making the assumption that the rate of increase of the adsorbed gas is proportional jointly to the concentration of the external dissociated oxygen and to the area of unoccupied platinum surface, whilst the rate of breaking up is proportional to the amount present, a formula is obtained which agrees with the experimental results.

This formula is that the ionisation \( i = \frac{Ap}{B+P} \), where \( P = (kP + \frac{1}{2}k^2) - \frac{1}{2}k \), \( P \) being the external pressure and \( k \) the dissociation constant of oxygen. \( A \), \( B \) and \( k \) are constants depending on the temperature and are of the general form \( a\theta e^{-ka} \). Thus this view accounts for both the temperature and pressure variation.

The positive ionisation from the outer surface of a hot platinum tube in air is increased when hydrogen is allowed to diffuse through from inside the apparatus. The increase in the ionisation is proportional at constant temperature to the quantity of hydrogen escaping from the surface in unit time. For different temperatures the effect produced by a given quantity of hydrogen is greater the higher the temperature.

The negative ionisation from hot platinum in air is unaltered when hydrogen is allowed to diffuse out through the platinum.
These results show that neither the negative nor the positive ionisations usually observed with hot platinum heated in air or oxygen are due to residual traces of absorbed hydrogen.

Careful measurements were made to see if the negative ionisation in oxygen at low pressures varied with the pressure of the oxygen at constant temperature. Although the addition of oxygen increased the positive leak by a factor of ten, the change in the negative leak was constant within the experimental error, in agreement with the work of previous observers.

The negative ionisation was found to have very nearly the same absolute value and the same temperature variation for two wires of different dimensions when heated in oxygen.

A wire which has been heated in hydrogen furnishes a negative ionisation which is very big compared with that from a wire heated in oxygen at the same temperature. If the hydrogen is at a pressure of the order of 1 millim, the negative ionisation can be rapidly reduced to a much smaller value by applying a high negative potential to the wire. The wire subsequently recovers its ionising power if the potential is reduced again. Under these conditions the ionisation varies in an interesting way with the time. The reduction in the ionising power of the wire appears to be caused by the bombardment of the surface by positive ions produced by collisions.

Long-continued heating of a platinum wire, which has previously been allowed to absorb hydrogen, in a good vacuum so as to expel the gas does not appear to reduce its ionising power. The ionisation apparently is not a definite function of the quantity of gas absorbed by the wire. The amount of hydrogen which a platinum wire will absorb at a low pressure is much greater than is usually suspected.

These results indicate that the increase in the negative ionisation in hydrogen at a low pressure is not caused by the hydrogen directly, but is rather a result of some change it produces in the surface of the platinum.

In conclusion the writer wishes to thank Professor Thomson for his valuable encouragement and advice during the course of this investigation which was carried out in the Cavendish Laboratory. He also wishes to record his indebtedness to the Government Grant Committee for Scientific Investigations for assistance in defraying the cost of some of the apparatus used.
II. Second Memoir on the Compositions of Numbers.

By Major P. A. MacMahon, R.A., D.Sc., F.R.S.

Received August 23,—Read December 6, 1906.

PREAMBLE.

In a Memoir on the Theory of the Compositions of Numbers, read before the Royal Society, November 24, 1892, and published in the ‘Philosophical Transactions’ for 1893, I discussed the compositions of multipartite numbers by a graphical method. The generating function produced by the method was of the form

\[ \frac{1}{1 - \Sigma \alpha_i + (1 - \lambda) \Sigma \alpha_i \alpha_j - (1 - \lambda)^2 \Sigma \alpha_i \alpha_j \alpha_k + \ldots} \]

a symmetrical function of the quantities \( \alpha \).

The investigation of the present paper leads, in part, to the same generating function which is subjected to a close examination. Moreover, the whole research has to do with the compositions of numbers, and appropriately follows the Memoir of 1893.

The problem under investigation, which was brought to my notice by Professor Simon Newcomb, may be stated as follows:

A pack of cards of any specification is taken—say that there are \( p \) cards marked 1, \( q \) cards 2, \( r \) cards 3, and so on—and, being shuffled, is dealt out on a table; so long as the cards that appear have numbers that are in descending order of magnitude, they are placed in one pack together—equality of number counting as descending order—but directly the descending order is broken a fresh pack is commenced, and so on until all the cards have been dealt. The result of the deal will be \( m \) packs containing, in order, \( a \), \( b \), \( c \), ... cards respectively, where, \( n \) being the number of cards in the whole pack,

\( \text{abc} \ldots \)

is some composition of the number \( n \), the numbers of parts in the composition being \( m \).

We have, then, for discussion—

(1) The number of ways of arranging the cards so as to yield a given composition

\( \text{abc} \ldots \); 

(2) The number of arrangements which lead to a distribution into exactly \( m \) packs.

These problems, and many others of a like nature, are solved in this paper.
The first of the two questions has given rise to two new symmetric functions, 

\[ h_{abc...}, \ a_{abc...}, \]

of great interest, which supply the complete solution. The second gives rise to the same generating function that presented itself in the first Memoir. It is here attacked by the calculus of symmetric function differential operators, and a number of new results obtained.

If the whole pack be specified by the partition

\[ (pqr...), \]

there is a one-to-one correspondence between the arrangements which lead to a distribution into \( m \) packs and the principal compositions, involving \( m-1 \) essential nodes, of the multipartite number

\[ (pqr...). \]

Part I. is concerned with an elementary theory of the case in which the cards are all numbered differently.

The general case, which is more difficult, is dealt with in Part II.

To make what follows clear to the reader, I commence with some elementary notions concerning the connection between the partitions and compositions of numbers on the one hand, and permutations and combinations of things on the other hand, and I also specify and describe the nomenclature and notation that I have found it convenient to adopt. A suitable notation is, indeed, of the first importance in this subject, as I hope to make evident as the investigation proceeds.

**Introductory.**

Art. 1. Any succession of numbers, written down from left to right at random, such as

\[ 142771, \]

is termed a "composition" of the number which is the sum of the numbers.

If the numbers be arranged in descending order from left to right,

\[ 774211, \]

the succession is termed a "descending partition," or simply a "partition" of the number which is the sum of the numbers.

Or, if we arrange in ascending order of magnitude,

\[ 112477, \]

the succession may be termed an "ascending partition."

Generally, in speaking of partitions, we understand that the descending order is meant; but it is convenient sometimes to consider them as being defined by an ascending order.
There is no other method of ordering a collection of numbers which is of general application.

We see that the same collection of numbers gives rise to only one partition, but, by permutation, to more than one composition.

Art. 2. Both partitions and compositions have an appropriate graphical representation. That of a partition was first given by Ferrers, and the notion was elaborated by Sylvester during the time he was at the Johns Hopkins University in Baltimore, U.S.A. It consisted merely in writing a row of nodes, or units, corresponding to each number (or part) of the partition, the left-hand nodes of the rows being placed in a vertical line. Thus

is denoted by

\[
\begin{array}{cccccc}
\bullet & \bullet & \bullet & \bullet & \bullet & \bullet \\
\end{array}
\]

Art. 3. A trial will show that this method is not suited to compositions. One method, effective for certain purposes, was given by the author.* To indicate it, consider the composition

of the number 7.

\[
\begin{array}{cccc}
\ast & \ast & \ast & \ast \\
\end{array}
\]

We take seven segments on a line, and place nodes, *, so that the line is divided off into 1, 4 and 2 segments respectively in order. The conjugate composition is reached from this by suppressing the existing nodes and placing nodes at the points of division which are free from nodes.

Thus

\[
\begin{array}{cccc}
\ast & \ast & \ast & \ast \\
\end{array}
\]

denotes the composition

\[
\begin{array}{cccc}
\ast & \ast & \ast & \ast \\
\end{array}
\]

Art. 4. There is a more illuminating mode of representation which is here given, it is believed, for the first time; it is akin to the method of Ferrers, and enables methods of research which Sylvester's exertions have made familiar.

It consists in taking rows of nodes in order and placing the left-hand node of any row vertically beneath the right-hand node of the previous row.

Thus

is denoted by

\[
\begin{array}{cccc}
\bullet & \bullet & \bullet & \\
\end{array}
\]

This graph is read horizontally; the conjugate is obtained by reading vertically, giving

or, in brief notation,

We may also read the graph horizontally from bottom to top and vertically from right to left, obtaining generally four compositions from the graph.

The graph is a zig-zag one and will be, without doubt, an important instrument of research.

Part I.—Section 1.

Art. 5. Consider the permutations of the first \( n \) integers, and for simplicity take \( n = 9 \).

Writing down a permutation at random,

it is clear that lines can be drawn separating the numbers into compartments in such wise that in each compartment the numbers are in descending order of magnitude. We can then write down a succession of numbers which describe the size of the compartments, proceeding from left to right, and thus arrive at a composition

of the number 9.

I say that the permutation under examination has a descending specification

Similarly, from the ascending character

of the same permutation, I say that the ascending specification is

where it is to be noticed that 142\( ^a \) is the composition of 9 which is conjugate to 21\( ^22^1 \), the composition which specifies the descending character. This is shown by the zig-zag graph
Art. 6. We can now formulate the question: Of the permutations of the first $n$ numbers, how many have a descending specification denoted by a given composition of the number $n$? Whatever the answer, it is clear that the same answer must, in general, be given for three other compositions, viz., the three others associated with the zig-zag graph. In fact, from

we derive

$314592768$ of specification $211221$,

$867295413$,

$2241$;

and from these two by changing the number $m$ into $n-m+1$,

$796518342$ of specification $1422$,

$243815679$,

$122112$.

and so forth.

In two cases there are two associated compositions instead of four, viz.:

(i) When the composition reads the same as its inverse (that is the same from left to right as from right to left),

(ii) When the conjugate and the inverse are identical, as in $221$, whose conjugate is $122$.

*The number of self-inverse compositions of an even number $2m$ and of an uneven number $2m+1$ is

$2^m$.

The number of inverse-conjugate compositions of an uneven number $2m+1$ is

$2^m$.

Hence, in the present theory, the number of different numbers that appear in the case of an even number $2m$ is, since the whole number of compositions is $2^{2m-1}$,

$$
\frac{1}{2} \cdot 2^m + \frac{1}{4} (2^{2m-1} - 2^m),
$$

$$
= 2^{m-2} (2^{m-1} + 1);
$$

and, in the case of an uneven number $2m+1$,

$$
\frac{1}{2} 2^m + \frac{1}{2} 2^m + \frac{1}{4} (2^{2m} - 2^{m+1}),
$$

$$
= 2^{m-1} (2^{m-1} + 1);
$$

viz., it is

$2^{n-3} + 2^{1/2(n-4)}$,

or

$2^{n-3} + 2^{1/2(n-3)}$,

according as $n$ is even or uneven.

* See "Memoir on the Theory of the Compositions of Numbers," 'Phil. Trans. Roy. Soc.,' 1893,
Art. 7. Let $N(abc...)$ denote the number of permutations of the first $n$ integers which have a descending specification denoted by the composition 

$$(abc...)$$

of the number $n$.

Obviously

$$N(a) = 1, \quad a = n.$$ 

To determine $N(ab)$, $a+b = n$, separate the $n$ integers into two groups, a left-hand group of $a$ numbers chosen at random and a right-hand group of the remaining $b$ numbers. This can be done in

$$\binom{n}{a}$$

different ways.

[I write $\frac{n!}{a!(n-a)!} = \binom{n}{a}$ in a common notation] now arrange each group of numbers in descending order of magnitude for each of the $\binom{n}{a}$ separations; we thus obtain each of the permutations enumerated by $N(a, b)$ and the one permutation enumerated by $N(a+b)$.

Hence

$$N(ab) + N(a+b) = \binom{n}{a},$$

or

$$N(ab) = \binom{n}{a} - \binom{n}{a+b} = \binom{n}{a} - 1.$$ 

Again, to find $N(abc)$, we separate the $n$ integers into three groups containing $a$, $b$, and $c$ integers respectively; this can be done in

$$\frac{n!}{a!b!c!}$$

different ways; placing the numbers in each group in descending order, we obtain all the permutations enumerated by

$$N(abc), \quad N(a+b, c), \quad N(a, b+c), \quad N(a+b+c).$$

Hence

$$N(abc)+N(a+b, c)+N(a, b+c)+N(a+b+c) = \frac{n!}{a!b!c!},$$

leading to

$$N(abc) = \frac{n!}{a!b!c!} - \frac{n!}{(a+b)!c!} - \frac{n!}{a!(b+c)!} + \frac{n!}{(a+b+c)!},$$

where $a+b+c = n$.

Similarly we find

$$N(abcd) = \frac{n!}{a!b!c!d!} - \frac{n!}{(a+b)!c!d!} - \frac{n!}{a!(b+c)!d!} - \frac{n!}{a!b!(c+d)!} + \frac{n!}{(a+b)!c!(d)!} + \frac{n!}{(a+b+c)!d!} + \frac{n!}{a!(b+c+d)!} - \frac{n!}{(a+b+c+d)!},$$

where $a+b+c+d = n$. 

The general law is clear; the letters $a$, $b$, $c$, $d$ are always in order in the denominators and the sign of a fraction depends upon the number of factors in its denominator.

We can thus calculate the number of permutations appertaining to each of the $2^{n-1}$ compositions of $n$.

It has been established independently, by the aid of the zig-zag graph, that these numbers

$$N(...)
$$

are equal in four’s or in two’s.

Art. 8. The sum of the numbers $N(...)$ is of course $n!$

The details of the above results for

$$n = 2, 3, 4, 5, 6$$

are given for easy reference.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$N(2)$</th>
<th>$N(3)$</th>
<th>$N(4)$</th>
<th>$N(5)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>6</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

$$n = 2, 3, 4, 5, 6$$

$$2 = 2!$$

$$6 = 3!$$

$$24 = 4!$$

$$120 = 5!$$
Some simple summations are obtainable from elementary considerations. In regard to the permutations of the first \( n \) integers, let

\[
\Sigma N (s...) = s \binom{n}{s+1} \frac{n!}{(s+1)!},
\]

where \( s < n \), denote the sum of all numbers \( N (...) \), such that \( s \) is the first number in the specifying composition. Take any \( s+1 \) of the numbers

\[1, 2, 3, \ldots n,\]

and arrange them from left to right in such wise that the first \( s \) numbers are in descending order and the \( s+1 \)th number greater than the \( s \)th; this can be done in

\[s \binom{n}{s+1} \text{ ways};\]

the remaining \( n-s-1 \) numbers can be arranged in \((n-s-1)!\) ways, so that, placing them to the right of the former, we arrive at the result

\[
\Sigma N (s...) = s \frac{n!}{(s+1)!}.
\]

Art. 10. Again, denoting by \( \Sigma N (1^{s-1}...) \) the sum of all numbers \( N (...) \) of which the specifying compositions commence with exactly \( s-1 \) units, the consideration of the properties of conjugate zig-zag graphs establishes that

\[
\Sigma N (1^{s-1}...) = \Sigma N (s...),
\]

with a single exception where \( s = n \); e.g.,

\[
\Sigma N (1^0...) = \ast \Sigma N (1...) = \frac{n!}{2!},
\]

\[
\dagger \Sigma N (1...) = \Sigma N (2...) = 2 \frac{n!}{3!},
\]

and so on.

* No restriction is placed upon the number next to the unit in this case.

† Here the number following the unit must be > 1.
Art. 11. Again, for the summation

$$\sum N (1^s \ldots),$$

where the composition begins with at least $s$ units, we easily obtain the value

$$\frac{n!}{(s+1)!}.$$

The Multiplication Theorem.

Art. 12. A fundamental property of the numbers $N (...)$ will be established from elementary considerations; it will, later on in the paper, be generalised.

Let

$$N (a_1 a_2 \ldots a_s)$$

be derived from the permutations of $p$ different integers, and

$$N (a_{s+1} a_{s+2} \ldots a_{s+t})$$

from the permutations of $n-p$ different integers; it is to be shown that

$$\left(\begin{array}{c} n \\ a_1 + a_2 + \ldots + a_s \end{array}\right) N (a_1 a_2 \ldots a_s) N (a_{s+1} a_{s+2} \ldots a_{s+t})$$

$$= N (a_1 a_2 \ldots a_{s+t}) + N (a_{s+1} a_{s+2} \ldots a_{s+t+1}).$$

where on the right the reference is to the permutations of $n$ different integers.

Out of the $n$ numbers

$$1, 2, 3, \ldots, n,$$

we can select

$$a_1 + a_2 + \ldots + a_s$$

numbers in

$$\left(\begin{array}{c} n \\ a_1 + a_2 + \ldots + a_s \end{array}\right)$$

ways, and arrange each selection, so as to have a descending specification

$$(a_1 a_2 \ldots a_s),$$

in

$$N (a_1 a_2 \ldots a_s)$$

ways;

the remaining numbers can be arranged, to have a descending specification

$$(a_{s+1} a_{s+2} \ldots a_{s+t}),$$

in

$$N (a_{s+1} a_{s+2} \ldots a_{s+t})$$

ways;

placing the latter to the right of the former there appears

$$\left(\begin{array}{c} n \\ a_1 + a_2 + \ldots + a_s \end{array}\right) N (a_1 a_2 \ldots a_s) N (a_{s+1} a_{s+2} \ldots a_{s+t})$$

arrangements.
Now, combining the two sets of numbers, we find that either there is or there is not a break in the descending order between

\[ a_s \text{ and } a_{s+1}; \]

hence the number of arrangements is also

\[ N(a_1a_2...a_{s+1}) + N(a_1a_2...a_{s-1}, a_s + a_{s+1}, a_{s+2}...a_{s+t}). \quad \text{Q.E.D.} \]

Art. 13. Regarded as a numerical theorem, the multiplication is commutative, but in regard to form it is not commutative; thus, by considering the multiplication

\[ N(a_{s+1}a_{s+2}...a_{s+t})N(a_2...a_s), \]

we obtain the linear relation

\[ N(a_1a_2...a_{s+1}) + N(a_1a_2...a_{s-1}, a_s + a_{s+1}, a_{s+2}...a_{s+t}) \]

\[ = N(a_{s+1}a_{s+2}...a_{s+t+1}) + N(a_{s+1}...a_{s+t-1}, a_{s+t} + a_1, a_2...a_s). \]

Observe also that the order of the numbers in brackets in any number \( N(...) \) can be reversed at pleasure and thus new forms of results obtained.

As a verification: from the tables

\[ \begin{align*}
\left(\frac{5}{3}\right) & N(12) N(11) = N(121^2) + N(131) = N(1^32) + N(12^2); \\
10 & 2 & 1 = 9 + 11 = 4 + 16 \\
N(123) + N(15) = N(312) + N(42). \\
35 & + 5 = 26 + 14
\end{align*} \]

The fact that the multiplication is not commutative formally is of great importance in the theory of these numbers.

Art. 14. Extending the theorem to the product of three numbers

\[ N(a_1a_2...a_s), \; N(b_1b_2...b_i), \; N(c_1c_2...c_u), \]

we find

\[ \frac{n!}{(\Sigma a)! (\Sigma b)! (\Sigma c)!} N(a_1a_2...a_s) N(b_1b_2...b_i) N(c_1c_2...c_u) \]

\[ = N(a_1...a_s b_1...b_i c_1...c_u) + N(a_1...a_{s-1}, a_s + b_1, b_2...b_i c_1...c_u) \]

\[ + N(a_1...a_{s-1}, b_1 + c_1, c_2...c_u) + N(a_1...a_{s-1}, a_s + b_1, b_2...b_{i-1}, b_i + c_1, c_2...c_u). \]

We may, in general, give the right-hand side 3! different forms corresponding to the 3! permutations of the numbers \( N(...) \) on the sinister.

If we take the product of \( m \) numbers \( N(...) \), to form the dexter, we combine the last integer of a number \( N(...) \) with the first integer of the next following number \( N(...) \),
0 times in 1 way,
1 \" \binom{m-1}{1} \" ways,
2 \" \binom{m-1}{2} \" ,
\ldots 
\binom{m-1}{m-1} \" ;

hence \(2^{m-1}\) numbers \(N(...)\) present themselves on the dexter.

Not counting reversals of order, the dexter can, in general, be given as many different forms as there are permutations of the numbers \(N(...)\) on the sinister. Counting reversals, the number of different forms is further multiplied by \(2^m\), subject to a diminution when one or more of the numbers \(N(...)\) is self-inverse.

Applications of the Theorem.

Art. 15. The theorems, already arrived at above, are particular cases of multiplication. Thus the formulæ, of which

\[ N(abc) + N(a + b, c) + N(a, b + c) + N(a + b + c) = \frac{n!}{a! b! c!} \]

is a type, are equivalent to results, of which

\[ \frac{n!}{a! b! c!} N(a) N(b) N(c) = N(abc) + N(a + b, c) + N(a, b + c) + N(a + b + c) \]

is representative, since \(N(a) = N(b) = N(c) = 1\).

That the sum of all numbers \(N(...)\), of given weight \(n\), is \(n!\) is shown by the formula

\[ n! \{N(1)\}^n = \Sigma N(...) ; \]

since on the dexter occurs an \(N(...)\) corresponding to every composition of \(n\).

Art. 16. Suppose that it is required to find the sum of all numbers \(N(...)\), of given weight, which are such that each associated composition commences with a given series of numbers \(a_1 a_2 \ldots a_m\),

or, in other words, suppose we wish to make the summation indicated by

\[ \Sigma N(a_1 a_2 \ldots a_m \ldots) ; \]

the solution is given at once by

\[ \frac{n!}{(\Sigma a + 1)!} N(a_1 a_2 \ldots a_m 1) \{N(1)\}^{n - \Sigma a - 1} = \Sigma N(a_1 a_2 \ldots a_m \ldots) ; \]

for, by the multiplication process, the unit which terminates \(N(a_1 a_2 \ldots a_m 1)\), combined with

\[ \{N(1)\}^{n - \Sigma a - 1}, \]

\(1, 2\)
gives every composition of the number \( n - \sum a \).

Hence, since \( N(1) = 1 \),
\[
\sum N(a_1a_2...am...) = \frac{n!}{(\sum a + 1)!} N(a_1a_2...am1).
\]

Art. 17. By varying the order of the factors, on the sinister of the multiplication formula, a variety of interesting results present themselves; thus
\[
\frac{n!}{(\sum a + 1)!} \{N(1)\}^{n-\sum a-p-1} N(a_1a_2...am1) = \Sigma \Sigma N(...a'_1a_2a_3...am...);
\]
where after \( a_m \), on the dexter, occurs every composition of
\[
n - \sum a - p;
\]
and the portion
\[
...a'_1
\]
includes every composition of
\[
p + a_1
\]
which terminates with a number not less than \( a_1 \).

Hence, for such a summation,
\[
\Sigma \Sigma N(...a'_1a_2...am...) = \frac{n!}{(\sum a + 1)!} N(a_1a_2...am1);
\]
a formula which is independent of \( p \).

Art. 18. In particular from
\[
\{N(1)\}^{n-\sum a-1} N(a_1a_2...am1)
\]
we obtain
\[
\Sigma N(...a'_1a_2...am1) = \frac{n!}{(\sum a + 1)!} N(a_1a_2...am1);
\]
wherein the summation is for every composition of
\[
n - a_2 - ... - a_m - 1
\]
which terminates with a number not less than \( a_1 \).

E.g., for \( n = 6, a_1 = 1, a_2 = 1 \),
\[
N(41^2) + N(131^2) + N(2^21^2) + N(1^221^3) = \frac{6!}{4!} N(211).
\]
\[
10 + 26 + 35 + 19 = 653.
\]

Art. 19. As another example of the power of the theorem, let
\[
\Sigma N(a_1a_2...am...b_1b_2...b_m)
\]
(the numbers \( a_1, a_2...a_m, b_1, b_2...b_m \) being given) denote a summation in regard to compositions of
\[
n - \sum a - \sum b
\]
placed between \( \alpha_m \) and \( b_1 \); we obtain

\[
\sum N (\alpha a_2 \ldots \alpha s b_2 \ldots b_m)
\]

\[
= \frac{n!}{(\Sigma a + 1)! (\Sigma b + 1)!} \{N (1)\}^{n-2s-2} N (1) b_1 b_2 \ldots b_m,
\]

\[
= \frac{n!}{(\Sigma a + 1)! (\Sigma b + 1)!} \{N (1)\}^{n-2s-2} N (1) b_1 b_2 \ldots b_m,
\]

\[
= \frac{n!}{(\Sigma a + \Sigma b + 2)!} \{N (1)\}^{n-2s-2} N (1) b_1 b_2 \ldots b_m.
\]

By varying the order of the factors, other summations, leading to the same numerical result, can be effected.

Art. 20. Consider next the multiplication

\[
\frac{n!}{(s_1 + 2)! (s_2 + 2)! (s_3 + 2)!} \times \{N (1)\}^{s-1} N (1) \{N (1)\}^{s_1-2} N (1) \{N (1)\}^{s_2-2} N (1) \{N (1)\}^{s_3-1}.
\]

wherein, \( \Sigma w + \Sigma s = n \),

\( w_1, w_2, w_3, w_4 \) are numbers not less than unity,

\( s_1, s_2, s_3 \) are any numbers, zero not excluded.

The result of the multiplication consists of numbers \( N (...) \), such that there is

(i) A composition of \( w_1 \) followed by \( s_1 \) units, succeeded by

(ii) A composition of \( w_2 \) followed by \( s_2 \) units, succeeded by

(iii) A composition of \( w_3 \) followed by \( s_3 \) units, succeeded by

(iv) A composition of \( w_4 \);

and the dexter is the sum of all such numbers \( N (...) \).

Denoting this sum by

\[
\sum N (w_1 w_2 w_3 w_4),
\]

we find that its value is

\[
\frac{n!}{(s_1 + 2)! (s_2 + 2)! (s_3 + 2)!},
\]

since each number \( N (...) \) occurring in the product on the sinister has unity for its value.

Hence, in general, the remarkable theorem,

\[
\sum N (w_1 w_2 w_3 w_4 \ldots) = \frac{n!}{(s_1 + 2)! (s_2 + 2)! (s_3 + 2)! \ldots};
\]

showing that the sum depends merely upon the numbers

\( s_1, s_2, s_3, \ldots \).
and not at all upon the numbers
\[ w_1, w_2, w_3, \ldots. \]

Observe that \( w_1 \) and the final number of the composition may or may not be unity, and that every composition of \( n \) may be written in the form
\[ w_1^{s_1}w_2^{s_2}w_3^{s_3}w_4^{s_4}\ldots. \]

If
\[ s_1 = s_2 = s_3 = \ldots = 0, \]
\[ \Sigma N(w_1w_2w_3w_4\ldots) = \frac{n!}{2!2!2!\ldots}; \]
and, in particular,
\[ \Sigma N(w_1w_2\ldots w_m) = \frac{n!}{(2!)^{m-1}}, \]
wherein \( w_2, w_3, \ldots w_{m-1} \) are non-unitary, but \( w_1, w_m \) may or may not be unitary.

As a simple example take
\[ w_1 = 1, \quad s_1 = 4, \quad w_2 = 1, \]
so that
\[ N(1^4) = \Sigma N(1, 1^4, 1) = \frac{6!}{(4+2)!} = 1, \]
a verification.

Art. 21. A more general theorem is yielded by
\[ \frac{n!}{(\Sigma p+2)! (\Sigma q+2)! (\Sigma r+2)!} \]
\[ \times (N(1))^{w_r-1}N(1p_1\ldots p_m, 1) \{N(1))^{w_s-2}N(1q_1\ldots q_m, 1) \{N(1))^{w_t-2}N(1r_1\ldots r_m, 1) \{N(1))^{w_u-1}, \]
\[ = \Sigma N(w_1p_1\ldots p_m, w_2q_1\ldots q_m, w_3r_1\ldots r_m, w_4), \]
wherein
\[ p_1 \ldots p_m, \]
\[ q_1 \ldots q_m, \]
\[ r_1 \ldots r_m, \]
are given integers and the summation indicated on the dexter is in respect of the whole of the compositions of the numbers
\[ w_1, \quad w_2, \quad w_3, \quad w_4, \]
where
\[ 0 \geq w_1-1, \quad w_2-2, \quad w_3-2 \quad \text{and} \quad w_4-1. \]

The value of the sum is thus
\[ \frac{n!}{(\Sigma p+2)! (\Sigma q+2)! (\Sigma r+2)!} \]
\[ N(1p_1\ldots p_m, 1)N(1q_1\ldots q_m, 1)N(1r_1\ldots r_m, 1), \]
which, by the multiplication theorem, may be given the form

\[
\frac{n!}{(\Sigma p + \Sigma q + \Sigma r + 6)!} \times \left[ N \left( 1p_1 \ldots p_m q_1 \ldots q_m r_1 \ldots r_m \right) \right]
\]

Evidently, from the above, comprehensive results can be obtained from the multiplication theorem.

**Section 2.**

Art. 22. The next problem I propose to solve is that of determining the number of the permutations of the first \( n \) integers, whose descending specifications contain a given number of integers, or, in other words, whose associated compositions involve a given number of parts. The solution is implicitly contained in a paper I wrote in the year 1888.*

Let \( N_m \) denote the number of permutations associated with compositions containing exactly \( m \) parts.

In the paper quoted, I had under view a collection of objects of any species—say \( p \) of one sort, \( q \) of a second sort, \( r \) of a third, and so on—and defined the objects as to species by these numbers placed in brackets. I thus formed a partition

\[
(pqr\ldots)
\]

of the number \( n \), such partition being the species definition of the objects.

As equalities may occur between the numbers \( p, q, r, \ldots \), I took, as a more general definition, the partition

\[
(p_1^{s_1}p_2^{s_2}p_3^{s_3}\ldots)
\]

where \( \Sigma p = n \).

In the case under consideration, where the integers (or objects) are all different, the species definition is the partition

\[
(1^r).
\]

I proved, in the general case, that the number of ways of distributing the objects, into \( m \) different parcels, is given by the series

\[
F_m = \left( m+p_1-1 \right)^{s_1} \left( m+p_2-1 \right)^{s_2} \left( m+p_3-1 \right)^{s_3} \ldots
\]

\[
- \left( m \right)^{s_1} \left( m+p_1-2 \right)^{s_2} \left( m+p_2-2 \right)^{s_3} \left( m+p_3-2 \right)^{s_4} \ldots
\]

\[
+ \left( m \right)^{s_1} \left( m+p_1-3 \right)^{s_2} \left( m+p_2-3 \right)^{s_3} \left( m+p_3-3 \right)^{s_4} \ldots
\]

\[
- \ldots
\]

For the case in hand, \( p_1 = 1, \pi_1 = n \),

\[
F_m = m^n - \binom{m}{1} (m-1)^n + \binom{m}{2} (m-2)^n - \binom{m}{3} (m-3)^n + \ldots.
\]

Art. 23. I shall prove that

\[
N_m = m^n - \binom{n+1}{1} (m-1)^n + \binom{n+1}{2} (m-2)^n - \binom{n+1}{3} (m-3)^n + \ldots.
\]

For consider the arrangements enumerated by \( F_m \). Place the compartments (or parcels) in order, from left to right, in any one such arrangement, and, in each compartment, place the integers in descending order of magnitude. The arrangement is obviously one of those enumerated by

\[
N_m, N_{m-1}, N_{m-2}, \ldots \text{ or } N_1.
\]

In the whole of the arrangements, enumerated by \( F_m \), thus treated, each arrangement enumerated by \( N_m \) will occur once only.

\[
\begin{array}{cccccc}
1 & | & 2 & | & 3 & | & 4 & | & \cdots & | & m-1 \text{ or } m-s.
\end{array}
\]

Let the illustration denote an arrangement enumerated by \( N_{m-1} \). Each segment denotes an integer, and the \( m-2 \) vertical lines separate the integers into compartments.

By placing an extra vertical line at one of the unoccupied points of division, we obtain an arrangement enumerated by \( F_m \). This can be done in \( (n-1)-(m-2) \) different ways, showing that the particular arrangement, enumerated by \( N_{m-1} \), is derivable by obliteration of a vertical line from \( n-m+1 \) different arrangements enumerated by \( F_m \).

Hence, the forms \( F_m \) include the forms \( N_{m-1} \) each \( n-m+1 \) times.

Again, let the illustration denote an arrangement enumerated by \( N_{m-s} \). By placing \( s \) extra vertical lines, at unoccupied points of division, we obtain an arrangement enumerated by \( F_m \). This can be done in

\[
\binom{n-m+s}{s}
\]

different ways; showing that the particular arrangement, enumerated by \( N_{m-s} \), is derivable, by obliteration of \( s \) vertical lines, from

\[
\binom{n-m+s}{s}
\]

different arrangements enumerated by \( F_m \).
Hence the forms $F_m$ include the forms $N_{m-s}$ each

$\binom{n-m+s}{s}$ times.

Hence

$$F_m = N_m + \left(\frac{n-m+1}{1}\right)N_{m-1} + \left(\frac{n-m+2}{2}\right)N_{m-2} + \ldots + \left(\frac{n-1}{m-1}\right)N_1.$$  

Thence it is easy to show that

$$N_m = F_m - \left(\frac{n-m+1}{1}\right)F_{m-1} + \left(\frac{n-m+2}{2}\right)F_{m-2} - \ldots + (-)^{m+1}\left(\frac{n-1}{m-1}\right)F_1;$$

and also

$$N_m = m^n - \left(\frac{n+1}{1}\right)(m-1)^n + \left(\frac{n+1}{2}\right)(m-2)^n - \ldots + (-)^{m+1}\left(\frac{n+1}{m-1}\right)1^n.$$  

The relation $\sum N_m = n!$ may be verified.

Art. 24. It follows at once, from the zig-zag graphs, that

$$N_m = N_{n-m+1}.$$  

Some of the simplest results are

<table>
<thead>
<tr>
<th>$n$</th>
<th>$N_1$</th>
<th>$N_2$</th>
<th>$N_3$</th>
<th>$N_4$</th>
<th>$N_5$</th>
<th>$N_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>1</td>
<td>4</td>
<td>1</td>
<td></td>
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<tr>
<td>4</td>
<td>1</td>
<td>11</td>
<td>11</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>26</td>
<td>66</td>
<td>26</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>57</td>
<td>302</td>
<td>302</td>
<td>57</td>
<td>1</td>
</tr>
</tbody>
</table>

Art. 25. There is another interesting series for $N_m$.

Let

$$(p+s)^n_{-1,0}$$

denote the expansion of

$$(p+s)^n$$

when deprived of the term which is linear in $p$ and of the term independent of $p$; and put

$$P_s = (1+s)^n_{-1,0};$$

then

$$N_m = P_{m-1} - \frac{m-2}{m-1}\binom{n}{1}P_{m-3} + \frac{m-3}{m-1}\binom{n}{2}P_{m-3} - \ldots + (-)^m\frac{1}{m-1}\binom{n}{m-2}P_1.$$
Art. 26. Considering next \( p \) different numbers, defined by the partition 

\[
(1^p),
\]

we have, by a previous definition,

\[
\Sigma N (a_1a_2...a_m) = N_{m,1^p};
\]

where \( a_1, a_2, a_3, ... \) are each \(<1\) and such that

\[
\Sigma a = p.
\]

I have written

\[
N_{m,1^p}
\]

instead of \( N_m \), in order to specify the number of objects (or numbers) subjected to permutation.

Art. 27. I shall now prove that

\[
\Sigma \Sigma N (a_1a_2...a_m...) = \frac{n!}{(p+1)!} (p-m+1) N_{m,1^p},
\]

where

\[
N (a_1a_2...a_m...)
\]

the number of objects subjected to permutation is \( n \), and the summation is in respect of all permutations such that the sum of the first \( m \) numbers in the descending specification is equal to \( p \).

For, by Art. 16,

\[
\Sigma N (a_1a_2...a_m...) = \frac{n!}{(p+1)!} N (a_1a_2...a_m1);
\]

hence

\[
\Sigma \Sigma N (a_1a_2...a_m...) = \frac{n!}{(p+1)!} \Sigma N (a_1a_2...a_m1);
\]

and, by the multiplication theorem,

\[
(p+1) N (a_1a_2...a_m) N (1) = N (a_1a_2...a_m1) + N (a_1a_2...a_m+1);
\]

so that

\[
\Sigma N (a_1a_2...a_m1) = (p+1) N_{m,1^p} - \Sigma N (a_1a_2...a_m+1);
\]

and since

\[
\Sigma N (a_1a_2...a_m+1) = N_{m,1^{p+1}} - \Sigma N (a_1a_2...a_{m-1}1),
\]

\[
\Sigma N (a_1a_2...a_m1) - \Sigma N (a_1a_2...a_{m-1}1) = (p+1) N_{m,1^p} - N_{m,1^{p+1}};
\]

whence, by summation,

\[
\Sigma N (a_1a_2...a_m1) = (p+1) \Sigma N_{m,1^p} - \Sigma N_{m,1^{p+1}};
\]

but since

\[
N_{m,1^p} = m^p - \binom{p+1}{1} (m-1)^p + \binom{p+1}{2} (m-2)^p - \ldots
\]

\[
\Sigma N_{m,1^p} = m^p - \binom{p}{1} (m-1)^p + \binom{p}{2} (m-2)^p - \ldots,
\]
so that, substituting,
\[ \Sigma N(\alpha_1\alpha_2\ldots\alpha_m1) = (p-m+1)N_{m,1^p}; \]

hence
\[ \Sigma\Sigma\Sigma N(\alpha_1\alpha_2\ldots\alpha_m\ldots) = \frac{n!}{(p+1)!} (p-m+1)N_{m,1^p}. \]

Art. 28. Further, summing each side with respect to \( m \),
\[ \Sigma\Sigma\Sigma N(\alpha_1\alpha_2\ldots\alpha_m\ldots) \]
\[ = \frac{n!}{(p+1)!} \left\{ pN_{1,1^p} + (p-1)N_{2,1^p} + \ldots + pN_{p,1^p} \right\} \]
\[ = \frac{n!}{(p+1)!} \left\{ N_{1,1^p} + 2N_{2,1^p} + \ldots + pN_{p,1^p} \right\}; \]

but the sinister is of the form
\[ \Sigma N(w_1w_2) \quad (\text{see Art. 20}) \]

and thus has the value \( \frac{1}{2}n! \); hence
\[ N_{1,1^p} + 2N_{2,1^p} + \ldots + pN_{p,1^p} = \frac{1}{2} (p+1)!, \]

an interesting result.

Art. 29. From a previous result
\[ \Sigma N(\alpha_1\alpha_2\ldots\alpha_m+1) = (p+1)N_{m,1^p} - \Sigma N(\alpha_1\alpha_2\ldots\alpha_m1) = mN_{m,1^p}; \]

hence
\[ \Sigma N(\alpha_1\alpha_2\ldots\alpha_m+1) = \Sigma N(\alpha_1\alpha_2\ldots\alpha_p\ldots+1) = mN_{m,1^p}; \]

and it may be observed that the numbers, included in
\[ \Sigma N(\alpha_1\alpha_2\ldots\alpha_m+1), \]

are the conjugates of those included in
\[ \Sigma N(\alpha_1\alpha_2\ldots\alpha_p\ldots+1). \]

Art. 30. Also since
\[ \Sigma N(\alpha_1\alpha_2\ldots\alpha_m+1) = N_{m,1^p+1} - \Sigma N(\alpha_1\alpha_2\ldots\alpha_m-1), \]
\[ \Sigma N(\alpha_1\alpha_2\ldots\alpha_m-1) + \Sigma N(\alpha_1\alpha_2\ldots\alpha_p+1) = N_{m,1^p+1}; \]

and this leads to the relation
\[ (p-m+2)N_{p-m+2,1^p} + mN_{m,1^p} = N_{m,1^p+1}. \]

E.g., for \( p = 3, m = 2, p-m+2 = 3, \)
\[ 3N_{2,1^p} + 2N_{2,1^p} = N_{2,1^p}; \]

verified by
\[ 3.1 + 2.4 = 11. \]
The result is convenient for the calculation of the numbers $N_{m,1^p+1}$ from the numbers $N_{m,1^p}$.

We have also the remarkable result that the probability of obtaining a permutation, such that the sum of the first $m$ numbers of the descending specification is $p$, is independent of $n$, and has the value

$$\frac{(p-m+1)}{(p+1)!} N_{m,1^p};$$

whenever $p$ is $n-1$ or less.

Art. 31. From the definition we have in respect of the permutations of $n$ numbers

$$N_1 + N_2 + N_3 + \ldots = n!$$

I shall now show that

$$N_n - \theta + 1 \binom{n-\theta+1}{1} N_n - \theta + 2 \binom{n-\theta+2}{2} N_n - \theta + 3 + \ldots$$

$$= \sum_{\nu_1, \nu_2, \ldots, \nu_n} \frac{n!}{\nu_1! \nu_2! \ldots \nu_n!} \cdot \theta!,$$

the summation being for all values of

$$\nu_1, \nu_2, \ldots$$

such that

$$\sum \nu = \theta,$$

$$\sum \nu_\nu = n.$$

The theorem is the outcome of the multiplication theorem of Art. 12.

Observing that, for all values of $s$,

$$N(1^s) = 1,$$

we have

$$\frac{(s_1 + s_2)!}{s_1! s_2!} N(1^s) N(1^s) = N(1^s + s_3) + N(1^s - 21^s),$$

$$\frac{(s_1 + s_2 + s_3)!}{s_1! s_2! s_3!} N(1^s) N(1^s) N(1^s) = N(1^s + s_4) + N(1^s - 21^s - 21^s),$$

and generally, for the product

$$\{N(1)\}^n \{N(1^2)\}^n \ldots \{N(1^p)\}^n,$$

since $\sum \nu_\nu = n$,

$$\frac{n!}{(1!)^n (2!)^n \ldots (p!)^n} = a \text{ linear function of numbers } N(...).$$

We may write down a similar result for every permutation of the factors of

$$\{N(1)\}^n \{N(1^2)\}^n \ldots \{N(1^p)\}^n$$

and, by addition, obtain

$$\frac{n!}{(1!)^n (2!)^n \ldots (p!)^n} \cdot \frac{\theta!}{\nu_1! \nu_2! \ldots \nu_n!} = \text{ linear function of numbers } N,$$

where $\sum \nu = \theta$. 

Further, we obtain a result of this nature for all values of
\[ \nu_1, \nu_2, \ldots \nu_p, \]
such that \( \Sigma \nu_\alpha = n, \Sigma \nu = \theta \); and, by addition, we obtain
\[
\sum \frac{n!}{(1!)^{\nu_1}(2!)^{\nu_2} \cdots (p!)^{\nu_p}} \cdot \frac{\theta!}{\nu_1! \nu_2! \cdots \nu_p!} = \text{linear function of numbers } N,
\]
where \( \Sigma \nu_\alpha = n, \Sigma \nu = \theta \).

We have now to determine the linear function of numbers \( N \) which appears on the dexter.

If one such number be \( N (abc\ldots) \),
it is evident that
\( (abc\ldots) \)
is some composition of the number \( n \).

Consider the product of \( \theta \) factors
\[ N(1^s)N(1^s)\ldots N(1^s), \]
where \( \Sigma s = n \).

The process of multiplication produces \( N \) numbers of \( \theta \) different kinds.

In the first place we throw all the units together,
\[ N(1^{s_2+s_3+\cdots+s_\theta}), \]
one \( N \) number containing \( n \) parts.

In the second place we combine a consecutive pair of factors and throw the remainder of the units together, thus producing \( \theta - 1 \) \( N \) numbers each containing \( n - 1 \) parts, viz.,
\[
N(1^{s_2-1}2^{s_3-1}s_4+\cdots+s_\theta), \quad N(1^{s_2-s_3}2^{s_4-1}s_5+\cdots+s_\theta), \quad \cdots \quad N(1^{s_2+s_3+\cdots+s_{\theta-1}}-121^{s_{\theta-1}}). \]

In the third place we combine two consecutive pairs (including, of course, a consecutive three) of factors and throw the remainder of the units together, thus producing
\[
\left( \begin{array}{c} \theta - 1 \\ 2 \end{array} \right)
\]
\( N \) numbers each containing \( n - 2 \) parts, viz., the series of which one is
\[ N(1^{s_2-1}2^{s_3-2}21^{s_4-1}s_5+\cdots+s_\theta). \]

Notice that, if \( s_2 = 1 \), this becomes
\[ N(1^{s_2-1}31^{s_3-1}s_4+\cdots+s_\theta). \]
We proceed in this manner until finally we combine $\theta - 1$ consecutive pairs and throw the remainder of the units together, thus producing
\[
\binom{\theta - 1}{\theta - 1}
\]
N numbers, each containing $n - \theta + 1$ parts.
Hence the compositions that present themselves are included in those enumerated by
\[
N_n, N_{n-1}, \ldots, N_{n-\theta+1}.
\]
We have to consider the product
\[
N(1^n)N(1^n)\ldots N(1^n)
\]
in all of its permutations and for every system of values of
\[
s_1, s_2, \ldots, s_\theta,
\]
such that
\[
s_1 + s_2 + \ldots + s_\theta = n.
\]
Hence, from considerations of symmetry, and attending to the modus operandi of the multiplication theorem, we find that the whole of the compositions enumerated by
\[
N_n, N_{n-1}, \ldots, N_{n-\theta+1}
\]
present themselves.
Hence the linear function we seek is a linear function of
\[
N_{n-\theta+1}, N_{n-\theta+2}, \ldots, N_{n-1}, N_n,
\]
and it remains to determine the coefficients.
The number of products, including permutations,
\[
N(1^n)N(1^n)\ldots N(1^n),
\]
which we have to consider, is equal to the numbers of compositions of $n$ into $\theta$ parts, viz., it is
\[
\binom{n-1}{n-\theta};
\]
each of these produces
\[
\binom{\theta - 1}{m}
\]
N numbers, each containing $n - m$ parts.
There are thus
\[
\binom{n-1}{n-\theta}\binom{\theta - 1}{m}
\]
N numbers, each containing $n - m$ parts.
But there are only
\[
\binom{n-1}{m}
\]
different $N$ numbers, each containing $n-m$ parts, because
\[
{n-1 \choose m}
\]
is equal to the number of compositions of $n$ into $n-m$ parts.
Hence, each $N$ number, comprised in
\[
N_{n-m},
\]
will occur
\[
\frac{(n-1) \binom{\theta-1}{m}}{(n-\theta) \binom{\theta-1}{m}} = {n-m-1 \choose n-\theta}
\]
times.

Hence the required linear function is
\[
\Sigma {n-m-1 \choose n-\theta} N_{n-m},
\]
or
\[
N_{n-\theta+1} + {n-\theta+1 \choose 1} N_{n-\theta+2} + \cdots + {n-\theta+2 \choose 2} N_{n-\theta+3} + \cdots + \frac{n-1}{\Theta-1} N_n,
\]
and the final result is
\[
\Sigma \frac{n!}{(1!)^n (2!)^r \cdots (p!)^r} \cdot \nu_1 \nu_2 \cdots \nu_p
\]
\[
= N_{n-\theta+1} + {n-\theta+1 \choose 1} N_{n-\theta+2} + \cdots + {n-\theta+2 \choose 2} N_{n-\theta+3} + \cdots + \frac{n-1}{\Theta-1} N_n,
\]
where
\[
\Sigma \nu_i = n, \Sigma \nu = \Theta.
\]

PART II.—SECTION 3.

Art. 32. In the preceding pages we have had under view the permutations of $n$ different numbers. As I am now taking in hand the general case of numbers which possess any number of similarities, I find it convenient to slightly alter the point of view.

Let
\[
a, \beta, \gamma, \ldots
\]
denote numbers in descending order of magnitude, and suppose there are $p$ number equal to $a$,
\[
q, \beta,
\]
\[
r, \gamma
\]
so that, placed in descending order, the assemblages may be written
\[
a^p \beta^q \gamma^r \ldots
\]
I say that the assemblage is specified by the composition
\[
(pqr \ldots).
\]
As equalities may occur between the numbers \( p, q, r, \ldots \), I take, for greater generality, the specifying composition

\[
(p_1^n p_2^n \ldots).
\]

It will be seen later that the order of occurrence of the parts of this composition is immaterial, so that we may consider the parts \( p_1, p_2, \ldots \) to be in descending order of magnitude and the specification to be denoted by a partition

\[
(p_1^n p_2^n \ldots).
\]

E.g., we obtain the same results for each of the six assemblages,

\[
\alpha \alpha \alpha \beta \beta \gamma, \quad \alpha \alpha \alpha \gamma \gamma \gamma, \quad \alpha \alpha \beta \beta \beta \gamma,
\]

\[
\alpha \alpha \beta \gamma \gamma \gamma, \quad \alpha \beta \beta \gamma \gamma \gamma, \quad \alpha \beta \gamma \gamma \gamma,
\]

the specification of each assemblage being

\[
(321).
\]

Every permutation has a descending specification.

E.g.,

\[
\alpha \beta \alpha \alpha \gamma \beta
\]

has the descending specification

\[
(231).
\]

In the case considered in Part I. the assemblage of numbers had the specification

\[
(1^n)
\]

since there were no similarities, and the numbers \( N(\ldots) \) were expressed in terms of the coefficients obtained by the multinomial expansion

\[
(a_1 + a_2 + a_3 + \ldots)^n.
\]

E.g., we found

\[
N(a) = \text{coefficient of symmetric function } (a) \text{ in the expansion,}
\]

\[
N(ab) + N(a+b) = \quad (ab)
\]

where, in the first case, \( a = n \), and in the second, \( a+b = n \).

In a usual notation let

\[
h_1, h_2, h_3, \ldots
\]

denote the homogeneous product sums, of the successive orders, of the roots of the equation

\[
x^n - \alpha_1 x^{n-1} + \alpha_2 x^{n-2} - \alpha_3 x^{n-3} + \ldots = 0;
\]

we may say that, in Part I., the auxiliary generating function was

\[
(a_1 + a_2 + a_3 + \ldots)^n = h_1^n,
\]

\( \alpha_1, \alpha_2, \alpha_3, \ldots \) being the roots of the equation.

Art. 33. In the present case the auxiliary generating function is

\[
h_{p_1}^{x_1} h_{p_2}^{x_2} h_{p_3}^{x_3} \ldots,
\]

as will appear.
For it was shown, _loc. cit._, that the number of ways of distributing the objects, as specified, into different parcels containing $a$, $b$, $c$... objects respectively is the coefficient of the symmetric function

$$(abc...)$$

in the development of the symmetric function

$$h_{p_1}h_{p_2}h_{p_3}...$$

as a sum of monomial symmetric functions.

Let this coefficient be denoted by

$$C(abc...)$$

and let the number of arrangements of the objects, which have a descending specification

$$(abc...)$$

be denoted by

$$N(abc...)$$

Let the whole number of objects be

$$\Sigma \pi p = n.$$ 

Then, when $a = n$, clearly

$$N(a) = C(a) = 1,$$

and when $a + b = n$, $C(ab)$ is the number of arrangements into two different parcels containing $a$, $b$ objects respectively, and by previous reasoning

$$N(ab) + N(a + b) = C(ab);$$

and, when $a + b + c = n$,

$$N(abc) + N(a + b, c) + N(a, b + c) + N(a + b + c) = C(abc),$$

and so forth as in the simple case already considered. Hence

$$N(ab) = C(ab) - C(a + b),$$

$$N(abc) = C(abc) - C(a + b, c) - C(a, b + c) + C(a + b + c),$$

$$N(abcd) = C(abcd) - C(a + b, c, d) - C(a, b + c, d) - C(a, b, c + d) + C(a + b, c + d) + C(a, b + c + d) + C(a + b + c, d) - C(a + b + c + d),$$

&c.,

the numbers $N$ being all expressible in terms of coefficients of the auxiliary generating function.

Art. 34. _E.g._ Take objects $aaba\beta\gamma$, where $\alpha$, $\beta$, $\gamma$ are in descending order of magnitude.

Since

$$h_3 h_2 h_1 = (6) + 3(51) + 5(42) + 8(41^2) + 6(3^2) + 12(321)$$

$$+ 19(31^3) + 15(2^5) + 24(2^21^2) + 38(21^4) + 60(1^6),$$

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we calculate, from the above formulæ,
\[
\begin{align*}
N (6) &= 1, \\
N (51) &= 3 - 1 = 2, \\
N (3^2) &= 6 - 1 = 5, \\
N (321) &= 12 - 5 - 2 - 1 = 4
\end{align*}
\]
and so on.

The five arrangements, enumerated by \( N (3^2) \), are
\[
\begin{align*}
\alpha\alpha\beta\alpha\beta\gamma \\
\alpha\alpha\gamma\alpha\beta \beta \\
\alpha\beta\gamma\alpha\alpha \beta \\
\alpha\beta\beta\alpha\alpha \gamma \\
\beta\beta\gamma\alpha\alpha \alpha,
\end{align*}
\]
each having the descending specification \((3^2)\).

The four arrangements, enumerated by \( N (321) \), are
\[
\begin{align*}
\alpha\alpha\beta\alpha\gamma \beta \\
\alpha\alpha\gamma\beta\alpha \beta \\
\alpha\beta\gamma\alpha\beta \alpha \\
\alpha\beta\beta\alpha\gamma \alpha,
\end{align*}
\]
each having the descending specification \((321)\).

The complete results that numbers specified by \((321)\) are
\[
\begin{align*}
N (31^3), N (1^33), N (21^4), N (1^42), N (2112) \quad & \text{each } 0 \quad \ldots \quad 0 \\
N (121^3), N (1^221), N (1^221^2), N (1^3) \quad & \text{each } 0 \quad \ldots \quad 0 \\
N (6), N (41^3), N (1^34), N (131^3), N (1^331) \quad & \text{ each } 1 \quad \ldots \quad 9 \\
N (2^31), N (1^22^3), N (2121), N (1212) \quad & \text{ each } 1 \quad \ldots \quad 9 \\
N (51), N (15), N (312), N (213) \quad & \text{ each } 2 \quad \ldots \quad 8 \\
N (141), N (1221) \quad & \text{ each } 3 \quad \ldots \quad 6 \\
N (42), N (24), N (321), N (123) \quad & \text{ each } 4 \quad \ldots \quad 16 \\
N (3^2), N (231), N (132) \quad & \text{ each } 5 \quad \ldots \quad 15 \\
N (2^3) \quad & \text{ each } 6 \quad \ldots \quad 6 \\
\end{align*}
\]
60 being, of course, the total number of permutations of the objects.
Art. 35. The method of calculation establishes that the number $N (...) \text{ is unaltered by reversal of the order of the numbers in the bracket. Also that the results are only dependent upon the magnitudes of the parts in the specification of the assemblage and not upon the order of their occurrence.}$

**General Investigation of a Generating Function.**

Art. 36. I have shown above that, for numbers specified by an auxiliary generating function is

\[ (p_1^n p_2^n \ldots), \]

\[ h_{p_1^n} h_{p_2^n} \ldots, \]

for, from its expansion in terms of monomial symmetric functions, the numbers

\[ N (abc \ldots) \]

can be successively calculated.

For present convenience I take the above generating function to be

\[ h_h h_h \ldots \]

and recall that

\[ N (abc \ldots) + N (a+b, c, \ldots) + N (a, b+c, \ldots) + \ldots \]

is equal to the coefficient of symmetric function

\[ (abc \ldots) \]

in the expansion of

\[ h_h h_h h_h \ldots \]

The above linear function of the numbers

\[ N (...) \]

is formed by adding adjacent numbers

\[ 0, 1, 2, 3, \ldots, k \text{ at a time,} \]

where the numbers $a, b, c, \ldots$ are $k$ in number.

It thus comprises $2^{k-1}$ terms in general.

Art. 37. Let this linear function be denoted by

\[ \theta_N \{ (a)(b)(c) \ldots \}, \]

so that if we write

\[ h_h h_h h_h \ldots = \Sigma C (abc \ldots) (abc \ldots), \]

\[ \theta_N \{ (a)(b)(c) \ldots \} = C (abc \ldots). \]

From this system of linear relations is determined the set

\[ N (a) = C (a), \text{ where } a = n, \]

\[ N (ab) = C (ab) - C (a+b), \text{ where } a+b = n, \]

\[ N (abc) = C (abc) - C (a+b, c) - C (a, b+c) + C (a+b+c), \text{ where } a+b+c = n, \text{ and so on;} \]

\[ N \quad 2 \]
the law of formation of the linear functions of the numbers

\[ C(...) \]

being similar to that which occurs in

\[ \theta_N \{(a)(b)(c)\ldots\}, \]

with the exception that the signs are alternately positive and negative, depending upon the numbers of integers in the brackets.

Art. 38. Denote this linear function of the numbers \( C(...) \) by

\[ \phi_C \{(a)(b)(c)\ldots\}, \]

so that

\[ N(abc\ldots) = \phi_C \{(a)(b)(c)\ldots\}. \]

When it is necessary to put in evidence the numbers whose permutations are under examination we may write the two formulae

\[ \theta_N \{(a)(b)(c)\ldots\}_{(pqr\ldots)} = C(abc\ldots)_{(pqr\ldots)}; \]

\[ N(abc\ldots)_{(pqr\ldots)} = \phi_C \{(a)(b)(c)\ldots\}_{(pqr\ldots)}. \]

Section 4.

_Digression on the Forms \( \theta_N, \phi_C \)._

Art. 39. Define in general, so that

\[ \theta_N \{(a_1\ldots a_{s-1}a_s)(b_1b_2\ldots b_{t-1}b_t)(c_1c_2\ldots c_{u-1}c_u)(d_1d_2\ldots d_v)(k_1k_2\ldots k_z)\}, \]

where there are \( k \) symbols \( a, b, c, d, \ldots, k \), denotes the \( 2^{k-1} \) terms forming the series

\[ N(a_1\ldots k_z) + N(a_1\ldots a_{s-1}, a_s+b_1, b_2\ldots k_z) + N(a_1\ldots b_{t-1}, b_t+c_1, c_2\ldots k_z) + \ldots + N(a_1\ldots a_{s-1}, a_s+b_1, b_2\ldots b_{t-1}, b_t+c_1, c_2\ldots k_z) + \ldots, \]

where additions take place,

\[ 0, 1, 2, \ldots, k-1 \] at a time between the pairs \( a_s, b_1; b_t, c_1; c_u, d_1; \ldots. \]

Art. 40. Similarly define

\[ \phi_C \{(a_1\ldots a_{s-1}a_s)(b_1b_2\ldots b_{t-1}b_t)(c_1c_2\ldots c_{u-1}c_u)(d_1d_2\ldots d_v)(k_1k_2\ldots k_z)\} \]

to denote the \( 2^{k-1} \) terms forming the series

\[ C(a_1\ldots k_z) \]
\[ -C(a_1\ldots a_{s-1}, a_s+b_1, b_2\ldots k_z) \]
\[ -C(a_1\ldots b_{t-1}, b_t+c_1, c_2\ldots k_z) \]
\[ -\ldots + C(a_1\ldots a_{s-1}, a_s+b_1, b_2\ldots b_{t-1}, b_t+c_1, c_2\ldots k_z) \]
\[ +\ldots, \]
formed according to the same law, but the successive blocks of terms having alternately positive and negative signs.

Art. 41. I proceed to generalise the two results

\[ \theta_N \{(a)(b)(c)\ldots\} = \phi_C \{(a)(b)\ldots\}, \]

\[ \theta_N \{(abc)\ldots\} = \phi_C \{(a)(b)(c)\ldots\}. \]

By definition

\[ \theta_N \{(a_1\ldots a_{n-1} a_n) (b_1 b_2 \ldots b_l)\} \]

\[ = N (a_1 \ldots b_l) + N (a_1 \ldots a_{n-1}, a_n + b_1, b_2 \ldots b_l); \]

and since

\[ N (abc)\ldots = \theta_N (abc)\ldots = \phi_C \{(a)(b)(c)\ldots\}, \]

this

\[ = \phi_C \{(a_1)(a_2)\ldots(b_l)\} + \phi_C \{(a_1)\ldots(a_{n-1})(a_n+b_1)(b_2)\ldots(b_l)\}. \]

Now the sum of these two terms is precisely

\[ \phi_C \{(a_1)(a_2)\ldots(a_{n-1})(a_n b_1)(b_2)\ldots(b_l)\}, \]

because the terms involving \( a_n + b_1 \)

in

\[ \phi_C \{(a_1)(a_2)\ldots(b_l)\} \]

are the same, with opposite sign, as those involved in

\[ \phi_C \{(a_1)\ldots(a_{n-1})(a_n+b_1)(b_2)\ldots(b_l)\}, \]

and therefore cancel them.

Hence the result

\[ \theta_N \{(a_1\ldots a_{n-1} a_n) (b_1 b_2 \ldots b_l)\} = \phi_C \{(a_1)(a_2)\ldots(a_{n-1})(a_n b_1)(b_2)\ldots(b_l)\}. \]

Art. 42. Again

\[ \theta_N \{(a_1\ldots a_n) (b_1\ldots b_l) (c_1\ldots c_n)\} \]

\[ = N (a_1 \ldots c_n) + N (a_1 \ldots a_{n-1}, a_n + b_1, b_2 \ldots c_n) \]

\[ + N (a_1 \ldots b_{l-1}, b_l + c_1, c_2 \ldots c_n) \]

\[ + N (a_1 \ldots a_{n-1}, a_n + b_1, b_2 \ldots b_{l-1}, b_l + c_1, c_2 \ldots c_n), \]

\[ = \theta_N (a_1 \ldots c_n) + \theta_N (a_1 \ldots a_{n-1}, a_n + b_1, b_2 \ldots c_n) \]

\[ + \theta_N (a_1 \ldots b_{l-1}, b_l + c_1, c_2 \ldots c_n) + \theta_N (a_1 \ldots a_{n-1}, a_n + b_1, b_2 \ldots b_{l-1}, b_l + c_1, c_2 \ldots c_n), \]

\[ = \phi_C \{(a_1)\ldots(c_n)\} + \phi_C \{(a_1)\ldots(a_{n-1})(a_n + b_1)(b_2)\ldots(c_n)\} \]

\[ + \phi_C \{(a_1)\ldots(b_{l-1})(b_l + c_1)(c_2)\ldots(c_n)\} + \phi_C \{(a_1)\ldots(a_{n-1})(b_1 + c_1)(c_2)\ldots(c_n)\}, \]

\[ = \phi_C \{(a_1)\ldots(a_{n-1})(a_n b_1)(b_2)\ldots(c_n)\} \]

\[ + \phi_C \{(a_1)\ldots(a_{n-1})(a_n b_1)(b_2)\ldots(b_l + c_1)(c_2)\ldots(c_n)\}, \]

\[ = \phi_C \{(a_1)\ldots(a_{n-1})(a_n b_1)(b_2)\ldots(b_{l-1})(b_l c_1)(c_2)\ldots(c_n)\}, \]

by successive use of the formula Art. 41 above.
Also, clearly, if \( t = 1 \)
\[
\theta_N \{ (a_1 \ldots a_t)(b_1 \ldots b_s) \} = \phi_C \{ (a_1 \ldots (a_{s-1})(a_s b_1 c_1) \ldots c_s \ldots c_s) \}.
\]

Art. 43. Therefore, by induction, we can express any form
\[
\theta_N \{ \quad \}
\]
as a form
\[
\phi_C \{ \quad \}.
\]

The law is well seen by a particular case, viz.,
\[
\theta_N \{ (a)(b)(c)(d) \} = \phi_C \{ abcd \},
\]
\[
\theta_N \{ (ab)(c)(d) \} = \phi_C \{ (a)(bcd) \},
\]
\[
\theta_N \{ (a)(bc)(d) \} = \phi_C \{ (ab)(cd) \},
\]
\[
\theta_N \{ (a)(bc)(d) \} = \phi_C \{ (abc)(d) \},
\]
\[
\theta_N \{ (abc)(d) \} = \phi_C \{ (a)(b)(cd) \},
\]
\[
\theta_N \{ (abcd) \} = \phi_C \{ (a)(b)(c)(d) \}.
\]

We have, in respect of the four letters, \( 8 = 2^3 \) relations; the letters always occur in the order
\( a, b, c, d, \)
and to obtain the form \( \phi_C \{ \quad \} \), which is equated to a form \( \theta_N \{ \quad \} \), we may make use of the zig-zag conjugate law; e.g., connect with
\[
(ab)(cd)
\]
the composition \( 22 \); take the zig-zag conjugate of this, viz., \( 121 \), and then write
\[
\theta_N \{ (ab)(cd) \} = \phi_C \{ (a)(bc)(d) \},
\]
and
\[
\theta_N \{ (a)(bc)(d) \} = \phi_C \{ (ab)(cd) \} ;
\]
and so in every case.

Art. 44. In the general case of \( p \) letters we obtain \( 2^{p-1} \) relations corresponding to the \( 2^{p-1} \) compositions of \( p \); the relations are obtainable from zig-zag conjugation of such compositions and, in any relation
\[
\theta_N \{ \quad \} = \phi_C \{ \quad \},
\]
we may interchange the form-symbols
\( \theta_N, \phi_C \).

Art. 45. In the above investigation we obtained incidentally certain linear relations between the forms
\[
\theta_N,
\]
and also between the forms $\phi_c$, which must now be set forth in a regular manner.

The former relations are of the type

$$\theta_N\{(a_1 \ldots a_s)(b_1 \ldots b_t)(c_1 \ldots c_u)\}$$

$$= \theta_N(a_1 \ldots a_s b_1 \ldots b_t c_1 \ldots c_u)$$

$$+ \theta_N(a_1 \ldots a_{s-1}, a_s + b_1, b_2 \ldots b_{t-1}, b_t + c_1, c_2 \ldots c_u)$$

$$+ \theta_N(a_1 \ldots a_s b_1 \ldots b_{t-1}, b_t + c_1, c_2 \ldots c_u)$$

$$+ \ldots$$

$$+ \theta_N(a_1 \ldots a_{s-1}, a_s + b_1, b_2 \ldots b_{t-1}, b_t + c_1, c_2 \ldots c_u)$$

$$+ \ldots ;$$

this follows directly from the definition of the form $\theta_N\{ \}$, since

$$\theta_N(abc \ldots) = N(abc \ldots).$$

Art. 46. The latter relations are of the type

$$\phi_c\{(a_1 \ldots a_s)(b_1 \ldots b_t)(c_1 \ldots c_u)\}$$

$$= \phi_c(a_1 \ldots a_s b_1 \ldots b_t c_1 \ldots c_u)$$

$$- \phi_c(a_1 \ldots a_{s-1}, a_s + b_1, b_2 \ldots b_{t-1}, b_t + c_1, c_2 \ldots c_u)$$

$$- \phi_c(a_1 \ldots a_s b_1 \ldots b_{t-1}, b_t + c_1, c_2 \ldots c_u)$$

$$- \ldots$$

$$+ \phi_c(a_1 \ldots a_{s-1}, a_s + b_1, b_2 \ldots b_{t-1}, b_t + c_1, c_2 \ldots c_u)$$

$$+ \ldots ;$$

which also follows directly from the definition of the form $\phi_c\{ \}$, since

$$\phi_c(abc \ldots) = C(abc \ldots).$$

Art. 47. We have other linear relations of the type

$$\theta_N\{(a_1 \ldots a_s)(b_1 \ldots b_t)(c_1 \ldots c_u)\}$$

$$= \theta_N\{(a_1 \ldots b_t)(c_1 \ldots c_u)\}$$

$$+ \theta_N\{(a_1 \ldots a_{s-1}, a_s + b_1, b_2 \ldots b_t)(c_1 \ldots c_u)\};$$

$$\phi_c\{(a_1 \ldots a_s)(b_1 \ldots b_t)(c_1 \ldots c_u)\}$$

$$= \phi_c\{(a_1 \ldots b_t)(c_1 \ldots c_u)\}$$

$$- \phi_c\{(a_1 \ldots a_{s-1}, a_s + b_1, b_2 \ldots b_t)(c_1 \ldots c_u)\}.$$

In fact, the law may be taken to operate as between any sets of consecutive factors in $\phi_N\{ \}$ and $\phi_c\{ \}$ respectively, leaving the remaining factors untouched.
Thus it is easy to verify the three relations

\[
\theta_N \{(ab)(cd)(ef)(gh)\} = \theta_N \{(abcd)(ef)(gh)\} + \theta_N \{(a, b+c, d)(ef)(gh)\},
\]

\[
= \theta_N \{(ab)(cd)(efgh)\} + \theta_N \{(ab)(cd)(e, f+g, h)\},
\]

\[
= \theta_N \{(abcd)(efgh)\} + \theta_N \{(abcd)(e, f+g, h)\} + \theta_N \{(a, b+c, d)(e, f+g, h)\};
\]

and the further three

\[
\phi_C \{(ab)(cd)(ef)(gh)\} = \phi_C \{(abcd)(ef)(gh)\} - \phi_C \{(a, b+c, d)(ef)(gh)\},
\]

\[
= \phi_C \{(ab)(cd)(efgh)\} - \phi_C \{(ab)(cd)(e, f+g, h)\},
\]

\[
= \phi_C \{(abcd)(efgh)\} - \phi_C \{(abcd)(e, f+g, h)\} + \phi_C \{(a, b+c, d)(e, f+g, h)\}.
\]

Art. 48. From these relations we may obtain new relations by transforming from \(\theta_N\) to \(\phi_C\), or vice versa.

Thus from relations of type

\[
\theta_N \{(a)(b)(c)\} = \theta_N (abc) + \theta_N (a+b, c) + \theta_N (a, b+c) + \theta_N (a+b+c),
\]

we obtain those of type

\[
\phi_C (abc) = \phi_C \{(a)(b)(c)\} + \phi_C \{(a+b)(c)\} + \phi_C \{(a)(b+c)\} + \phi_C (a+b+c);
\]

and from those of type

\[
\phi_C \{(a)(b)(c)\} = \phi_C (abc) - \phi_C (a+b, c) - \phi_C (a, b+c) + \phi_C (a+b+c),
\]

we obtain others of type

\[
\theta_N (abc) = \theta_N \{(a)(b)(c)\} - \theta_N \{(a+b)(c)\} - \theta_N \{(a)(b+c)\} + \theta_N (a+b+c).
\]

These new expressions for

\[
\theta_N (abc...) \text{ and } \phi_C (abc...),
\]

with an obviously analogous law to that we have frequently met with, are of great importance.
From the relation

\[ \phi_c\{(a)(b)(c)(d)\} = \phi_c\{(ab)(cd)\} - \phi_c\{(a+b)(c+d)\} + \phi_c\{(a+b)(c+d)\}, \]

we obtain

\[ \theta_N\{abcd\} = \theta_N\{(a)(bc)(d)\} - \theta_N\{(a+b, c)(d)\} - \theta_N\{(a)(b, c+d)\} + \theta_N\{(a+b, c+d)\}; \]

and there is no necessity to give further examples.

Section 5.

Art. 49. The differential operator, of order \(s\), that is so frequently of use in the theory of symmetric functions, viz.:

\[ \frac{1}{s!}(\partial_{a_1} + a_1\partial_{a_2} + a_2\partial_{a_3} + \ldots)' = D_s, \]

can now be employed.

Remembering that operating upon monomial symmetric functions,

\[ D_a(a) = 1, \]
\[ D_a(b) = 0 \text{ unless } b = a, \]
\[ D_aD_bD_c \ldots (abc \ldots) = 1; \]

and generally that \(D_a\) obliterates a number \(a\) from the partition of a function and causes it to vanish if no such number presents itself, it is clear that

\[ D_aD_bD_c \ldots h_lh_qh_r \ldots = C(abc \ldots)_{pqr \ldots}; \]

and thence if we write

\[ \phi_D\{(a)(b)(c)\ldots\} = D_aD_bC_c \ldots - D_{a+b}D_c \ldots - D_{a+b+c} \ldots - \ldots \]

according to a law derivable from that which defines

\[ \phi_c\{(a)(b)(c)\ldots\} \text{ (see Art. 38),} \]

we find

\[ N(abc \ldots)_{pqr \ldots} = \phi_D\{(a)(b)(c)\ldots\} h_lh_qh_r \ldots. \]

Art. 50. Observe that in the paper to which reference has been made it was shown that

\[ C(abc \ldots)_{pqr \ldots} = C(pqr \ldots)_{abc \ldots}. \]

Two consequences flow from this fact.

Firstly

\[ \theta_N\{(a)(b)(c)\ldots\}_{pqr \ldots} = \theta_N\{(p)(q)(r)\ldots\}_{abc \ldots}, \]

which is a theorem of reciprocity for the numbers

\[ N(...). \]
Secondly, since
\[ D_1 D_2 D_3 \ldots h_1 h_2 h_3 \ldots = D_1 D_2 D_3 \ldots h_1 h_2 h_3 \ldots, \]

\[ N(abc\ldots)_{(pqr\ldots)} = D_1 D_2 D_3 \ldots (h_1 h_2 h_3 \ldots h_{a+b+c} \ldots \ldots); \]

where, on the dexter, the operand is a function formed from the functions \( h_1, h_2, h_3, \ldots \) in the same manner as

\[ \phi_{D}\{\{(a)(b)(c)\ldots\}\}. \]

is formed from the operators \( D_1, D_2, D_3, \ldots \).

Hence

\[ N(abc\ldots)_{(pqr\ldots)} = D_1 D_2 D_3 \ldots \phi_{D}\{\{(a)(b)(c)\ldots\}\}, \]

where

\[ \phi_{D}\{\{(a)(b)(c)\ldots\}\} = h_1 h_2 h_3 \ldots h_{a+b+c} \ldots \ldots \ldots. \]

Art. 51. I now write

\[ \phi_{D}\{\{(a)(b)(c)\ldots\}\} = h_{abc\ldots}; \]

so that

\[ N(abc\ldots)_{(pqr\ldots)} = D_1 D_2 D_3 \ldots h_{abc\ldots}; \]

and it appears that

\[ h_{abc\ldots} \]

is the true generating function of the numbers

\[ N(abc\ldots) \]

for the permutations of assemblages of numbers of all specifications.

In fact,

\[ h_{abc\ldots} = \Sigma N(abc\ldots)_{(pqr\ldots)} \cdot (pqr\ldots); \]

and the expansion of

\[ h_{abc\ldots} \]

as a linear function of monomial symmetric functions gives a complete account of numbers

\[ N(abc\ldots). \]

Art. 52. Before proceeding to a rapid examination of this new and most important symmetric function

\[ h_{abc\ldots}, \]

never before I believe introduced into algebraic analysis, I give complete tables of the numbers \( N(\ldots) \) as far as \( n = 6 \).

\[ n = 2. \]

\[ \begin{array}{|c|c|c|}
\hline
 & (2) & (1^2) \\
\hline
N(2) & 1 & 1 \\
N(1^2) & 1 \\
\hline
\end{array} \]

= specification.
### $n = 3$.

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<th>(21)</th>
<th>(2)</th>
<th>= specification.</th>
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<td>1</td>
<td>1</td>
<td></td>
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<tr>
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<th>(2)</th>
<th>(21)</th>
<th>(12)</th>
<th>= specification.</th>
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<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>N (31)</td>
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<tr>
<td>N (2)</td>
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<td>2</td>
<td>3</td>
<td>5</td>
<td></td>
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</tr>
<tr>
<td>N (121)</td>
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<td>2</td>
<td>5</td>
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<td>N (212)</td>
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### $n = 5$.

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</tr>
<tr>
<td>N (31)</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N (132)</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N (123)</td>
<td>1</td>
<td>3</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N (2)</td>
<td>1</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N (1)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

\[ o 2 \]
To explain—it will be found that

\[ h_{131} = h_2 h_1^2 - 2h_4 h_1 + h_5, \]

\[ = (32) + 2(31^3) + 3(2^21) + 6(21^3) + 11(1^5), \]

corresponding to row 4 of the table for \( n = 5 \).

Art. 53. Another symmetric function

is formed from the elements

\[ a_1, a_2, a_3, \ldots \]

in the same manner as the symmetric function

from the elements

\[ h_{p_1, p_2, p_3, \ldots} \]

\[ h_1, h_2, h_3, \ldots \]
The Symmetric Functions $h_{p_1 p_2 \ldots}, a_{p_1 p_2 \ldots}$

Art. 54. These two new functions are of fundamental importance, not only in this investigation, but in the theory of symmetric functions generally.

In regard to the algebraic equation

$$x^n - a_1 x^{n-1} + a_2 x^{n-2} - \ldots = 0,$$

$h_1, h_2, h_3, \ldots$ are the homogeneous product sums of the roots and the two sets of elements

$$a_1, a_2, a_3, \ldots,$$

$$h_1, h_2, h_3, \ldots$$

have reciprocal properties which it is useful to briefly glance at.

We have

$$h_1 = a_1 = (1),$$

$$h_2 = a_1^2 - a_2 = (2) + (1^2),$$

$$h_3 = a_1^3 - 2a_1a_2 + a_3 = (3) + (21) + (1^3),$$

and, in general,

$$h_n = \Sigma (-1)^{n+k} \frac{(\Sigma k)!}{k_1! k_2! \ldots k_s!} a_1^{k_1} a_2^{k_2} \ldots a_s^{k_s}.$$ 

The two series of elements are connected in such wise that, in any relation between the elements, the symbols $a, h$ may be interchanged. Thus, from

$$\alpha_1^2 - 3\alpha_2 = -2h_1^2 + 3h_2$$

is derived

$$h_1^2 - 3h_2 = -2\alpha_1^2 + 3\alpha_2.$$

As a particular case it is found that $\alpha_s$ is the same function of the elements $h_1, h_2, h_3, \ldots$ that $h_s$ is of the elements $a_1, a_2, a_3, \ldots$

If functions of the elements $h_1, h_2, h_3, \ldots$ be denoted by

$$f(h), \quad \phi(h),$$

we see that, if

$$f(h) = \phi(a),$$

so that

$$\phi(h) = f(a),$$

then

$$f(h)\phi(h) = f(a)\phi(a);$$

showing that

$$f(h)\phi(h)$$

is an absolute invariant quâd the transformation which replaces the elements

$$h_1, h_2, h_3, \ldots$$

by the elements

$$a_1, a_2, a_3, \ldots.$$
Art. 55. With these necessary preliminary remarks I define a new function of weight \( n \), viz.:

\[ h_{p_1 p_2 p_3 \ldots}, \]

where \( p_1 p_2 p_3 \ldots \) is any composition of the number \( n \); of the given weight there are

\[ 2^{n-1} \]
such functions, one of which is clearly

\[ h_n. \]

The complete definition is given by the multiplication law

\[ h_{p_1 p_2 \ldots p_r} h_{q_1 q_2 \ldots q_t} = h_{p_1 p_2 \ldots p_r q_1 q_2 \ldots q_t} + h_{p_1 p_2 \ldots p_r q_1 + q_t, q_2 \ldots q_t}, \]

where the functions

\[ h_{p_1 p_2 \ldots p_r}, \quad h_{q_1 q_2 \ldots q_t} \]

are, or are not, of the same weight.

Art. 56. A second new function

\[ a_{p_1 p_2 p_3 \ldots} \]

is similarly defined by the same law; viz.,

\[ a_{p_1 p_2 \ldots p_r} a_{q_1 q_2 \ldots q_t} = a_{p_1 p_2 \ldots p_r q_1 q_2 \ldots q_t} + a_{p_1 p_2 \ldots p_r q_1 + q_t, q_2 \ldots q_t}. \]

What follows applies generally to both of the new functions.

Art. 57. Since the multiplication is commutative, we have the first important property, viz.,

\[ h_{p_1 p_2 \ldots p_r q_1 q_2 \ldots q_t} + h_{p_1 p_2 \ldots p_r q_1 + q_t, q_2 \ldots q_t} = h_{q_1 q_2 \ldots q_t p_1 p_2 \ldots p_r + q_1, q_2 \ldots q_t}. \]

Art. 58. Every product of elementary functions is expressible in terms of the new functions, e.g.,

\[ h_{y} h_{q} = h_{y q} + h_{y + q}, \]

\[ h_{y} h_{q} h_{r} = h_{y q r} + h_{y + q} r + h_{y + q} r + h_{y + q + r}; \]

and in general

\[ h_{x}, h_{y}, h_{z}, \ldots h_{p_r} = \theta_{s} \{(p_1)(p_2)(p_3)\ldots(p_s)\}, \]

where, in \( \theta_{s} \{ \quad \}, \) the sum of the coefficients is

\[ 2^{s-1}. \]

These relations show that

\[ h_{p_1 p_2 \ldots p_r} = h_{p_1 \ldots p_r}. \]

Art. 59. Similarly

\[ h_{pq} = h_{p} h_{q} - h_{p + q}, \]

\[ h_{pqr} = h_{p} h_{q} h_{r} - h_{p + q} h_{r} - h_{p} h_{q + r} + h_{p + q + r}; \]

and in general

\[ h_{p_1 p_2 \ldots p_r} = \phi_{s} \{(p_1)(p_2)\ldots(p_s)\}. \]

If, moreover, we define

\[ \theta_{s} \{(p_1 p_2 \ldots p_s) (q_1 q_2 \ldots q_t) (r_1 r_2 \ldots r_u)\} \]
as denoting
\[ h_{p_1 \cdots p_{t-1} q_{t-1} r} + h_{p_1 \cdots p_{t-1} q_{t} r} + h_{p_1 \cdots p_{t-1} q_{t} r} \]
and
\[ \phi_h \{ (p_1 \cdots p_{t-1} q_{t} ) (q_{t-1} q_{t} q_{t} ) (r_1 r_2 \cdots r_u) \} \]

as denoting
\[ h_{p_1 \cdots p_{t-1} q_{t} r} - h_{p_1 \cdots p_{t-1} q_{t} r} + h_{p_1 \cdots p_{t-1} q_{t} r} \]
and
\[ \phi_h \{ (p_1 \cdots p_{t-1} q_{t} ) (q_{t-1} q_{t} q_{t} ) (r_1 r_2 \cdots r_u) \} \]

according to the law usual in this subject; we find
\[ \theta_h \{ (p_1 \cdots p_{t-1} q_{t} ) (q_{t-1} q_{t} q_{t} ) (r_1 r_2 \cdots r_u) \} = h_{p_1 \cdots p_{t-1} q_{t} r} ; \]
and
\[ \phi_h \{ (p_1 \cdots p_{t-1} q_{t} ) (q_{t-1} q_{t} q_{t} ) (r_1 r_2 \cdots r_u) \} = \phi_h \{ (p_1 \cdots p_{t-1} q_{t} ) (q_{t} q_{t} q_{t} ) (r_1 r_2 \cdots r_u) \} = \phi_h \{ (p_1 \cdots p_{t-1} q_{t} ) (q_{t} q_{t} q_{t} ) (r_1 r_2 \cdots r_u) \} = \phi_h \{ (p_1 \cdots p_{t-1} q_{t} ) (q_{t} q_{t} q_{t} ) (r_1 r_2 \cdots r_u) \} = h_{p_1 \cdots p_{t-1} q_{t} r} .

The reader may verify that
\[ \phi_h \{ (p \) (q) (r) \}, \phi_h \{ (pq) (r) \}, \phi_h \{ (p) (qr) \}, \phi_h \{ (pqr) \} \]
have each the same value
\[ h_{pq} h_{pr} - h_{pq} h_{pr} - h_{pq} h_{qr} + h_{pq} + h_{qr} , \]
which we have denoted by
\[ h_{pqr} . \]

Art. 60. I pass on to drag into the light some important relations connecting
\[ h_{p_1 \cdots p_n} \text{ and } a_{p_1 \cdots p_n} . \]

When the relation
\[ h_n = \Sigma (-)^{n+k} \frac{\Sigma k!}{k_1 ! \cdots k_s !} a_1^{k_1} \cdots a_s^{k_s} \]
was under observation just now, it will not have escaped notice that this is precisely the expansion of
\[ a_n , \]
for
\[ a_{11} = a_1^2 - a_2 , \]
\[ a_{111} = a_1^3 - 2a_1a_2 + a_3 ; &c. , \]
and by the law of formation we see that
\[ a_1 = h_n , \]
and hence
\[ a_n = h_n . \]
The known value of \( h_n \) is thus given by a law identical with the multiplication law of this paper, and the expression of \( h_n \) in terms of \\
\\n\[
\alpha_1, \alpha_2, \alpha_3, \ldots
\]
\\n
is completely given by \\
\\n\[
h_n = \alpha_1.
\]
\\n
This new statement, of a well-known law, immediately suggests the generalization to which I proceed.

Observe that \\
\\n\[
n \text{ and } 1^n
\]

are zig-zag conjugate compositions.

From the relation \\
\\n\[
\alpha_{pq} = \alpha_{p} \alpha_{q} - \alpha_{p+q}
\]

is now deduced \\
\\n\[
\alpha_{pq} = h_{pq} h_{1^2} - h_{1^p+q};
\]

and, since \\
\\n\[
h_{pq} h_{1^2} = h_{1^p+q} + h_{1^{p-1} q^2 - 1},
\]

and we again observe that \\
\\n\[
pq \text{ and } 1^{p-1} 2^{1^{q-1}}
\]

are zig-zag conjugate compositions.

Hence writing \\
\\n\[
(1^{p-1} 2^{1^{q-1}}) = (pq)',
\]

\[
\alpha_{(pq)} = h_{(pq)};
\]

and, in general, I have established (but reserve the proof for another occasion) that \\
\\n\[
\alpha_{(p_1 p_2 \ldots)} = h_{(p_1 p_2 \ldots)};
\]

where \\
\\n\[
(p_1 p_2 \ldots), (p_1 p_2 \ldots)'
\]

are zig-zag conjugate compositions.

Art. 61. The theorem has an interest of its own, but it is also of vital importance in this investigation. This importance consists partly in the circumstance that the functions \\
\\n\[
h_{pqr}
\]

are those which naturally arise in the present theory of permutations. The present theorem enables the immediate expression of them in terms of the elementary symmetric functions \\
\\n\[
\alpha_1, \alpha_2, \alpha_3, \ldots
\]

and thus they may be more easily dealt with by symmetric functions differential operators. In fact, the homogeneous product sums \\
\\n\[
h_1, h_2, h_3, \ldots
\]

can be made to disappear from the investigation; but, as will be seen, it is sometimes advantageous to retain them wholly or in part.
Art. 62. To gain familiarity with the new functions I give without proof some of their elementary properties.

\[ s_n = a_1^1 - a_2^1 + \alpha_{21}^2 - a_3^3 - ... (-)^{n+1} a_n \]

\[ = (-)^{n+1} \{ n_1^1 - h_{21}^2 + h_{31}^3 - ... (-)^{n+1} h_n \}, \]

where \( s_n \) is the sum of the \( n \)th power of the roots.

The following expression for \( a_{s1}^{n-z} \)

\[ a_{s1}^{n-z} = \alpha_{s-1}^1 h_{n-s+1} - \alpha_{s-2}^1 h_{n-s+2} + ... (-)^{s+1} h_n. \]

The result of operations with \( D_p \), viz.,

\[ D_p a_{s1}^{n-z} = \alpha_{s-1}^1 h_{n-s-p+1}. \]

If \( s_n, t \) denote the sum of the symmetric functions whose partitions contain exactly \( t \) parts, we have the companion tables, in which the law is obvious.

<table>
<thead>
<tr>
<th>( s_{n,1} )</th>
<th>( s_{n,2} )</th>
<th>( s_{n,3} )</th>
<th>( s_{n,4} )</th>
<th>( s_{n,5} )</th>
<th>( s_{n,6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_1^* )</td>
<td>1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>( a_{21}^{n-z} )</td>
<td>1</td>
<td>+2</td>
<td>+3</td>
<td>+4</td>
<td>+5</td>
</tr>
<tr>
<td>( a_{31}^{n-z} )</td>
<td>1</td>
<td>+3</td>
<td>+6</td>
<td>+10</td>
<td></td>
</tr>
<tr>
<td>( a_{41}^{n-z} )</td>
<td>1</td>
<td>+4</td>
<td>+10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a_{51}^{n-z} )</td>
<td>1</td>
<td>+5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a_{61}^{n-z} )</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( s_{n,1} )</th>
<th>( a_{21}^{n-z} )</th>
<th>( a_{31}^{n-z} )</th>
<th>( a_{41}^{n-z} )</th>
<th>( a_{51}^{n-z} )</th>
<th>( a_{61}^{n-z} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( s_{n,1} )</td>
<td>1</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>( s_{n,2} )</td>
<td>1</td>
<td>-2</td>
<td>+3</td>
<td>-4</td>
<td>+5</td>
</tr>
<tr>
<td>( s_{n,3} )</td>
<td>1</td>
<td>-3</td>
<td>+6</td>
<td>-10</td>
<td></td>
</tr>
<tr>
<td>( s_{n,4} )</td>
<td>1</td>
<td>-4</td>
<td>+10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( s_{n,5} )</td>
<td>1</td>
<td>-5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( s_{n,6} )</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fundamental properties of these new symmetric functions were communicated by me to Section A of the British Association for the Advancement of Science, at the York meeting, 1906, August 1–8.

Art. 63. The generating function of \( N(abc...) \) is either

\[ h_{abc...} \quad \text{or} \quad \alpha_{(abc...)}. \]
We can now determine the highest symmetric function, in dictionary order of the parts, which occurs in the development of $h_{abc...}$. This, by the known theory of symmetric functions, is obtained from the form

$$a_{(abc...)}$$

by expressing $(abc...)'$ as a partition and taking the Ferrers conjugate $(abc...)''$; then we see that no symmetric function, prior in dictionary order to

$$(abc...)''$$

can appear.

Also the highest integer in

$$(abc...)$$

is the lower limit of the number of parts, occurring in the partition of a symmetric function, arising from the development of

$$h_{abc...}.$$  

*E.g., since*

$h_{141} = a_{21^2}$,

we arrange $21^2$ as a partition, obtaining $2^21^2$, and taking the Ferrers conjugate from the graph

we reach (42) as the highest symmetric function in dictionary order that occurs in the development of $h_{141}$.

Hence

$$N(141)_6 = N(141)_{51} = 0.$$  

(See the table of weight 6.)

Numerous relations such as

$$h_{141} + h_{51} = h_{412} + h_{42}$$

can be verified by the same table.

Art. 64. Before proceeding to establish the multiplication theorem, the generalization of that in Part I., it is necessary to examine the mode of operation of the differential operator

$$D_a$$

upon a product

$$h_p \alpha h_p^{\alpha'},$$
or

$$a_p \alpha a_p^{\alpha'}.$$  

It is clear that

$$D_a h_p = h_{p-a}.$$  

In the paper it was shown that

$$D_a h_p h_q = \Sigma (D_a h_p)(D_a h_q),$$

where $\alpha'\alpha''$ denotes a composition of $\alpha$ into two parts, zero not excluded, and the summation is for every such composition.
Hence

\[ D_n h \cdot h_q = \sum_{x-y} h_{x-y} \cdot h_{y-x}. \]

*E.g.*,\n
\[ D_{4} h_{4} = h_{4} + h_{3} + h_{2} + h_{1} = 2h_{2} + 2h_{1}, \]

where the compositions of 4 have been taken in the order

40, 31, 13, 22.

In general

\[ D_{a} h_{p} h_{p} \ldots h_{p} = \sum_{x-y} h_{p-x} h_{p-y} \ldots h_{p-y}, \]

where

\[ a' a'' \ldots a^{(s)} \]

is a composition of \( a \) into \( s \) or fewer parts.

It is to be noted that in forming the compositions zeros are parts, so that, for instance,

400, 040, 004

count as different compositions.

If the operand be

\[ a_{p} a_{p} \ldots a_{p}, \]

since

\[ D_{a} (a_{p}) = 0 \] unless \( a = 1 \),

we need only attend to the compositions composed of units and zeros.

Thus

\[ D_{a} h_{a} a_{a} a_{a} a_{a} = a_{a} a_{a} a_{a} a_{a} + a_{a} a_{a} a_{a} a_{a} + a_{a} a_{a} a_{a} a_{a} + a_{a} a_{a} a_{a} a_{a} + a_{a} a_{a} a_{a} a_{a} + a_{a} a_{a} a_{a} a_{a}. \]

It is easy to show that

\[ D_{a} h_{a} = h_{a-1} + h_{a-1} + h_{a-1}, \]

from which

\[ N (a b)_{pq} = N (a-1, b)_{pq} + N (a, b-1)_{pq} + N (a + b-1)_{pq}; \]

and, particularly,

\[ N (42)_{pq} = N (32)_{pq} + N (41)_{pq} + N (5)_{pq} \]

\[ 7 = 4 + 2 + 1 \]

from the table.

Similar formulæ can be established at pleasure.

*The Conjugate Law.*

Art. 65. It has been seen (Art. 6) that, when the numbers permuted are specified by

\[ 1^{n}, \]

\[ N (pq \ldots) = N (pq \ldots)' , \]

where

\[ (pq \ldots), (pq \ldots)' \]

denote conjugate compositions.

We write the theorem

\[ N (pq \ldots)_{(a)} = N (pq \ldots)'_{(a)} ; \]

and we may inquire into the existence of an analogous theorem when the numbers permuted have any other specification.
Consider the expression

\[ h_{(pq...)} - h_{(pq...y)}, \]

which is the generating function for the difference between

\[ N (pq...) \quad \text{and} \quad N (pq...y), \]

for all specifications of the numbers permuted.

The generating function may be written

\[ h_{pq...} - a_{pq...}, \]

according to the theorem proved above.

The differential operation

\[ D_1 \]

has the equivalent forms

\[ \partial_n h_{pq...} + \alpha_1 \partial_{n_1} + \alpha_2 \partial_{n_2} + \ldots \]

\[ \partial_n h_{pq...} + h_1 \partial_{n_1} + h_2 \partial_{n_2} + \ldots ; \]

hence

\[ D_1^n h_{pq...} \]

is the same function of

\[ h_1, h_2, h_3, \ldots \]

that

\[ D_1^n a_{pq...} \]

is of

\[ a_1, a_2, a_3, \ldots. \]

It follows at once that

\[ D_1^n (h_{pq...} - a_{pq...}) = 0, \]

equivalent to the known result

\[ N (pq...)_{(a)} = N (pq...)'_{(a)} \]

already found.

Art. 66. Now, considering the generating functions

\[ h_{(pq...)} + h_{(pq...y)} \]

or

\[ h_{(pq...)} + a_{(pq...)}, \]

\[ D_1^{a-2} \{ h_{pq...} + a_{pq...} \} \]

must be of the form

\[ Ah_2 + Bh_1^2 + Aa_2 + Ba_1^2, \]

or

\[ (A + 2B) \{ (2) + 2 (1^2) \}. \]

Hence

\[ D_1^{a-2} D_2 (h_{pq...} + a_{pq...}) \]

\[ = \frac{1}{2} D_1^a (h_{pq...} + a_{pq...}) \]

\[ = D_1^a h_{pq...}, \]

equivalent to

\[ N (pq...)_{(a-1)} + N (pq...)'_{(a-1)} = N (pq...)_{(a)}. \]

Thus, from the table \( n = 6, \)

\[ \begin{array}{c c c}
N (33)_{(a)} & + & N (1^2 2^1)_{(a)} = N (33)_{(a)} \\
13 & + & 6 & = & 19.
\end{array} \]
Art. 67. Again, operating with $D_1^{s-2}$,
upon
$$h_{pq...} - \alpha_{pq...},$$
we obtain a result of the form
$$A (h_3 - \alpha_3) + B (h_2 h_1 - \alpha_2 \alpha_1)$$
or
$$(A + B) ((3) + (21));$$
hence
$$D_1^{s-2} D_3 (h_{pq...} - \alpha_{pq...}) = D_1^{s-2} D_2 (h_{pq...} - \alpha_{pq...}),$$
equivalent to
$$N (pq...)(31-\eta) - N (pq...)'(31-\eta) = N (pq...)(31-\eta) - N (pq...)'(31-\eta);$$
and, particularly, from the table
$$N (321)(31\eta) - N (2^21^1)(31\eta) = N (321)(31\eta) - N (2^21^1)(31\eta),$$
$$8 - 3 = 20 - 15.$$

No new result is obtained by taking
$$h_{pq...} + \alpha_{pq...}$$
as the operand.
Art. 68. Further,
$$D_1^{s-4} (h_{pq...} - \alpha_{pq...})$$
has the form
$$A (h_4 - \alpha_4) + B (h_3 h_1 - \alpha_3 \alpha_1) + C (h_2^2 - \alpha_2^2) + D (h_2 h_1^2 - \alpha_2 \alpha_1^2),$$
reducing to
$$(A + B + C + D)(4) + (A + 2B + 2C + 2D) ((31) + (2^3) + (21^3)),$$
equivalent to the new result
$$N (pq...)(21-\eta) - N (pq...)'(21-\eta) = N (pq...)(21-\eta) - N (pq...)'(21-\eta);$$
and, particularly, from the table
$$N (2^3)(21\eta) - N (12^21)(21\eta) = N (2^3)(21\eta) - N (12^21)(21\eta),$$
$$18 - 13 = 11 - 6.$$

Art. 69. If we take here the operand to be
$$h_{pq...} + \alpha_{pq...},$$
a new result is obtained, viz.,
$$2N (pq...)(41-\eta) + 2N (pq...)'(41-\eta) + N (pq...)(21-\eta) + N (pq...)'(21-\eta)$$

The above is sufficient to indicate the nature of the results which present themselves; I have not attempted to generalise them. The question appears to be a difficult one.
Generalisation of the Multiplication Theorem.

Art. 70. I will establish the result

\[ \sum \sum \sum \{N(a_1 a_2 a_3 \ldots )_{(pqr, \ldots )} N(b_1 b_2 b_3 \ldots )_{(pqr, \ldots )} N(c_1 c_2 c_3 \ldots )_{(pqr, \ldots )} \} \]

\[ = \theta_N \{(a_1 a_2 a_3 \ldots )_1 (b_1 b_2 b_3 \ldots )_2 (c_1 c_2 c_3 \ldots )_3 \}_1 \]

where the summation is for all solutions of the diophantine equations

\[ p_1 + q_1 + r_1 + \ldots = \Sigma a, \]
\[ p_2 + q_2 + r_2 + \ldots = \Sigma b, \]
\[ p_3 + q_3 + r_3 + \ldots = \Sigma c, \]
\[ \ldots \ldots \ldots \ldots \ldots \]
\[ p_1 + p_2 + p_3 + \ldots = p, \]
\[ q_1 + q_2 + q_3 + \ldots = q, \]
\[ r_1 + r_2 + r_3 + \ldots = r, \]
\[ \ldots \ldots \ldots \ldots \ldots \]

For consider

\[ \theta_N \{(a_1 a_2)_1 (b_1 b_2)_2 \} \]
\[ = \phi_C \{(a_1 a_2)_1 (b_1 b_2)_2 \}, \]
\[ = C(a_1 a_2 b_1 b_2)_{(pqr, \ldots )} - C(a_1 a_2, b_1 + b_2)_{(pqr, \ldots )} - C(a_1 a_2, b_1 + b_2)_{(pqr, \ldots )} + C(a_1 + a_2, b_1 + b_2)_{(pqr, \ldots )} \]
\[ = (D_a D_1 D_2 D_3 - D_{a_1 + a_2} D_1 D_2 D_3 - D_{a_1 + a_2} D_1 D_2 D_3 + D_{a_1 + a_2} D_1 D_2 D_3) h_1 h_2 h_3 \]
\[ = (D_a D_1 - D_{a_1 + a_2}) (D_1 D_2 - D_{b_1 + b_2}) h_1 h_2 h_3 \]
\[ = D_a D_1 D_2 D_3 h_1 h_2 h_3 \]

Now

\[ D_p D_q D_r \ldots h_{a_1 a_2} h_{b_1 b_2} \]

\[ = \sum \sum \sum (D_p D_q D_r)_{(a_1 a_2)} (D_p D_q D_r)_{(b_1 b_2)} \]

the summation being for all solutions of the diophantine equations

\[ p_1 + q_1 + r_1 + \ldots = a_1 + a_2, \]
\[ p_2 + q_2 + r_2 + \ldots = b_1 + b_2, \]
\[ p_1 + p_2 = p, \]
\[ q_1 + q_2 = q, \]
\[ r_1 + r_2 = r, \]
\[ \ldots \ldots \ldots \ldots \]

Moreover,

\[ D_p D_q D_r \ldots h_{a_1 a_2} = N(a_1 a_2)_{p/q/r, \ldots } \]

Hence

\[ \theta_N \{(a_1 a_2)_1 (b_1 b_2)_2 \}_{(pqr, \ldots )} = \sum N(a_1 a_2)_{p/q/r, \ldots } N(b_1 b_2)_{p/q/r, \ldots } \]

and, by like reasoning, the theorem as enunciated follows.
As examples,

\[ N(321)_{(222)} + N(33)_{(222)} = 3N(32)_{(221)}, \]

derived from

\[ \theta_N \{(32)\}_{(222)}; \]

and

\[
\begin{align*}
N(24)_{(222)} + N(231)_{(222)} + N(213)_{(222)} + N(222)_{(222)} \\
+ N(2211)_{(222)} + N(2121)_{(222)} + N(2112)_{(222)} + N(21111)_{(222)} \\
= 6N(21)_{(011)} + 18N(21)_{(21)},
\end{align*}
\]

derived from

\[ \theta_N \{(21)\}_{(1^2)} \{222\}, \]

Art. 71. The enumeration of the permutations, whose specifications contain a given largest integer, will now be investigated.

Let

\[ I_m, J_m, K_m \]

denote respectively

\[ \sum N(abc\ldots) \]

in which

(i.) the highest of the integers a, b, c, \ldots is m or less;

(ii.) \ldots or greater;

(iii.) \ldots exactly;

so that, when \(a+b+c+\ldots = n\),

\[
\begin{align*}
I_m &= K_1 + K_2 + \ldots + K_m, \\
J_m &= K_m + K_{m+1} + \ldots + K_m, \\
I_m - I_{m-1} &= J_m - J_{m+1} = K_m, \\
\theta_N (n) &= N(n) = J_n = K_n = I_n - I_{n-1};
\end{align*}
\]

and, since

\[
\begin{align*}
\theta_N \{(n-1)\}_{(1)} &= N(n-1, 1) + N(n), \\
\theta_N \{(1)\}_{(n-1)} &= N(1, n-1) + N(n),
\end{align*}
\]

we find

\[ 2\theta_N \{(n-1)\}_{(1)} = K_{n-1} + 2K_n = J_{n-1} + J_n = -I_{n-1} - I_{n-2} + 2I_n; \]

also

\[
\begin{align*}
\theta_N \{(n-2)\}_{(1^2)} &= N(n-2, 1^2) + N(n-1, 1) + N(n-2, 2) + N(n), \\
\theta_N \{(1) \}_{(n-2)}(1) &= N(1, n-2, 1) + N(n-1, 1) + N(1, n-1) + N(n), \\
\theta_N \{(1)\}_{(n-2)}(1^2) &= N(1^2, n-2) + N(1, n-1) + N(2n-2) + N(n),
\end{align*}
\]

and by addition

\[
\begin{align*}
3\theta_N \{(n-2)\}_{(1^2)} &= K_{n-2} + 2K_{n-1} + 3K_n, \\
&= J_{n-2} + J_{n-1} + J_n, \\
&= -I_{n-3} - I_{n-2} - I_{n-1} + 3I_n,
\end{align*}
\]

the law apparent here obtains so long as a number \(n - \nu\) appearing in

\[ N(\quad), \]
on the right-hand side, is not equal to any other number in the same bracket; so that, when \( s < \frac{1}{2} n \),

\[
(s+1) \theta_N \left\{ (n-s) \left( 1 \right)^s \right\} \\
= K_{n-s} + 2K_{n-s+1} + 3K_{n-s+2} + \ldots + (s+1)K_n,
\]

\[
= J_{n-s} + J_{n-s+1} + J_{n-s+2} + \ldots + J_n,
\]

\[
= -I_{n-s-1} - I_{n-s} - I_{n-s+1} - \ldots + (s+1)I_n.
\]

Hence

\[
J_m = (n-m+1) \theta_N \left\{ (m) \left( 1 \right)^{n-m} \right\} - (n-m) \theta_N \left\{ (m+1) \left( 1 \right)^{n-m-1} \right\},
\]

\[
K_m = (n-m+1) \theta_N \left\{ (m) \left( 1 \right)^{n-m} \right\} - 2(n-m) \theta_N \left\{ (m+1) \left( 1 \right)^{n-m-1} \right\}
+ (n-m-1) \theta_N \left\{ (m+2) \left( 1 \right)^{n-m-2} \right\},
\]

and, the specification of the numbers permuted being

\[
I_m = \frac{n!}{p!q!r!} \ldots -(n-m) \theta_N \left\{ (m+1) \left( 1 \right)^{n-m-1} \right\} + (n-m-1) \theta_N \left\{ (m+2) \left( 1 \right)^{n-m-2} \right\}.
\]

Now

\[
\theta_N \left\{ (\alpha) (\beta) (\gamma) \ldots \right\} = C (\alpha \beta \gamma \ldots) = D_\alpha D_\beta D_\gamma \ldots h_\alpha h_\beta h_\gamma \ldots;
\]

hence

\[
J_m = \{ (n-m+1) D_m D_1^{n-m} -(n-m) D_{m+1} D_1^{n-m-1} \} h_\alpha h_\beta h_\gamma \ldots,
\]

\[
= D_p D_q D_r \ldots \{ (n-m+1) h_m h_1^{n-m} -(n-m) h_{m+1} h_1^{n-m-1} \} ;
\]

or, \( m \) not being less than the greatest integer in \( \frac{1}{2} (n+1) \),

\[
(n-m+1) h_m h_1^{n-m} -(n-m) h_{m+1} h_1^{n-m-1}
\]

is the generating function of the number \( J_m \).

Similarly

\[
K_m = D_p D_q D_r \ldots \{ (n-m+1) h_m h_1^{n-m} - 2(n-m) h_{m+1} h_1^{n-m-1} + (n-m-1) h_{m+2} h_1^{n-m-2} \} ;
\]

and, \( m \) not being less than the greatest integer in \( \frac{1}{2} (n+1) \),

\[
(n-m+1) h_m h_1^{n-m} - 2(n-m) h_{m+1} h_1^{n-m-1} + (n-m-1) h_{m+2} h_1^{n-m-2}
\]

is the generating function of the number \( K_m \).

Similarly, but subject now to the condition that \( m \) must not be less than the greatest integer in \( \frac{1}{2} (n-1) \),

\[
(n-m-1) h_{m+2} h_1^{n-m-2} -(n-m) h_{m+1} h_1^{n-m-1}
\]

is the function which generates the number

\[
I_m = \frac{n!}{p!q!r!} \ldots
\]

Subject to the conditions mentioned, we have a complete solution of the problem, but when \( m \) has other values, the solution is less simple and I see no way of effecting it.
Section 8.

Art. 72. I recall that the number of ways of distributing numbers (or objects) specified by 

\[(p_1^r p_2^s p_3^t \ldots),\]

into \(m\) different parcels, is given by the series

\[F_m = \frac{(m+p_1-1)^r}{p_1} \left(\frac{m+p_2-1}{p_2}\right)^s \left(\frac{m+p_3-1}{p_3}\right)^t \ldots\]

and this, for brevity, I write

\[F_m = G_m - \text{terms} - \ldots\]

Let

\[N_{m, p_1^r p_2^s p_3^t \ldots},\]

denote the number of distributions, associated with a descending specification containing exactly \(m\) parts, and write this

\[N_m,\]

when there is no risk of misunderstanding.

Following the proof of Art. 23, it may be proved that

\[F_m = N_m + \binom{n-m+1}{1} N_{m-1} + \binom{n-m+2}{2} N_{m-2} + \ldots + \binom{n-1}{m-1} N_1;\]

and also

\[N_m = F_m - \binom{n-m+1}{1} F_{m-1} + \binom{n-m+2}{2} F_{m-2} + \ldots + (-1)^{n+1} \binom{n-1}{m-1} F_1;\]

and thence

\[N_m = G_m - \binom{n+1}{1} G_{m-1} + \binom{n+1}{2} G_{m-2} - \ldots + (-1)^{n+1} \binom{n+1}{m-1} G_1.\]

Art. 73. From this relation the following results are obtained:

\[n = 3.\]

<table>
<thead>
<tr>
<th>(N_1)</th>
<th>(3).</th>
<th>(21).</th>
<th>(1^2).</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
MAJOR P. A. MACMAHON ON THE COMPOSITIONS OF NUMBERS.

\[ n = 4. \]

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\hline
N_1 & 1 & 1 & 1 & 1 & 1 \\
\hline
N_2 & 3 & 4 & 7 & 11 & \\
\hline
N_3 & 1 & 4 & 11 & & \\
\hline
N_4 & & & & 1 & \\
\hline
\end{array}
\]

\[ n = 5. \]

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\hline
N_1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\hline
N_2 & 4 & 6 & 10 & 12 & 18 & 26 & \\
\hline
N_3 & 3 & 9 & 15 & 33 & 66 & & \\
\hline
N_4 & & 2 & 8 & 26 & & & \\
\hline
N_5 & & & & 1 & & & \\
\hline
\end{array}
\]

\[ n = 6. \]

\[
\begin{array}{|c|c|c|c|c|c|c|c|c|c|}
\hline
\hline
N_1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\hline
N_2 & 5 & 8 & 13 & 9 & 17 & 25 & 20 & 29 & 41 & 57 & & \\
\hline
N_3 & 6 & 16 & 9 & 33 & 67 & 48 & 93 & 171 & 302 & & \\
\hline
N_4 & 1 & 9 & 27 & 20 & 53 & 131 & 302 & & & & \\
\hline
N_5 & & 1 & 4 & 16 & 57 & & & & & & \\
\hline
N_6 & & & & & & & & & & 1 & \\
\hline
\end{array}
\]

To explain, observe that the number at the intersection of the row \( N_3 \) and the column \((2^21^2)\) shows that

\[ N_{3,221} = 93. \]

These tables will be of constant service in verifying results to be obtained.

Art. 74. From the relation

\[ N_m = G_m - \binom{n+1}{1} G_{m-1} + \binom{n+1}{2} G_{m-2} - \ldots, \]

we can obtain a system, for, summing each side from \( m = 1 \) to \( m = m \),

\[ N_m + N_{m-1} + \ldots + N_1 = G_m - \binom{n}{1} G_{m-1} + \binom{n}{2} G_{m-2} - \ldots, \]
and, repeating the summation $\theta$ times,

\[ N_m + \binom{\theta+1}{1} N_{m-1} + \binom{\theta+2}{2} N_{m-2} + \ldots + \binom{\theta+m-1}{m-1} N_1 = G_m - \binom{n-\theta}{1} G_{m-1} + \binom{n-\theta}{2} G_{m-2} - \ldots; \]

so that, when $\theta = n$,

\[ N_m + \binom{n+1}{1} N_{m-1} + \ldots + \binom{n+m-1}{m-1} N_1 = G_m. \]

Again, taking differences instead of summing, we get the series

\[ N_m - N_{m-1} = G_m - \binom{n+2}{1} G_{m-1} + \binom{n+2}{2} G_{m-2} - \ldots, \]

\[ N_m - 2N_{m-1} + N_{m-2} = G_m - \binom{n+3}{1} G_{m-1} + \binom{n+3}{2} G_{m-2} - \ldots, \]

and in general

\[ N_m - \binom{p}{1} N_{m-1} + \ldots \pm N_{m-p} = G_m - \binom{n+p+1}{1} G_{m-1} + \binom{n+p+1}{2} G_{m-2} - \ldots. \]

These results are all given by the two formulæ

\[ N_m + \binom{p}{1} N_{m-1} + \binom{p+1}{2} N_{m-2} + \ldots = G_m - \binom{n+p+1}{1} G_{m-1} + \binom{n+p+1}{2} G_{m-2} - \ldots; \]

\[ N_m - \binom{p}{1} N_{m-1} + \binom{p}{2} N_{m-2} - \ldots = G_m - \binom{n+1+p}{1} G_{m-1} + \binom{n+1+p}{2} G_{m-2} - \ldots; \]

which become the same when $p = 0$.

Curious Expression for $N_m$.

Art. 75. I shall now prove that

\[ N_m = P_{m-1} - \frac{m-2}{m-1} \binom{n}{1} P_{m-2} + \frac{m-3}{m-2} \binom{n}{2} P_{m-3} + \ldots + (-)^m \frac{1}{m-1} \binom{n}{m-2} P_1, \]

where

\[ P_z = \left( \frac{p_1 + s - 1}{p_1} \right)^{s_1} \left( \frac{p_2 + s - 1}{p_2} \right)^{s_2} \ldots \{ (p_1 + s)^n (p_2 + s)^n \ldots \}^{z_1, z_2 \ldots} \]

\[ \text{where} \quad \{ (p_1 + s)^n (p_2 + s)^n \ldots \}_{-1, 0} \]

denotes the expansion of

\[ (p_1 + s)^n (p_2 + s)^n \ldots. \]
when deprived of the terms linear in \( p_1, p_2, \ldots \), and of the term independent of \( p_1, p_2, \ldots \).

For it is easy to show that two consecutive terms

\[
(-)^{m-t-1} \binom{n}{m-1} \frac{p_{n-m-1} + \cdots + p_{n-m-2}}{p_{n-m-1}} + (-)^{m-t-2} \binom{n}{m-1} \frac{p_{n-m-2} + \cdots + p_{n-m-3}}{p_{n-m-2}}
\]

may be given the form

\[
(-)^{m-t-1} \binom{n}{m-1} \frac{p_{n-m-1} + \cdots + p_{n-m-2}}{p_{n-m-1}} + (-)^{m-t-2} \binom{n}{m-1} \frac{p_{n-m-2} + \cdots + p_{n-m-3}}{p_{n-m-2}}
\]

and, giving \( t \) the values 0, 2, 4, \ldots, and summing and simplifying, we obtain

\[
\frac{(p_{m-1} + \cdots + p_{m-2})^2}{p_1} \cdot \frac{(p_{m-2} + \cdots + p_{m-3})^2}{p_2} + \cdots
\]

which we know to be the value of \( N_m \).

Art. 76. The symmetry of the numbers \( N_m \) will not escape the notice of the reader.

**Section 9.**

Art. 77. My purpose now is to connect the preceding pages with my Memoir on the Compositions of Numbers, to which attention has already been directed. In the course of that investigation I had occasion to consider the permutations of the letters in

\[\alpha \beta \gamma,\]

with the object of determining the number of permutations containing given numbers of

\[\beta \alpha\text{ contacts},\]

\[\gamma \alpha, \begin{array}{c}\gamma \beta, \\gamma\end{array}\]

If we take any permutation

\[\ldots \beta \alpha \ldots \gamma \alpha \ldots \gamma \beta \ldots \gamma \beta \alpha \ldots\]

and particularly notice all of such contacts, it is clear that the numbers of parts in the descending specification \( \alpha, \beta, \gamma, \ldots \), being numbers in descending order of
magnitude, is necessarily one greater than the number of such contacts; in the present instance there are 6 parts in the descending specification and 5 contacts. The problem of the determination of the permutations having descending specifications containing \(m\) parts is identical with that which is concerned with those having \(m-1\) contacts of the nature specified.

Art. 78. I established in the Memoir that the letters in

\[ a^r b^s \gamma^r \]

can be permuted in

\[ \binom{s_1+s_2}{s_1} \binom{p}{s_1+s_2} \binom{q}{s_2} \binom{q+s_3}{s_1+s_2} \binom{r}{s_3+s_2} \]

ways so as to have exactly

\[ s_1 \beta \alpha \text{ contacts,} \]
\[ s_3 \gamma \alpha \]
\[ s_2 \gamma \beta \]

and I further discovered that this number is the coefficient of

\[ \lambda_1^{s_1} \lambda_2^{s_2} \lambda_3^{s_3} a^r b^s \gamma^r \]

in the development of the function

\[ (a+\lambda_1 \beta+\lambda_3 \gamma)^s (a+\beta+\lambda_2 \gamma)^s (a+\gamma)^s \]

Art. 79. In the same paper I showed that for this function may be substituted the function

\[ 1 \]
\[ 1-(a+\beta+\gamma)+(1-\lambda_1) \alpha \beta +(1-\lambda_3) \alpha \gamma +(1-\lambda_2) \beta \gamma -(1-\lambda_1) (1-\lambda_3) \alpha \beta \gamma \]

which does not involve \(p, q, r\), and may therefore be regarded as the general generating function of the numbers.

Art. 80. Reserving for the present the generalizations, which were also given in the papers referred to, it is clear that the application to the present question is obtained by putting

\[ \lambda_1 = \lambda_3 = \lambda_2 = \lambda, \]

when we find that the number of permutations of

\[ a^r b^s \gamma^r, \]

which have descending specifications containing \(m\) parts, is the coefficient of

\[ \lambda^{m-1} a^r b^s \gamma^r \]

in the development of

\[ (a+\lambda \beta+\lambda \gamma)^s (a+\beta+\lambda \gamma)^s (a+\beta+\gamma)^s, \]

or of

\[ 1 \]
\[ 1-(a+\beta+\gamma)+(1-\lambda) (\alpha \beta + \alpha \gamma + \beta \gamma)-(1-\lambda)^2 \alpha \beta \gamma. \]

This, therefore, is the true generating function of the numbers \(N_m\).
It may be verified, for example, that the complete coefficient of
\[ \alpha^2 \beta^2 \gamma^2 \]
is
\[ (1 + 20\lambda + 48\lambda^2 + 20\lambda^3 + \lambda^4), \]
which agrees with a previous result.

From a previous result also the coefficient of
\[ \lambda^{m-1} alpha^p \beta^q \gamma^r \]
is
\[ \left( \frac{m+p-1}{p} \right) \left( \frac{m+q-1}{q} \right) \left( \frac{m+r-1}{r} \right) \]
\[ - \left( \frac{n+1}{1} \right) \left( \frac{m+p-2}{p} \right) \left( \frac{m+q-2}{q} \right) \left( \frac{m+r-2}{r} \right) \]
\[ + \left( \frac{n+1}{2} \right) \left( \frac{m+p-3}{p} \right) \left( \frac{m+q-3}{q} \right) \left( \frac{m+r-3}{r} \right) \]
where \( n = p+q+r \).

Art. 81. Observe that the generating function is a symmetric function of \( \alpha, \beta, \gamma \), verifying a previous conclusion that an \( N_m \) number is not altered by any interchange of the letters \( \alpha, \beta, \gamma \).

When the numbers \( p, q, r \) are equal, that is when the objects are specified by the partition
\[ (p^3), \]
we can establish a symmetrical property of the numbers \( N \).

For coefficient
\[ \lambda^{m-1} (a \beta \gamma)^p \]
in \( (\alpha + \lambda \beta + \lambda \gamma)^p (\alpha + \beta + \gamma)^p \)
is, by writing
\[ \frac{1}{\lambda} \]
for \( \lambda \alpha, \lambda \beta, \lambda \gamma \) for \( \alpha, \beta, \gamma \),
equal to coefficient of
\[ \lambda^{p-m+1} (a \beta \gamma)^p \]
in \( (\lambda \alpha + \beta + \gamma)^p (\lambda \alpha + \lambda \beta + \lambda \gamma)^p \)
equal to coefficient of
\[ \lambda^{p-m+1} (a \beta \gamma)^p \]
in \( (\lambda \alpha + \beta + \gamma)^p (\lambda \alpha + \lambda \beta + \gamma)^p (\alpha + \beta + \gamma)^p \),
equal to coefficient of
\[ \lambda^{p-m+1} (a \beta \gamma)^p \]
in \( (\alpha + \lambda \beta + \lambda \gamma)^p (\alpha + \beta + \gamma)^p \).

Art. 82. Hence
\[ N_m = N_{2p-m+2}, \]
and the numbers \( N \) range from \( N_1 \) to \( N_{2p+1} \),
showing that \( 2p+1 \) is the maximum number of parts in the descending specification, when the objects are specified by the partition
\[ (p^3). \]
Art. 83. In general, when there are \( k \) different letters, the number of permutations of
\[ \alpha_1, \alpha_2, \ldots, \alpha_k, \]
which have descending specifications containing \( m \) parts, is the coefficient of
\[ \lambda^{m-1}\alpha_1^m\alpha_2^m\ldots\alpha_k^m \]
in the development of
\[ \{\alpha_1 + \lambda(\alpha_2 + \ldots + \alpha_k)\}^m \{\alpha_1 + \alpha_2 + \lambda(\alpha_3 + \ldots + \alpha_k)\}^m \ldots \{\alpha_1 + \alpha_2 + \ldots + \alpha_k\}^{m-1} \]
or of
\[ \frac{1}{1 - \Sigma \alpha_1 + (1 - \lambda) \Sigma \alpha_2 \alpha_3 - (1 - \lambda)^2 \Sigma \alpha_1 \alpha_2 \alpha_3 + \ldots + (-)^k (1 - \lambda)^{k-1} \alpha_1 \alpha_2 \ldots \alpha_k} \]
This is the general generating function of the numbers \( N_m \).

Art. 84. Since it is symmetrical in regard to
\[ \alpha_1, \alpha_2, \ldots, \alpha_k, \]
the value of \( N_m \) is not affected by permutation of the letters
\[ \alpha_1, \alpha_2, \ldots, \alpha_k. \]

Art. 85. It can be shown also, as in the simpler case, that when
\[ p_1 = p_2 = \ldots = p_k = p, \]
the coefficient of
\[ \lambda^{m-1}(\alpha_1 \alpha_2 \ldots \alpha_k)^p \]
is equal to the coefficient of
\[ \lambda^{(k-1)p-m+1}(\alpha_1 \alpha_2 \ldots \alpha_k)^p; \]
so that
\[ N_m = N_{(k-1)p-m+2}; \]
the numbers \( N \) range from \( N_1 \) to \( N_{(k-1)p+1} \);
and \( (k-1)p+1 \) is the maximum number of parts in a descending specification.

SECTION 10.

Art. 86. The generating function
\[ \frac{1}{1 - \Sigma \alpha_1 + (1 - \lambda) \Sigma \alpha_1 \alpha_2 - (1 - \lambda)^2 \Sigma \alpha_1 \alpha_2 \alpha_3 + \ldots + (-)^k (1 - \lambda)^{k-1} \alpha_1 \alpha_2 \ldots \alpha_k} \]
now presents itself for examination.
Introducing the elementary functions
\[ \alpha_1, \alpha_2, \ldots, \]
and writing \( 1 - \lambda = b \), it is written

\[
\frac{1}{1 - a_1 + b a_2 - b^2 a_3 + \ldots + (-1)^k b^{k-1} a_k};
\]
or

\[
\frac{1}{1 - A};
\]

where

\[ A = a_1 - b a_2 + b^2 a_3 - \ldots \]

For the present purpose we may consider \( k \) to be infinite, and write

\[ A = a_1 - b a_2 + b^2 a_3 - \ldots \]

Art. 87. Taking the symmetric function operators

\[
d_s = \partial a_s + a_1 \partial a_{s+1} + a_2 \partial a_{s+2} + \ldots ;
\]

\[
D_s = \frac{1}{s!} (\partial a_s + a_1 \partial a_s + a_2 \partial a_s + \ldots)^s = \frac{1}{s!} (d_s^s),
\]

and an auxiliary fictitious equation

\[ x^r - D_1 x^{r-1} + D_2 x^{r-2} - D_3 x^{r-3} + \ldots = 0, \]
r being an infinite number, it is necessary to remind the reader of the relations existing between the operators.

Successive linear operations of \( d_\lambda, d_\mu, d_\nu, \ldots \)

are denoted by placing them in separate brackets, thus,

\[(d_\lambda)(d_\mu)(d_\nu)\ldots,\]

but when they are multiplied, as in Taylor's theorem, so as to produce a single operator of higher order, they will be placed in one bracket, thus,

\[(d_\lambda d_\mu d_\nu)\ldots.\]

Art. 88. Let monomial symmetric functions of the fictitious relation

\[ x^r - D_1 x^{r-1} + D_2 x^{r-2} - \ldots = 0 \]

be denoted by a partition in brackets with subscript \( D \), thus,

\[ (\quad)_D. \]

Then I have shown, in a previous paper,

\[
\begin{align*}
d_1 &= D_1 = (1)_D, \\
d_2 &= D_1^2 - 2D_2 = (2)_D, \\
&\quad \ldots \ldots \ldots \ldots \ldots \ldots \\
d_3 &= \ldots = (s)_D,
\end{align*}
\]

and, in general,

\[
\frac{1}{\pi_1! \pi_2! \ldots} (d_1^{n_1} d_2^{n_2} \ldots) = (p_1^{n_1} p_2^{n_2} \ldots) n.
\]
Art. 89. Every symmetric function identity has corresponding to it a relation between the operators; thus corresponding to the set
\[(1)^2 = (2) + 2(1^2),\]
\[(1)^3 = (3) + 3(21) + 6(1^3),\]
\[(1)^4 = (4) + 4(31) + 6(2^2) + 12(21^2) + 24(1^4),\]
we have the set
\[(d_1)^2 = (d_2) + d_3 = 2(1^2) + (2)_d,\]
\[(d_2)^3 = (d_3)^3 + 3(d_1d_2) + d_3 = 6(1^3) + 3(21)_d + (3)_d,\]
\[(d_3)^4 = (d_4)^4 + 6(d_1d_2d_3) + 3(d_3) + 4(d_2d_1) + (d_4),\]
\[= (24)(1^4) + 12(21^2) + 6(2^3) + 4(31)_d + (4)_d,\]
and so on.

Art. 90. Also, corresponding to the set
\[2\alpha_2 = s_1^2 - s_2,\]
\[6\alpha_3 = s_1^3 - 3s_1s_2 + 2s_3,\]
\[24\alpha_4 = s_1^4 - 6s_1^2s_2 + 3s_2^2 + 8s_1s_3 - 6s_4,\]
&c., we have the set
\[2D_2 = (d_2)^2 = (d_2)^2 - d_2,\]
\[6D_3 = (d_3)^3 = (d_3)^3 - 3(d_1)(d_2) + 2d_3,\]
\[24D_4 = (d_4)^4 = (d_4)^4 - 6(d_1)(d_2)^2 + 3(d_3)^2 + 8(d_1)(d_3) - 6(d_4),\]
and so on.

Art. 91. For the special operand
\[\frac{1}{1-A}\]
these operator relations assume a special simple form which is of great importance in the theory of the generating function.

For
\[d_sA = (-)^{s-1}b^{s-1}(1-bA) = (-)^{s-1}b^{s-1}d_sA;\]
or, quâ the above operand,
\[d_s \equiv (-)^{s-1}b^{s-1}d_1;\]
and thence, from a set of relations given above,
\[2!D_2 \equiv D_1(D_1 + b),\]
\[3!D_3 \equiv D_1(D_1 + b)(D_1 + 2b),\]
\[\ldots\]
\[s!D_t \equiv D_1(D_1 + b)\ldots\{D_1 + (s-1)b\},\]
\[s!D_t \equiv t!D_1(D_1 + t)(D_1 + (t+1)b)\ldots\{D_1 + (s-1)b\}.\]

Art. 92. By means of these we can now arrive at a most important series of relations.
For
\[(p)_D = d_p = (-b)^{p-1}D_1;\]
\[(pq)_D = (d_p d_q) = (d_p) (d_q) - d_{p+q},\]
\[\equiv (-1)^{p+q-2} b^{p+q-2}D_1^2 + (-1)^{p+q-2} b^{p+q-1}D_1,\]
\[\equiv (-b)^{p+q-2} 2! D_2;\]
\[(pqr)_D = (d_p d_q d_r)\]
\[\equiv (d_p) (d_q) (d_r) - (d_{p+q}) (d_r) - (d_{p+r}) (d_q)\]
\[-(d_{q+r}) (d_p) + 2 d_{p+q+r},\]
\[\equiv (-b)^{p+q+r-3}D_1^3,\]
\[-3 (-b)^{p+q+r-2}D_2^2,\]
\[+ 2 (-b)^{p+q+r-1}D_1,\]
\[\equiv (-b)^{p+q+r-3} 3! D_3;\]

and generally
\[(p_1 p_2 \ldots p_s)_D \equiv (-b)^{2p-2s} 2! D_s;\]

and more generally
\[(p_1^{\pi_1} p_2^{\pi_2} \ldots)_D \equiv (-b)^{\sum \pi - \sum \pi} \frac{(\Sigma \pi) !}{\pi_1! \pi_2! \ldots} D_{\Sigma \pi};\]
or, if \(\Sigma \pi p = n, \Sigma \pi = \pi,\)
\[(p_1^{\pi_1} p_2^{\pi_2} \ldots)_D \equiv (-b)^{\sum \pi - \pi} \frac{\pi !}{\pi_1! \pi_2! \ldots} D_{\pi}.

Art. 93. From the relations
\[s ! D_s = D_1 (D_1 + b) \ldots (D_1 + (s-1)b);\]
we find the set
\[D_1^2 = 2D_2 - bD_1,\]
\[D_1^3 = 6D_3 - 6bD_2 + b^2D_1,\]
\[D_1^4 = 24D_4 - 36bD_3 + 14b^2D_2 - b^3D_1,\]
\[\ldots\]

Art. 94. And also the set
\[
\begin{align*}
\binom{s}{1} D_s &= D_{s-1} \left\{ D_1 + \binom{s-1}{1} b \right\}, \\
\binom{s}{2} D_s &= D_{s-2} \left\{ D_2 + \binom{s-2}{1} bD_1 + \binom{s-1}{2} b^2 \right\}, \\
\binom{s}{3} D_s &= D_{s-3} \left\{ D_3 + \binom{s-3}{1} bD_2 + \binom{s-2}{2} b^2D_1 + \binom{s-1}{3} b^3 \right\}, \\
\ldots & \\
\binom{s}{t} D_s &= D_{s-t} \left\{ D_t + \binom{s-t}{1} bD_{t-1} + \ldots + \binom{s-1}{t} b^t \right\},
\end{align*}
\]
\[sD_s = D_1 \left\{ D_{s-1} + bD_{s-2} + b^2D_{s-3} + \ldots + b^{s-1} \right\}.\]
The Expressibility of $D_s$.

Art. 95. The fundamental relation

$$s!D_s = D_1 (D_1 + b) (D_1 + 2b) \ldots \{D_1 + (s-1)b\},$$

exhibits $D_s$ in terms of powers of $D_1$.

It is clear, à priori, that $D_s$ is expressible in terms of $D_1$ and powers of $D_s$, e.g.,

$$\begin{align*}
\binom{3}{1} D_3 &= D_s (D_1 + 2b), \\
\binom{4}{2} D_4 &= D_s (D_3 + 2bD_1 + 3b^2), \\
\binom{5}{3} D_5 &= D_s (D_2D_1 + 8bD_2 + 9b^2D_1 + 12b^3), \\
\binom{6}{4} D_6 &= D_s (D_2^2 + 6bD_2D_1 + 29b^2D_2 + 24b^3D_1 + 30b^4),
\end{align*}$$

and so on, where notice, as a verification, that the sum of the numerical coefficients is the same on the two sides.

In every case $D_s$ appears as a factor.

In general the operator products, which appear on the right, are factors of $D_2D_1$, which contain the factor $D_s$, every weight of operator product being represented once, and once only, from the weight 2 up to the weight of the single operator on the left-hand side.

It is important to remark that

$$\binom{2k+1}{1}$$

is a perfect partition* of the number $2k+1$;

because every lower number can be composed in exactly one way by the parts of the partition.

Art. 96. It will now appear that there exists an expression for $D_s$

**corresponding to every perfect partition that can be constructed.**

The general expression of a perfect partition is

$$\ldots \{(1+\alpha) (1+\beta) (1+\gamma)\}^{s} \{(1+\alpha) (1+\beta)\}^{\gamma} (1+\alpha)^{\delta} 1^s;$$

where $\alpha, \beta, \gamma, \delta, \ldots$ are any positive integers, zero excluded.

The perfect partition

$$\binom{2k+1}{1}$$

is the particular case $\alpha = 1, \beta = k, \gamma = \delta = \ldots = 0.$

* 'Messenger,' 1890, p. 103.
In every case, if \( \sigma \) be the highest figure in the perfect partition, \( D_\sigma \) is a factor of the expression for \( D_\sigma \), e.g., taking the perfect partition 
\[
3^12,
\]
we have
\[
40D_6 = 2D_2^2 + 3bD_3D_1^2 + 15b^2D_3D_1 + 20b^3D_3.
\]

I do not interrupt the investigation by stopping to prove the theory of expressibility depending upon perfect partitions; its truth is intuitive.

Art. 97. It is necessary to labour the subject of the operator relations, quod the special operands, because the whole theory of the numbers \( N_m \) is involved.

Art. 98. Perhaps the most interesting of the operator relations are those which do not involve \( b \) (or \( \lambda \)).

Recalling the relation of Art. 92, viz.,
\[
(p_1^n p_2^m \ldots)_b = (-b)^{n-i} \frac{i!}{\pi_1! \pi_2!} D_i,
\]
where
\[
\Sigma \pi p = n, \quad \Sigma \pi = i,
\]
we may also write
\[
(q_1^n q_2^m \ldots)_b = (-b)^{v-j} \frac{j!}{\chi_1! \chi_2!} D_j,
\]
where
\[
\Sigma \chi q = v, \quad \Sigma \chi = j,
\]
and, if
\[
n - i = v - j,
\]
we may eliminate \( b \), obtaining
\[
\frac{j!}{\chi_1! \chi_2!} D_j (p_1^n p_2^m \ldots)_b = \frac{i!}{\pi_1! \pi_2!} D_i (q_1^n q_2^m \ldots)_b.
\]

Art. 99. The simplest formula thence obtained is found by putting
\[
(p_1^n p_2^m \ldots) = (2^2),
\]
\[
(q_1^n q_2^m \ldots) = (31);
\]
and this leads at once to
\[
d_1d_3 - d_2^2 = 0,
\]
or
\[
D_2D_1^2 - 4D_2^2 + 3D_3D_1 = 0;
\]
which also results by elimination of \( b \) from
\[
2D_3 = D_1(D_1 + b),
\]
\[
6D_3 = D_1(D_1 + b)(D_1 + 2b).
\]

Art. 100. To obtain some more relations in a simple manner, I write
\[
(s)_b = (-b)^{s-i}D_i,
\]
\[
(t)_b = (-b)^{t-i}D_i,
\]
\[
(u)_b = (-b)^{u-i}D_i,
\]
\[
(t + u)_b = (-b)^{t+u-i}D_i,
\]
\[
(u + s)_b = (-b)^{u+s-i}D_i,
\]
\[
(s + t)_b = (-b)^{s+t-i}D_i; 
\]
and then
\[(s+t)_{D}(u)_{D} = (s)_{D}(t+u)_{D} = (t)_{D}(u+s)_{D};\]
or, as these relations may be written,
\[d_{t+u} d_{u} = d_{t} d_{t+u} = d_{u} d_{t+u};\]
or
\[(s+t, u)_{D} = (s, t+u)_{D} = (t, u+s)_{D},\]
with the usual multiplier (viz., 2), if either
\[s+t = u, \text{ or } t+u = s, \text{ or } u+s = t.\]

Art. 101. We are led to the series
\[
\begin{align*}
(31)_{D} &= 2 (2^{2})_{D}, \\
(41)_{D} &= (32)_{D}, \\
(51)_{D} &= (42)_{D} = 2 (3^{2})_{D}, \\
(61)_{D} &= (52)_{D} = (43)_{D}, \\
(71)_{D} &= (62)_{D} = (53)_{D} = 2 (4^{2})_{D}, &c.,
\end{align*}
\]
and generally if
\[
(p_{1} p_{2} \ldots), \quad (q_{1} q_{2} \ldots)
\]
be functions of the same weight and degree, viz.,
\[
\Sigma x_{0} p = \Sigma x_{0} q; \Sigma x = \Sigma y = i,
\]
\[\pi_{1} ! \pi_{2} ! \ldots (p_{1} p_{2} \ldots)_{D} = \chi_{1} ! \chi_{2} ! \ldots (q_{1} q_{2} \ldots)_{D}.
\]

**Application of the Foregoing to the Generating Function.**

Art. 102. It has been established that
\[
\frac{1}{1 - a_{1} + (1 - \lambda) a_{2} - (1 - \lambda)^{2} a_{3} + \ldots} = \Sigma N_{m, p, p_{1}, p_{2}, \ldots}^{\lambda} \lambda a_{m-1} (p_{1} p_{2} \ldots).
\]
We will first of all examine the result of the equivalence of operators
\[2! D_{2} = D_{1}^{2} + (1 - \lambda) D_{1}\]
(see Art. 93 *quâ* the operand on the right-hand side). Write the operand
\[
\Sigma N_{m, 1^{c_{1}} 2^{c_{2}} 3^{c_{3}} \ldots}^{\lambda} \lambda a_{m-1} (1^{c_{2}} 2^{c_{3}} \ldots);
\]
then
\[
2! \Sigma N_{m, 1^{c_{1}} 2^{c_{2}} 3^{c_{3}} \ldots} = N_{m, 1^{c_{1}} 2^{c_{2}} 3^{c_{3}} \ldots} + (N_{m} - N_{m-1}) c_{1} 1^{c_{2}} 2^{c_{3}} \ldots,
\]
e.g., put
\[
c_{1} = 0, \quad c_{2} = 2, \quad c_{3} = c_{4} = \ldots = 0,
\]
\[m = 3,
\]
\[2N_{3, 2} = N_{3, 1^{2}} + (N_{3} - N_{2})_{2} ;
\]
verified (from the tables) by
\[2.48 = 93 + (15 - 12).\]
Art. 103. Again, in the same formula, put
\[c_1 = n - 2, \quad c_2 = 0, \quad c_3 = c_4 = \ldots = 0,\]
we find
\[2N_{m, 21^{n-2}} = N_{m, 1^n} + (N_m - N_{m-1})_1^{n-1}.\]

We obtain, from this, a useful result by writing
\[n - m + 1 \text{ for } m,
\]
for then
\[2N_{n-m+1, 21^{n-2}} = N_{n-m+1, 1^n} + (N_{n-m+1} - N_{n-m})_1^{n-1}.\]

Art. 104. Observe that
\[N_{m, 1^n} = N_{n-m+1, 1^n},\]
\[N_{m, 1^{n-1}} = N_{n-m, 1^{n-1}},\]
\[N_{m-1, 1^{n-1}} = N_{n-m+1, 1^{n-1}};\]
so that by addition and subtraction we obtain
\[N_{m, 21^{n-2}} + N_{n-m+1, 21^{n-2}} = N_{m, 1^n};\]
\[N_{m, 21^{n-2}} - N_{n-m+1, 21^{n-2}} = N_{m, 1^{n-1}} - N_{n-m+1, 1^{n-1}};\]
or, as we may conveniently write these relations,
\[(N_m + N_{n-m+1})_{21^{n-2}} = N_{m, 1^n};\]
\[(N_m - N_{n-m+1})_{21^{n-2}} = (N_m - N_{n-m+1})_1^{n-1};\]
\[= (N_m - N_{n-m-1})_1^{n-1}.\]

These are the relations connecting \(N_m\) and \(N_{n-m+1}\) _quā_ the subscript \(21^{n-2}\) analogous to those connecting the same symbols _quā_ the subscript \(1^n\).

Art. 105. From any operator relation we can immediately derive a relation between the numbers \(N_m\) by substituting for
\[b^* D_1 D_t \ldots\]
the expressions
\[\left\{ N_m - \binom{\sigma}{1} N_{m-1} + \binom{\sigma}{2} N_{m-2} - \ldots \right\}_{1^* D_1^*, 2^* D_2^* + \ldots};\]
and this it is convenient to denote by
\[N_{(\sigma)}_{m, 1^* D_1^*, 2^* D_2^* + \ldots}.\]

Art. 106. Thus, corresponding to the operator relation
\[6D_3 = D_1 (D_1 + b) (D_1 + 2b) = D_1^3 + 3b D_1^2 + 2b^2 D_1,
\]
we obtain
\[6N_{m, 1^* D_1^* + \ldots} = N_{m, 1^* D_1^* + \ldots} + 3N_m^{(0)}_{m, 1^* D_1^* + \ldots} + 2N_m^{(0)}_{m, 1^* D_1^* + \ldots};\]
As a particular case put
\[c_1 = n - 3, \quad c_2 = c_3 = c_4 = \ldots = 0,
\]
so that
\[6N_{m, 31^{n-2}} = N_{m, 1^n} + 3 (N_m - N_{m-1})_1^{n-1} + 2 (N_m - 2N_{m-1} + N_{m-2})_1^{n-2};\]
and thence
\[3 \left( N_m + N_{m-2} + N_{m-1} \right)_{m-2} = N_{m,1} + 2 \left( N_m - 2N_{m-1} + N_{m-2} \right)_{m-2};\]
\[\left( N_m - N_{m-1} \right)_{m-2} = (N_m - N_{m-1})_{m-1}.\]

For \( n = 6 \), these relations can be verified by the tables for all values of \( m \).

Art. 107. Similarly the theorems derived from
\[s! \cdot D_s = D_1 \left( D_1 + b \right) \left( D_1 + 2b \right) \ldots \left\{ D_1 + (s - 1) b \right\}\]
can be at once written down.

It is worth noting that this operator relation can, by putting \( D_1 = b \Delta_1 \), be written
\[D_s = b^s \left( \frac{\Delta_1 + s - 1}{s} \right).\]

If
\[s_1! s_2! \ldots D_{s_1} D_{s_2} \ldots = D_1^{s_1} + g_1 D_1^{s_1-1} + g_2 D_1^{s_1-2} + \ldots ;\]
we can write down the corresponding relation between the numbers \( N_m \).

It will be found that
\[\left( N_m + N_{m-1} \right)_{m-2} = N_{m,1} + N^{(2)}_{m,1} + N^{(4)}_{m,1} \ldots ;\]
and
\[\left( N_m - N_{m-1} \right)_{m-2} = N^{(1)}_{m,1} + N^{(2)}_{m,1} + N^{(3)}_{m,1} + N^{(4)}_{m,1} \ldots ;\]
and that the same obtains when instead of
\[s! \ldots 1^{n-2} \ldots\]
we take
\[s_1 s_2 \ldots 1^{n-2} \ldots\]

Art. 108. From the operator relation
\[(p_1^{m_1})^{n_1} (p_2^{m_2})^{n_2} \ldots D_{p_1}^{m_1} D_{p_2}^{n_2} \ldots = \prod_{p_1, m_1} D_t \left( D_1 + b \right) \ldots \left\{ D_1 + (m - 1) b \right\}^{m_1};\]
we find
\[D_{p_1}^{m_1} D_{p_2}^{n_2} \ldots = b^{m_1} \left( \frac{\Delta_1 + m - 1}{m} \right)^{n_1} \left( \frac{\Delta_1 + n - 1}{n} \right)^{n_2} \ldots ;\]

where \( u_0, u_1, u_2, \ldots \) are numerical coefficients that may be determined.

Thence is derived the relation
\[N^{(m,1)}_{m,1} = N^{m-1} \ldots \]
giving a hint to put
\[N_{m,1}^{m-1} = N_{m}^{m-1} \text{ symbolically,} \]
and then
\[N_{m,1}^{m-1} = \left( N_m + p_1 - 1 \right)^{m_1} \left( N_m + p_2 - 1 \right)^{n_2} \ldots \text{ symbolically.} \]

Art. 109. It must now be remarked that, since
\[N_{m}^{m-1} = \left\{ N_m - \left( \frac{t}{1} \right) N_{m-1} + \left( \frac{t}{2} \right) N_{m-2} \ldots \right\}^{m-1},\]
we obtain
\[ N_{n-m+1} = \left\{ N_{n-m+1} - \binom{t}{1} N_{n-m} + \binom{t}{2} N_{n-m-1} - \ldots \right\}_{n-t}; \]
and since
\[ N_{n-t} = N_{n-t} = N_{n-t} = N_{n-t} = (-1)^{n-t}; \]
and
\[ N_{n-m+1}, p_1^x p_2^y \ldots \]
\[ = u_0 N_{m-1} - u_1 N_{m-2} + u_2 N_{m-3} - \ldots \]
\[ = u_0 N_{m} - u_1 N_{m-1} + u_2 N_{m-2} - \ldots \]
\[ = \left( \begin{array}{c} N_m \\ p_1 \end{array} \right) \left( \begin{array}{c} N_m \\ p_2 \end{array} \right) \ldots ; \]
we obtain
\[ N_{n-m+1} = \left( \begin{array}{c} N_{n-m+1} \\ p_1 \end{array} \right) \left( \begin{array}{c} N_{n-m+1} \\ p_2 \end{array} \right) \ldots . \]

Art. 110. We have two alternative expressions for
in terms of numbers
\[ N_{n-t}. \]
I verify them in the case
\[ p_1^x p_2^y \ldots = 2^3; \]
(i.)
\[ N_m = \frac{1}{3} (N_m^2 + N_m^3); \]
or
\[ 8N_m = N_m^6 + 3N_m^5 + 3N_m^4 + N_m^3; \]
\[ = N_{m-1}^6 + 3(N_m - N_{m-1})^6 + 3(N_m - 2N_{m-1} + N_{m-2})^6 + (N_m - 3N_{m-1} + 3N_{m-2} - N_{m-3})^6, \]
agreeing with, for \( m = 3, \)
\[ 8.48 = 302 + 3(66 - 26) + 3(11 - 2.11 + 1) + (1 - 3.4 + 3.1). \]
(ii.)
\[ N_m = \frac{1}{3} (N_{7-m}^3 - N_{7-m})^3; \]
or
\[ 8N_m = N_{7-m}^6 - 3N_{7-m}^5 + 3N_{7-m}^4 - N_{7-m}^3; \]
and, for \( m = 3, \)
\[ 8N_3 = N_4^6 - 3N_4^5 + 3N_4^4 - N_4^3; \]
\[ = N_{4,1}^6 - 3(N_4 - N_3)_+ + 3(N_4 - 2N_3 + N_2)_+ - (N_4 - 3N_3 + 3N_2 - N_1)_+; \]
agreeing with
\[ 8.48 = 302 - 3(66 - 66) + 3(1 - 2.11 + 11) - (3.1 + 3.4 - 1). \]
Art. 111. We have seen that, in general, we have two expressions for

but, since

we have four expressions for

viz.,

Art. 112. It is clear that the operator relations afford unlimited scope for obtaining

theorems connecting the numbers

Relations, so far utilised, have involved the operator

but it is easy to construct them so as not to contain $D_1$ and generally so as not to contain $D_s$, where $s$ is less than a given integer.

E.g., from the symmetric function relation

we find

and generally the relation

leads to

or, throwing out the factor

the same relation as before.

Moreover, the relation

leads, after throwing out a power of $b$, to precisely the same relation.

Art. 113. This remarkable circumstance greatly limits the number of operator relations obtainable. It should be observed that any operator relation may be multiplied throughout by any power of $b$ and may be then used to obtain relations between the numbers

...
but no essentially new relations are thus obtainable; for take a simple case

leading to

$$2D_2 = D_1^2 + bD_1,$$

true for all values of $m$.

If we take

$$2bD_2 = bD_1^2 + b^2D_1,$$

we are led to

$$2(N_m-N_{m-1})x^{n+1}... = (N_m-N_{m-1})x^{n+2}x^{n+1}... + (N_m-2N_{m-1}+N_{m-2})x^{n+1}x^{n+k}...,$$

and if the former relation be written

$$f(m) = 0,$$

the latter is merely

$$f(m) - f(m-1) = 0;$$

and further multiplication by $b$ leads to the series of which the general term is

$$f(m) - (\frac{\sigma}{1})f(m-1) + (\frac{\sigma}{2})f(m-2)...;$$

so that no new information is obtained.

Art. 114. The operator relation of the form $D,D, = a$ linear function of

$$b^tD_s, b^{t-1}D_{s+1}, b^{t-2}D_{s+2},...$$

is not difficult to obtain.

I find that

$$(-)^tD_sD_t = (s\choose t) (t\choose s) b^tD_s - (s+1\choose t) (1\choose t) b^{t-1}D_{s+1}$$

and thence the formula for

$$D_sD_tD_u$$

follows by taking $D_u$ as the operand on each side and then reducing the products

by the formula for $D_sD_t$.

I find that

$$(-)^{t+n}D_sD_tD_u$$

$$= (s\choose u) (t\choose 0) (s\choose t) (u\choose 0) b^{t+n}D_s$$

$$- (s+1\choose u) \left\{ (t\choose 0) (s\choose t) (u\choose 1) + (t\choose 1) (s+1\choose t) (u\choose 0) \right\} b^{t+n-1}D_{s+1}$$

$$+ (s+2\choose u) \left\{ (t\choose 0) (s\choose t) (u\choose 2) + (t\choose 1) (s+1\choose t) (u\choose 1) + (t\choose 2) (s+2\choose t) (u\choose 0) \right\} b^{t+n-2}D_{s+2}$$

$$- ...;$$
and, generally, the product of any number of operators is expressible in the required linear form.

Art. 115. With the object of connecting this theory of the numbers \(N_m\) with that of the numbers \(N\ (abc\ldots)\), the generating function

\[
\frac{1}{1-\alpha_1 + (1-\lambda)\alpha_2 - (1-\lambda)^2\alpha_3 + \ldots}
\]

will now be expanded in ascending powers of \(\lambda\), the coefficients of \(\lambda\) being functions of the homogeneous product sums

\[h_1, h_2, h_3, \ldots\]

The point of departure is the elementary formula

\[
\frac{1}{1-\alpha_1 + \alpha_2 - \alpha_3 + \ldots} = 1 + h_1 + h_2 + h_3 + \ldots
\]

Remarking that

\[1-\alpha_1 + \alpha_2 - \alpha_3 + \ldots = (1-\alpha_1)\ (1-\alpha_2)\ (1-\alpha_3) \ldots\]

I write

\[(1-\lambda)\alpha_s\ \text{for}\ \alpha_s,
\]

equivalent to writing

\[(1-\lambda)^r\alpha_s\ \text{for}\ \alpha_s,
\]

and

\[(1-\lambda)^r h_s\ \text{for}\ h_s;
\]

then

\[
\frac{1}{1-(1-\lambda)\alpha_1 + (1-\lambda)^2\alpha_2 - (1-\lambda)^3\alpha_3 + \ldots} = 1 + (1-\lambda)h_1 + (1-\lambda)^2h_2 + (1-\lambda)^3h_3 + \ldots
\]

\[= u\ \text{suppose};
\]

and, as before, write

\[\alpha_1 - (1-\lambda)\alpha_2 + (1-\lambda)^2\alpha_3 - \ldots = A;
\]

so that

\[u = \frac{1}{1-(1-\lambda)A};
\]

whence, solving for \(A\),

\[A = \frac{1}{1-\lambda}\ \frac{u-1}{u},
\]

and

\[\frac{1}{1-A} = (1-\lambda)\ \frac{u}{1-\lambda u};
\]

where \(\frac{1}{1-A}\) is the generating function under consideration.

Write

\[H_1 = h_1 + h_2 + h_3 + h_4 + \ldots
\]

\[H_2 = h_2 + 2h_3 + 3h_4 + 4h_5 + \ldots
\]

\[H_3 = h_3 + 3h_4 + 6h_5 + 10h_6 + \ldots
\]

\[H_4 = h_4 + 4h_5 + 10h_6 + 20h_7 + \ldots
\]

\[
\ldots \ldots \ldots \ldots \ldots \ldots \ldots
\]

s 2
so that
\[ u = 1 + (1 - \lambda) h_1 + (1 - \lambda)^2 h_2 + (1 - \lambda)^2 h_3 + \ldots \]
\[ = 1 + H_1 - \lambda (H_1 + H_2) + \lambda^2 (H_2 + H_3) + \ldots + (-1)^{(t + 1) h_{t + 1}} + \ldots \]
\[ = 1 + (1 - \lambda) H_1 - \lambda (1 - \lambda) H_2 + \lambda^2 (1 - \lambda) H_3 - \ldots ; \]
therefore
\[ \frac{1 - \lambda H}{1 - \lambda} = 1 - \lambda H_1 + \lambda^2 H_2 - \lambda^3 H_3 + \ldots \]
and thence
\[ \frac{1}{1 - A} = 1 + \frac{H_1 - \lambda H_2 + \lambda^2 H_3 - \ldots}{1 - \lambda H_1 + \lambda^2 H_2 - \lambda^3 H_3 + \ldots}. \]
Now let functions
\[ A_1, A_2, A_3, A_4, \ldots \]
be connected with
\[ H_1, H_2, H_3, H_4, \ldots \]
in the same way that
\[ \alpha_1, \alpha_2, \alpha_3, \alpha_4, \ldots \]
are connected with
\[ h_1, h_2, h_3, h_4, \ldots \]
so that
\[ A_1 = H_1, \]
\[ A_2 = H_1^2 - H_2, \]
\[ A_3 = H_1^3 - 2H_1H_2 + H_3, \]
\[ \ldots \ldots \ldots \ldots \]
then
\[ \frac{1}{1 - \lambda H_1 + \lambda^2 H_2 - \lambda^3 H_3 + \ldots} = 1 + \lambda A_1 + \lambda^2 A_2 + \lambda^3 A_3 + \ldots ; \]
and
\[ \frac{1}{1 - A} = 1 + (H_1 - \lambda H_2 + \lambda^2 H_3 - \ldots) (1 + \lambda A_1 + \lambda^2 A_2 + \lambda^3 A_3 + \ldots). \]
On the dexter the co-factor of \( \lambda^t \) is
\[ H_1A_t - H_2A_{t-1} + H_3A_{t-2} - \ldots - (-1)^{(t + 1) h_{t + 1}}, \]
which has the value
\[ A_{t + 1}, \]
since
\[ \alpha_{t + 1} - h_1\alpha_2 + h_2\alpha_3 - \ldots - (-1)^{(t + 1) h_{t + 1}} = 0 \]
is a well-known identity in the elementary theory of symmetric functions. Hence
\[ \frac{1}{1 - A} = 1 + A_1 + \lambda A_2 + \lambda^2 A_3 + \lambda^3 A_4 + \ldots ; \]
or, as we may write it,
\[ \frac{1}{1 - a_1 + (1 - \lambda) a_2 - (1 - \lambda)^2 a_3 + \ldots} \]
\[ = 1 + A_1 + \lambda A_2 + \lambda^2 A_3 + \lambda^3 A_4 + \ldots, \]
\[ = 1 + H_1 + \lambda H_{11} + \lambda^2 H_{111} + \lambda^3 H_{1111} + \ldots, \]
\[ = 1 + H_1 + \lambda (H_1^2 - H_2) + \lambda^2 (H_1^3 - 2H_1H_2 + H_3) \]
\[ + \lambda^3 (H_1^4 - 3H_1^2H_2 + H_2^2 + 2H_1H_3 - H_4) + \ldots. \]
Art. 116. The preceding pages show that the coefficient of

\[ \lambda^{m-1} \]

in the expansion of

\[ \frac{1}{1 - \alpha_1 + (1 - \lambda) \alpha_2 - (1 - \lambda)^2 \alpha_3 + \ldots} \]

is equal to

\[ \sum N_{m, \{pqr\ldots\}} \]

the summation being for every partition

\( \{pqr\ldots\} \)

and this, from the theory of the numbers

\[ N(p_1p_2\ldots p_m) \]

\[ \sum \ldots \sum h_{p_1p_2\ldots p_m} \]

the summation being for all integer values of

\[ p_1, p_2, \ldots p_m \]

or, the same thing, for the compositions of all numbers into exactly \( m \) parts.

Hence

\[ \sum h_{p_1} = A_1 = H_1 \]

\[ \sum \sum h_{p_1p_2} = A_2 = H_{11} = H_1^2 - H_2 \]

\[ \sum \sum \sum h_{p_1p_2p_3} = A_3 = H_{111} = H_1^3 - 2H_1H_2 + H_3 \]

\[ \ldots \ldots \ldots \ldots \ldots \ldots \]

\[ \sum \sum \ldots \sum h_{p_1p_2\ldots p_m} = A_m = H_1^m, \]

a remarkable result.

Art. 117. Since

\[ \frac{1}{1 - \alpha_1 + (1 - \lambda) \alpha_2 - (1 - \lambda)^2 \alpha_3 + \ldots} \]

we find, putting \( \lambda = 1 \),

\[ \frac{1}{1 - \alpha_1} = 1 + \sum h_{p_1} + \sum h_{p_1p_2} + \sum h_{p_1p_2p_3} + \ldots, \]

and, since

\[ D_1 = d_1 = d_{n_1}, \]

\[ D_1' \left( 1 + \sum h_{p_1} + \sum h_{p_1p_2} + \sum h_{p_1p_2p_3} + \ldots \right) \]

\[ = s! \left( 1 + \sum h_{p_1} + \sum h_{p_1p_2} + \sum h_{p_1p_2p_3} + \ldots \right)^{s+1}; \]
and thence, as an easy deduction,

\[ D_r (1 + \Sigma h_{p_1} + \Sigma h_{p_2 p_1} + \Sigma h_{p_3 p_2 p_1} + \ldots) \]

\[ = (1 + \Sigma h_{p_1} + \Sigma h_{p_2 p_1} + \Sigma h_{p_3 p_2 p_1})^{r+1} \]

(for observe that, for the operand \( \frac{1}{1-\alpha_i} \), \( D_i^r \equiv s! D_r \)), and thence, by an easy step,

\[ D_{p_1} D_{p_2} \ldots (1 + \Sigma h_{p_1} + \Sigma h_{p_2 p_1} + \Sigma h_{p_3 p_2 p_1} + \ldots) \]

\[ = \frac{(\Sigma \pi p)!}{(p_1)!^n (p_2)!^{n_2} \ldots} (1 + \Sigma h_{p_1} + \Sigma h_{p_2 p_1} + \Sigma h_{p_3 p_2 p_1} + \ldots)^{s_{p+1}}. \]

By C. Cuthbertson and E. Parr Metcalfe, B.Sc.

Communicated by Professor F. T. Trouton, F.R.S.

Received October 23.—Read November 18, 1906.

We have continued, with more perfect apparatus, the enquiry recorded in a previous paper* on the refractive indices of the vapours of elements which are not gaseous at ordinary temperatures. The instrument employed was the refractometer of Jamin, and the arrangement of the apparatus has been fully described in the paper just cited, so that it requires only a brief recapitulation here.

Two similar exhausted tubes are placed in the paths of the rays of monochromatic light between the mirrors, and a known weight of the element is vaporised in one of them, of which the volume is known. The tubes are heated by means of a simple form of electric furnace, consisting of two coils of nickel wire embedded in asbestos.

The number of interference bands which pass a fiducial mark in the field of the observing telescope during the evaporation, or return during the condensation, combined with the other data, give the index for the wave-length employed.

The calculation is as follows:—

If \( N \) be the number of bands observed to pass the fiducial mark, \( \lambda \) the wave-length \( X \) the length of the tube, \( m \) the refractive index observed, and \( \mu \) the refractive index at the standard density selected, we have

\[
N\lambda = (m - 1)X
\]

and

\[
\frac{\mu - 1}{m - 1} = \frac{\text{standard density}}{\text{observed density}}
\]

\[
= \frac{0.00009 \times \text{atomic weight of element}}{\text{atomic weight of hydrogen}} \times \frac{\text{volume of tube}}{\text{weight of element volatilised}}
\]

Hence

\[
(\mu - 1) = \frac{N\lambda}{X} \times \frac{0.00009 \times \text{atomic weight of element} \times \text{volume of tube}}{\text{atomic weight of hydrogen} \times \text{weight volatilised}}
\]

* 'Phil. Trans.,' A, vol. 204, p. 323, 1905.
The standard density selected is that in which the number of atoms of the element per unit volume is equal to the number of atoms contained in unit volume of hydrogen at 0° C. and 760 millims.

In the present work the original procedure underwent several important improvements. Repeated failure had shown that the glass tubes formerly used, with plate-glass ends ground in and luted with shellac, were useless above 280° C., when the shellac charred and the tubes cracked.

Recourse was had, therefore, to tubes of fused silica, which were made with admirable skill by the firm of HERAEUS, of Hanau. The ends of the tubes, through which the interfering rays passed, were plates of the same material ground optically flat, fused into the tubes and again polished, so that the whole formed an air-tight, homogeneous enclosure, which could be heated to the highest temperature employed (about 850° C.) without fear of softening, and could be heated and cooled locally with great rapidity without cracking.

This property of the silica permitted the introduction of a second improvement in the procedure. In the earlier work the two sections of the furnace were joined up in the centre, and the whole length of the tubes was heated in one operation, so that the observer had sometimes to remain with his eye at the telescope for several hours while the furnace heated and cooled. This tedious method was now abolished. The two sections of the furnace were separated by a gap of about an inch, and their inner ends covered with thin asbestos boards. In these boards holes were punched, through which the silica tubes passed. In this way the greater part of the tubes could be raised to a high temperature while the gap in the middle remained comparatively cool. With the object of obtaining a reasonable equality in the temperature of the two halves of the furnace, the sections were made in all respects as nearly similar as possible, and the heating coils were connected in parallel to the lighting circuit.

When the furnace had reached the temperature which was found by experiment to be more than sufficiently high to evaporate the whole of the charge employed, cold water was dropped on the exposed part of the tube until it was certain that the temperature there must be below 100° C., and, consequently, that there could be practically none of the element in a state of vapour. The observer then noted the position of the bands in the telescope, in relation to a pointer fixed on the further mirror, and his colleague quickly heated the central portion of the tube with a Bunsen flame. The bands now moved rapidly and attained their maximum in a few minutes. The heating was continued for about a minute after the stopping of the bands indicated the complete vaporisation of the charge; the flame being then removed, a second reading was obtained as the element condensed. When nearly all the bands had passed, water was again dropped on the tube till it was certain that the zero had been reached. Meanwhile the temperature of the rest of the furnace was kept approximately constant, and thus many minor sources of error due to inequality of
the length of the tubes, or of the thickness of the ends, or to unequal heating of the air, which had given trouble previously, were avoided.

In the case of zinc, the temperature necessary was so high that the glass diaphragms used to close the outer ends of the furnace began to soften and buckle. This difficulty was overcome by substituting worked plates of fused silica.

In the course of the work it was found that the dispersion would be considerable. Arrangements were therefore made for determining the index for more than one wave-length. A mercury vapour lamp of Bastian's pattern was found to give an excellent green (\(\lambda = 4460\)), and red light (\(\lambda = 6562\)) was obtained from a hydrogen vacuum tube. But these methods proved unsatisfactory, and eventually it was found possible to work with approximately monochromatic light sifted out with a slit from the spectrum of the white light of a Nernst filament dispersed through four glass prisms. The light thus obtained was sufficiently monochromatic to give twenty or thirty sharp black interference bands, and it was used in all the later experiments.

Potassium.

Of the elements whose indices still remain to be measured in the gaseous state, the most important group is that of the alkalis. It was, therefore, decided to begin with potassium, which seemed likely to prove the easiest.

So far as we are aware, only one attempt has hitherto been made to measure the index of a member of this group. In the course of his brilliant research on the optical properties of sodium vapour, Professor R. W. Wood* measured the retardation of light in passing through a column of dense vapour, and compared its value at different points of the spectrum with that produced at the wave-length of the yellow helium line. By the application of the Sellmeier dispersion formula to his results he deduces an index of 1.0000275 for infinitely long waves for sodium vapour saturated at 644° C. Unfortunately the density of the vapour corresponding to this temperature is yet unknown, so that it is impossible from the data available to calculate the absolute atomic refractivity of sodium.

The relative values for different wave-lengths are, of course, independent of the density, and in themselves constitute a most interesting exemplification of the variation of the index in the neighbourhood of an absorption band. Thus, the index increases from the infra-red to the line D\(_1\), where it becomes very large. On the blue side of D\(_2\) the index increases rapidly from very small values, but remains less than unity even as far as \(\lambda = 2260\).

In view of these facts the investigation of the index of potassium seemed likely to yield results of similar interest. But, unfortunately, the chemical difficulties proved so great that, in spite of numerous attempts, it was found impossible to obtain absolute values with the apparatus employed. At the temperature at which

* 'Phil. Mag.' September, 1904.
potassium evaporates, it attacks both glass and silica, so that it is not possible to obtain, in vessels of these materials, a density of the vapour sufficient for a quantitative determination of the absolute index. Eventually, however, by adopting the device of heating all but a small portion of the refractometer tube to a sufficient temperature, and then rapidly heating the cool part, a sufficient density of vapour was attained to permit of some qualitative observations.

Since reliable numerical results could not be looked for, no attempt was made to purify the potassium beyond distilling it in vacuo after prolonged heating to expel occluded hydrogen. The distillate was run into capillary tubes, which were sealed off in short sections, and, by a device which need not be described, the operations of breaking the capillary and introducing it into the refractometer tube were performed entirely in vacuo.

Experiments were, at first, made with sodium light, but it was found that at a temperature of about 220° C. the interference bands disappeared, though the light was not wholly absorbed by the vapour. This effect might be accounted for by supposing that the potassium contained a small quantity of sodium, or that sodium was set free by the action of the potassium on the glass tube, for Wood has shown that the great dispersion of the vapour of sodium in the neighbourhood of the D lines has the effect of destroying interference bands formed by light of those wave-lengths, when even small quantities of vapour are present.

The sodium flame was therefore replaced by a Bastian mercury lamp which gave good bands with the wave-length 5460. Several experiments were made with this light with refractometer tubes both of glass and of silica; and it was found that the evaporation of the potassium was attended by a movement of the bands in the direction corresponding to a refractive index less than unity. On one occasion no less than four bands were observed to pass during the heating and to return during the cooling.

These experiments at first suggested that the quantity of sodium present was greater than had been suspected, and that its influence on the index dominated that of the potassium. If this were so we should find that an experiment with light of greater wave-length than that of the D lines would give a very high refractive index. In order to test this surmise, experiments were made with the red light supplied by a hydrogen vacuum tube whose Hᵡ line was so strong as to give good interference bands. But in this case also the bands moved in the same direction as those formed by the light of the mercury lamp. We are, therefore, driven to the conclusion that the index of potassium is less than unity both for \( \lambda = 5460 \) and for \( \lambda = 6562 \).

These results showed that no experiments on the indices of the alkali elements were likely to repay the labour involved until the chemical difficulties had been overcome and arrangements could be made for obtaining the index for very long waves. It was, therefore, determined to abandon the attempt for the present, and to turn to some other series.
Cadmium. (Atomic Weight 112.)

For experiments with this element the purest metal to be obtained from Kahlbaum was used. The arrangement described above acted very well. At a temperature between 600° C. and 700° C. enough cadmium evaporated to give a shift of 20 or 30 bands. There was no marked absorption. The principal difficulty in obtaining concordant results lay in the reading of the bands, which were unsteady owing to the mirage caused by currents of unequally heated air, and in many cases were badly illuminated. It was never possible to read to less than a quarter of a band; and if the conditions were bad, it was exceedingly easy to miss a whole band, or even two, or to count one twice. It was for this reason that the number of readings recorded is so large.

Table I. exhibits the results obtained. Those readings which appear obviously incorrect are enclosed in brackets. Four different charges of cadmium were used and numerous readings were made with each. The results obtained with the second charge may be neglected. In this case the bands were observed by the old method, while the whole furnace was heated in a single operation, and the correction for "end effects" was found to be of the order of 25 per cent. of the reading, and was not trustworthy. The other three charges gave fairly consistent results, as will be seen from the summary.

Zinc. (Atomic Weight 65.)

The next element dealt with was zinc, in the hope that the completion of the series zinc, cadmium, mercury might afford useful information. Again, in this case, the pure metal supplied by Kahlbaum was used. Only two charges of zinc were used, and much trouble was experienced in overcoming the effects of air convection currents. No absorption band was observed. It is to be regretted that the number of bands read was so small; but the furnace was not adapted for reaching a higher temperature than about 850° C., and it was not possible to evaporate a larger quantity at this temperature.

Table II. exhibits the results.

Arsenic. (Atomic Weight 75.)

Arsenic, free from iron, was obtained from two sources, and a series of determinations was made with each specimen.

This element proved the easiest of all those attempted, and concordant results were quickly obtained (see Table III.).

Selenium. (Atomic Weight 79.)

Experiments were made with two charges of this element. In the first series the readings were somewhat uncertain, and the result may be neglected. The second
Table I.—Refractions of gaseous Cadmium.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>January 16</td>
<td>34.8 centims.</td>
<td>48.17 cub. centims.</td>
<td>5893</td>
<td>0.00823</td>
<td>26½, 26</td>
<td>26½</td>
<td>2605</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.8 centims.</td>
<td>48.17</td>
<td>5460</td>
<td>0.00823</td>
<td>28½, 29 to 29½, 28½ to 29½</td>
<td>29.04</td>
<td>2675</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.8 centims.</td>
<td>48.17</td>
<td>5893</td>
<td>0.01141</td>
<td>35.8</td>
<td>35.8</td>
<td>2575</td>
<td></td>
</tr>
<tr>
<td>February 3</td>
<td>34.8 centims.</td>
<td>48.17</td>
<td>5893</td>
<td>0.00621</td>
<td>20, 20, 19½, 19½</td>
<td>19.8</td>
<td>2620</td>
<td></td>
</tr>
<tr>
<td>June 8</td>
<td>34.8 centims.</td>
<td>48.17</td>
<td>5460</td>
<td>0.00621</td>
<td>22, (20½), 22, 22½, 23, 23, 23</td>
<td>22.1</td>
<td>2725</td>
<td></td>
</tr>
<tr>
<td>June 8</td>
<td>34.8 centims.</td>
<td>48.17</td>
<td>6562</td>
<td>0.00777</td>
<td>22, 24, 22½, 23, 23, 23, 23</td>
<td>22.4</td>
<td>2675</td>
<td></td>
</tr>
<tr>
<td>June 8</td>
<td>34.8 centims.</td>
<td>48.17</td>
<td>5893</td>
<td>0.00777</td>
<td>25½, 25½, 25½, 25½</td>
<td>25.8</td>
<td>2675</td>
<td></td>
</tr>
<tr>
<td>June 8</td>
<td>34.8 centims.</td>
<td>48.17</td>
<td>5183</td>
<td>0.00777</td>
<td>(31)<em>, (29)</em>, (30½)<em>, (30½), 30½</em>, 30½, 30½, 29½, 29½, 29½</td>
<td>29.5</td>
<td>2780</td>
<td></td>
</tr>
</tbody>
</table>

\[ \lambda \]

\[ (\mu - 1) 10^6. \]

Refractions observed for . . .

\begin{align*}
5562 & \quad 2675 \\
5893 & \quad 2605, (2575), 2620, 2675 \\
5460 & \quad 2675, (2550), 2725 \\
5183 & \quad - \quad - \quad 2780
\end{align*}

Probable best values . . .

\begin{align*}
5562 & \quad 2675 \\
5893 & \quad 2675 \\
5460 & \quad 2725 \\
5183 & \quad 2780
\end{align*}

A bad experiment. A large correction for "end effects" was involved.

* Bad readings, owing to poor light and mirage.
### Table II.—Refractivities of gaseous Zinc.

<table>
<thead>
<tr>
<th>Date, 1906</th>
<th>Internal length of tube.</th>
<th>Volume of tube</th>
<th>Wave-length of light employed, A.U.</th>
<th>Weight of element.</th>
<th>Bands observed.</th>
<th>Mean (approx.)</th>
<th>Refractivity. ((\mu - 1) \times 10^6).</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>February 8 and 14</td>
<td>34.8 centims.</td>
<td>48.2 cub. centims.</td>
<td>5460</td>
<td>0.00379</td>
<td>(17\frac{3}{4}, 17\frac{1}{4}) or (18\frac{3}{4}, 17\frac{3}{4}), ((19\text{ or }18\frac{3}{4}), 17\text{ or }18, 17, 18\text{ or }17\frac{3}{4}, 18\frac{3}{4}, 18\frac{3}{4})</td>
<td>18.3</td>
<td>2150</td>
<td></td>
</tr>
<tr>
<td>June 12</td>
<td>34.8 centims.</td>
<td>48.2 centims.</td>
<td>5893</td>
<td>0.00544</td>
<td>(16\frac{1}{2}, 16\frac{1}{4}, 16\frac{3}{4}, 16\frac{1}{4}, 16, 16\frac{1}{4}, 16\frac{1}{2}, 20\frac{1}{2}, 21, 19\frac{3}{4}) or (20\frac{1}{2}, 19, 20)</td>
<td>16.2</td>
<td>2050</td>
<td>{Bad readings; much mirage.}</td>
</tr>
<tr>
<td>8 \text{ and } 14</td>
<td>34.8 centims.</td>
<td>48.2 centims.</td>
<td>6562</td>
<td>0.00544</td>
<td>(19\frac{3}{4}, 20\frac{3}{4}, (18), 20 \text{ or }21, 19\frac{3}{4}, 20 \text{ or }21, 21, 20\frac{1}{2}, 19\frac{3}{4})</td>
<td>20</td>
<td>1960</td>
<td>{Bad readings; much mirage.}</td>
</tr>
<tr>
<td>15</td>
<td>34.8 centims.</td>
<td>48.2 centims.</td>
<td>6562</td>
<td>0.00544</td>
<td>(20, 20, (19), (18\frac{3}{4}), 19\frac{3}{4}, 20, 20, 20, (18\frac{3}{4}), 20, (19\frac{3}{4}), 20)</td>
<td>20.25</td>
<td>2065</td>
<td>{Bad readings; much mirage.}</td>
</tr>
<tr>
<td>20</td>
<td>34.8 centims.</td>
<td>48.2 centims.</td>
<td>6562</td>
<td>0.00544</td>
<td>(23\frac{1}{4}, 23\frac{3}{4}, (23\frac{3}{4} \text{ or }24), 23\frac{1}{4}, 23\frac{1}{4}, 23\frac{3}{4}, 23\frac{1}{4})</td>
<td>23.25</td>
<td>2065</td>
<td>{Bad readings; much mirage.}</td>
</tr>
<tr>
<td>11</td>
<td>34.8 centims.</td>
<td>48.2 centims.</td>
<td>5893</td>
<td>0.00544</td>
<td>(24\frac{1}{4}, 24\frac{3}{4}, (24\frac{3}{4} \text{ or }24), 24, 24, 24)</td>
<td>24</td>
<td>2020</td>
<td>{Bad readings; much mirage.}</td>
</tr>
<tr>
<td>15</td>
<td>34.8 centims.</td>
<td>48.2 centims.</td>
<td>5630</td>
<td>0.00544</td>
<td>(26\frac{1}{4}, 26\frac{1}{4}, 26\frac{1}{4}, 26\frac{1}{4})</td>
<td>26.3</td>
<td>2070</td>
<td>{Bad readings; much mirage.}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>((\mu - 1) \times 10^6).</th>
</tr>
</thead>
<tbody>
<tr>
<td>{6562}</td>
<td>1960</td>
</tr>
<tr>
<td>5893</td>
<td>2050</td>
</tr>
<tr>
<td>5630</td>
<td>2065</td>
</tr>
<tr>
<td>5460</td>
<td>2150</td>
</tr>
<tr>
<td>5183</td>
<td>2070</td>
</tr>
</tbody>
</table>

Refractivities observed . . . .

Probable values range from 1960 in red \((\lambda = 6562)\) to 2100 in green \((\lambda = 5183)\)
### Table III.—Refractivities of gaseous Arsenic.

<table>
<thead>
<tr>
<th>Date, 1906</th>
<th>Internal length of tube.</th>
<th>Volume of tube.</th>
<th>Wave-length of light employed, A.U.</th>
<th>Weight of element.</th>
<th>Bands observed.</th>
<th>Mean (approx.)</th>
<th>Refractivity, $(\mu - 1) \times 10^6$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>February 19 and 22</td>
<td>centims. 34.8</td>
<td>c. centims. 48.07</td>
<td>5460</td>
<td>0.01784</td>
<td>$55\frac{1}{2}, 55\frac{1}{2} (55\frac{3}{4} \pm 1), 55\frac{1}{2}$</td>
<td>55.5</td>
<td>1580</td>
<td><em>(Good reading.)</em></td>
</tr>
<tr>
<td>&quot; 23</td>
<td>34.8</td>
<td>48.07</td>
<td>5893</td>
<td>0.01784</td>
<td>$(50\frac{1}{2} \pm 1), 50\frac{1}{2}$ to $\frac{1}{2}$</td>
<td>50.6</td>
<td>1550</td>
<td></td>
</tr>
<tr>
<td>&quot; 23</td>
<td>34.8</td>
<td>48.07</td>
<td>5460</td>
<td>0.01760</td>
<td>$(53 \pm 1), (53), 54, 54\frac{1}{2}$</td>
<td>54.5</td>
<td>1577</td>
<td></td>
</tr>
<tr>
<td>March 8</td>
<td>34.8</td>
<td>48.07</td>
<td>5893</td>
<td>0.01760</td>
<td>$49\frac{1}{2}, 50, 49\frac{1}{2}$</td>
<td>49.7</td>
<td>1554</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$(\mu - 1) \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractivities observed.</td>
<td></td>
</tr>
<tr>
<td>5893</td>
<td>1550, 1554, mean 1552</td>
</tr>
<tr>
<td>5460</td>
<td>1580, 1577, &quot; 1579</td>
</tr>
</tbody>
</table>

### Table IV.—Refractivities of gaseous Selenium.

<table>
<thead>
<tr>
<th>Date, 1906</th>
<th>Internal length of tube.</th>
<th>Volume of tube.</th>
<th>Wave-length of light employed, A.U.</th>
<th>Weight of element.</th>
<th>Bands observed.</th>
<th>Mean (approx.)</th>
<th>Refractivity, $(\mu - 1) \times 10^6$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>March 23</td>
<td>centims. 34.8</td>
<td>cub. centims. 48.2</td>
<td>5893</td>
<td>0.01347</td>
<td>$35, 36\frac{1}{2} (37 or 38), 38, 36$</td>
<td>37</td>
<td>1592</td>
<td></td>
</tr>
<tr>
<td>May 14</td>
<td>34.8</td>
<td>48.2</td>
<td>5893</td>
<td>0.00836</td>
<td>$23, 22 \frac{1}{2} (21 or 22), 21 \frac{1}{2}, (22\frac{1}{2}), 21\frac{1}{2}, 21\frac{1}{2}, 21\frac{1}{2}$</td>
<td>21.4</td>
<td>1505</td>
<td></td>
</tr>
<tr>
<td>&quot; 14</td>
<td>34.8</td>
<td>48.2</td>
<td>5460</td>
<td>0.00836</td>
<td>$24\frac{1}{2}, 24\frac{1}{2}, 24\frac{1}{2}, 24\frac{1}{2}$</td>
<td>24.1</td>
<td>1570</td>
<td></td>
</tr>
<tr>
<td>&quot; 28</td>
<td>34.8</td>
<td>48.2</td>
<td>6540</td>
<td>0.00836</td>
<td>$20, 19\frac{1}{2}, 20, 20, 20 (bare), 20, 19\frac{1}{2}$ to $19\frac{1}{2}$</td>
<td>19.5</td>
<td>1530</td>
<td></td>
</tr>
<tr>
<td>June 6</td>
<td>34.8</td>
<td>48.2</td>
<td>6562</td>
<td>0.00836</td>
<td>$19\frac{1}{2}$</td>
<td>19.5</td>
<td>1535</td>
<td></td>
</tr>
<tr>
<td>&quot; 6</td>
<td>34.8</td>
<td>48.2</td>
<td>5893</td>
<td>0.00836</td>
<td>$22\frac{1}{2}, 22\frac{1}{2}, 22\frac{1}{2}, 22\frac{1}{2}$ (full), $22\frac{1}{2}, 22\frac{1}{2}, 22\frac{1}{2}, 22\frac{1}{2}$</td>
<td>22.6</td>
<td>1565</td>
<td></td>
</tr>
<tr>
<td>&quot; 6</td>
<td>34.8</td>
<td>48.2</td>
<td>5540</td>
<td>0.00836</td>
<td>$23\frac{1}{2}, 24, 24, 24$</td>
<td>23.9</td>
<td>1560</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$(\mu - 1) \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractivities observed.</td>
<td></td>
</tr>
</tbody>
</table>
series gave values consistent with each other. The vapour exhibits a strong absorption band extending from the violet so far towards the red that no readings could be made at the wave-length 5183, as, when five or six bands had passed, the light was completely absorbed (see Table IV.).

Tellurium. (Atomic Weight 128.)

The specimen used was obtained from Kahlbaum and, for the first experiment, was redistilled. In this case also there is a strong absorption band in the violet, which prevented readings being made beyond \( \lambda = 5460 \). Tellurium was found to evaporate with difficulty at a temperature hardly lower than that required for zinc, and it was necessary to use very small quantities, so that the number of bands observed was small, and the values obtained possibly less accurate. Two charges were used. In the first day's work with the second charge the temperature was not taken sufficiently high, with the result that the band readings are about 6 per cent. too low; but they are nevertheless recorded, as they show relative numbers for the dispersion effect which are useful in corroborating the other results (see Table V.).

Mercury. (Atomic Weight 200.)

This was the first element dealt with by C. Cuthbertson three years ago. As a check on the older method of working, another measurement of the refractivity of mercury vapour was made by E. P. Metcalfe, the silica refractometer tubes and the divided furnace being now used. One charge only was employed, and observations were taken with light of four different wave-lengths. The value of the refractivity now obtained for D light (1866) is in good agreement with the previous determination (1857). The accuracy of the band readings seems to be, for the D line, to within about \( \frac{1}{3} \) per cent., for the other wave-lengths to within about 1 per cent. (see Table VI.).*

Remarks.

Dispersion.

The present research was designed to obtain a single value for each element, and it was only with the object of satisfying ourselves that the refractivity measured was not affected to an abnormal degree by the existence of an absorption band for a wave-length near to that by which the observations were made that readings were taken with different wave-lengths. Each band reading being completely independent of the rest, and the degree of accuracy being, apparently, not much greater than to

[* Subsequent work by Mr. Metcalfe renders it probable that the true value for \( \lambda = 6562 \) is \( 1\frac{1}{2} \) to 2 per cent. higher than that given in Table VI.—January 24, 1907.]
### Table V.—Refractivities of gaseous Tellurium.

<table>
<thead>
<tr>
<th>Date, 1906</th>
<th>Internal length of tube.</th>
<th>Volume of tube.</th>
<th>Wave-length of light employed, A.U.</th>
<th>Weight of element.</th>
<th>Bands observed.</th>
<th>Mean (approx.)</th>
<th>Refractivity. ( (\mu - 1) \times 10^6 )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 21</td>
<td>34.8 centims.</td>
<td>48.00 cub. centims.</td>
<td>6562</td>
<td>0.00402</td>
<td>9, (9 or 10), 9, 9_2, 9_3, 9_8, 9_9, 9_{10}, 9_{11}, 10_2</td>
<td>9.1</td>
<td>2405</td>
<td></td>
</tr>
<tr>
<td>&quot; 21</td>
<td>34.8 centims.</td>
<td>48.00 cub. centims.</td>
<td>5893</td>
<td>0.00402</td>
<td>11, 10_2, 11, 10_3, 12, 12, 12</td>
<td>10.7</td>
<td>2543</td>
<td></td>
</tr>
<tr>
<td>&quot; 26</td>
<td>34.8 centims.</td>
<td>48.00 cub. centims.</td>
<td>5460</td>
<td>0.00402</td>
<td>13, 13 or 14, 13_2, 13, 13_3, 13, 13_3, 12 (full)</td>
<td>13.1</td>
<td>2330</td>
<td></td>
</tr>
<tr>
<td>&quot; 28</td>
<td>34.8 centims.</td>
<td>48.00 cub. centims.</td>
<td>5893</td>
<td>0.00402</td>
<td>10_3 to 10_3, 10_3, 10_3, 13, 13_3, 12 (full), 12 (full)</td>
<td>11.7</td>
<td>2410</td>
<td></td>
</tr>
<tr>
<td>&quot; 28</td>
<td>34.8 centims.</td>
<td>48.00 cub. centims.</td>
<td>5460</td>
<td>0.00402</td>
<td>14, 14, 14, 14, 14_1, 14_1, 14_1, 14_1</td>
<td>14.1</td>
<td>2640</td>
<td></td>
</tr>
</tbody>
</table>

\[\lambda = \left\{ \begin{array}{l} 
6562 \quad 2405, 2335, \text{mean 2370} \\
5893 \quad 2543, 2410, " \quad 2495 \\
5460 \quad 2600, 2640, " \quad 2620 \\
\end{array} \right.\]

### Table VI.—Refractivities of gaseous Mercury.

<table>
<thead>
<tr>
<th>Date, 1906</th>
<th>Internal length of tube.</th>
<th>Volume of tube.</th>
<th>Wave-length of light employed, A.U.</th>
<th>Weight of element.</th>
<th>Bands observed.</th>
<th>Probable best number of bands</th>
<th>Refractivity. ( (\mu - 1) \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 13</td>
<td>34.8 centims.</td>
<td>48.46 cub. centims.</td>
<td>6562</td>
<td>0.01235</td>
<td>13.3, 13.5, 13.5, 13.5, 13.5</td>
<td>13.5</td>
<td>1799</td>
</tr>
<tr>
<td>&quot; 12</td>
<td>34.8 centims.</td>
<td>48.46 cub. centims.</td>
<td>5893</td>
<td>0.01235</td>
<td>15.5, 15.5, 15.5, 15.5, 15.5</td>
<td>15.6</td>
<td>1866</td>
</tr>
<tr>
<td>&quot; 12 and 13</td>
<td>34.8 centims.</td>
<td>48.46 cub. centims.</td>
<td>5459</td>
<td>0.01235</td>
<td>16.0, 16.0, 16.0, 16.0, 16.0</td>
<td>17.0</td>
<td>1882</td>
</tr>
<tr>
<td>&quot; 13</td>
<td>34.8 centims.</td>
<td>48.46 cub. centims.</td>
<td>5183</td>
<td>0.01235</td>
<td>18.0, 17.9, 17.9, 17.9, 17.9</td>
<td>17.9</td>
<td>1885</td>
</tr>
</tbody>
</table>
within about 2 per cent., an accurate record of the dispersion was hardly to be expected. We have not overlooked the importance of determining the dispersion in every case through a wide range of wave-lengths; but the difficulty of obtaining values sufficiently accurate to yield useful information when introduced into a dispersion formula was found to be insurmountable with the present apparatus in the time at our disposal. We hope, however, in the future, to make a further attempt to obtain the dispersion with improved apparatus.

The results appear interesting. In every case, except that of potassium, the dispersion observed is normal in direction.* But its magnitude is very great. Thus, in the case of tellurium, the refractivity varies from about 2370 for $\lambda = 6562$ to 2620 for $\lambda = 5460$, or nearly 10 per cent. For zinc the variation is about 7 per cent. for the same range.

Refraction and Refraction Equivalents.

It is probable that the refractive indices for infinitely long waves would be considerably smaller than those here observed. But even after making the most liberal deduction, it is certain that the indices of zinc, cadmium, and tellurium are higher than the highest (viz., that of iodine) of which we had previous knowledge. It is interesting to compare them with the refraction equivalents of GLADSTONE and others. This is done in Table VII.

### Table VII.

<table>
<thead>
<tr>
<th>Refraction equivalents.</th>
<th>Refractivities now found (gaseous).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gladstone.</td>
</tr>
<tr>
<td></td>
<td>Early.†</td>
</tr>
<tr>
<td>As</td>
<td>15.4</td>
</tr>
<tr>
<td>Zn</td>
<td>10.2</td>
</tr>
<tr>
<td>Cd</td>
<td>13.6</td>
</tr>
<tr>
<td>Se</td>
<td>—</td>
</tr>
<tr>
<td>H</td>
<td>1.3</td>
</tr>
</tbody>
</table>

* The apparent exceptions to this statement are attributable to errors of observation.
‡ 'American Journal of Science,' 3, 29, 1885, p. 57.
The results are very curious. Gladstone’s refraction equivalent for arsenic* is about twelve times that for hydrogen, while the gaseous refractivity is eleven times that of hydrogen. But the values of Gladstone for zinc and cadmium are just half those now obtained for the gaseous state. Haagen, however, has a value for zinc which corresponds fairly well with the refractivity. Finally, Gladstone’s value of selenium is about double that shown by the refractivity.

Relative Refractivities of the Elements.

Previous work in this field had brought to light certain relations between the refractivities of the elements which seemed too regular to be due to chance, and the present work was undertaken mainly with the object of ascertaining whether similar relations existed in the case of other elements.

The results have been partly successful and partly unsuccessful. It was at once manifest that, in view of the great dispersion and in the absence of trustworthy values for infinitely long wave-lengths, the search for simple integral ratios between the refractivities must be postponed. But in one group of elements traces of a tendency to conform to such a rule may, we think, be fairly claimed.

Table VIII. shows the elements arranged in the order of their atomic weights, with the refractivities appended in those cases in which they have been measured in the gaseous state for the D line. The form of the table is suggested by the ratios existing between the refractivities of some of the elements, and is, so far as we know, somewhat different from previous forms of the periodic table.

Thus, since the refractivities of nitrogen, oxygen, fluorine and neon are respectively one fourth of those of phosphorus, sulphur, chlorine and argon, it would seem that each of these groups should form a horizontal row, and since the refraction equivalents of potassium, rubidium and caesium are in the same ratio as those of argon, krypton,

* In this connection it is interesting to compare the values now found with those suggested by the indices of some compounds of the elements.

As an instance we may take the case of arsenic trichloride, whose index (as found by Haagen) is approximately 1.6. Converting this number into the corresponding one for a gas by the formula of Lorenz, \[
\frac{\mu^2 - 1}{\mu^2 + 2} \frac{\rho}{\mu} \] constant, we arrive at the figure 1.920; of this 1.152 may be subtracted for the chlorine atoms, leaving a balance 768 for one atom of arsenic, or 1536 for two atoms of arsenic, a result which corresponds well with the number 1550 now found. But the additive rule, as is well known, is not of universal application. It fails conspicuously in the case of the fluorine compounds of the sulphur, selenium, tellurium group. The present writers were, through the courtesy of Dr. E. B. R. Prideaux, afforded the opportunity of measuring the refractivities of these compounds. The results have been published already in Dr. Prideaux’ paper in ‘Trans. Chem. Soc.,’ 1906, vol. 89, p. 330. For the refractivities of the hexafluorides of sulphur, selenium, and tellurium we found the values 783, 895, and 991, the corresponding numbers deduced by the additive rule being 1116, 1336, and 1826 respectively.
### ON THE REFRACTIVE INDICES OF GASEOUS POTASSIUM, ETC.

<table>
<thead>
<tr>
<th>Table VII</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atom</strong></td>
</tr>
<tr>
<td>Li</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>Ne</td>
</tr>
<tr>
<td>Ar</td>
</tr>
<tr>
<td>Kr</td>
</tr>
<tr>
<td>X</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Symbol</strong></th>
<th><strong>Refractive Index</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.44 × 10^-2</td>
</tr>
<tr>
<td>He</td>
<td>1.44 × 10^-2</td>
</tr>
<tr>
<td>F</td>
<td>1.92 × 10^-2</td>
</tr>
<tr>
<td>Cl</td>
<td>1.92 × 10^-2</td>
</tr>
<tr>
<td>Br</td>
<td>1.85 × 2^-6</td>
</tr>
<tr>
<td>I</td>
<td>1.52 × 10^-6</td>
</tr>
<tr>
<td>N</td>
<td>2.97 × 10^-4</td>
</tr>
<tr>
<td>O</td>
<td>2.70 × 10^-4</td>
</tr>
<tr>
<td>P</td>
<td>2.99 × 10^-4</td>
</tr>
<tr>
<td>S</td>
<td>1.197 × 4</td>
</tr>
<tr>
<td>Se</td>
<td>3.298 × 6</td>
</tr>
<tr>
<td>As</td>
<td>3.43 × 6</td>
</tr>
<tr>
<td>Ga</td>
<td>20.60</td>
</tr>
<tr>
<td>In</td>
<td>280.70</td>
</tr>
<tr>
<td>Zn</td>
<td>34.80</td>
</tr>
<tr>
<td>Hg</td>
<td>188.6</td>
</tr>
</tbody>
</table>

---

#### Notes
- The refractive indices are given for gaseous potassium and other elements under specific conditions.
- The data is presented in a tabular format for easy reference.\n- The refractive indices are critical for understanding the behavior of light in different media.
and xenon (i.e., as 2:3:5) the table has been rearranged so as to bring these together in such a way that a single factor is characteristic of each row.*

From such a table we should expect the refractivities of selenium and tellurium to be to that of sulphur as 3 and 5 respectively to 2. The values found are in both cases rather low, but that for selenium is not notably so. In the other cases the regularity breaks down. The value for arsenic is much nearer $\frac{5}{4}$ that of phosphorus than $\frac{3}{4}$. The values for zinc do not bear to those for cadmium the ratio 3:5, while the refractivity of mercury is actually less than that of either, thus exhibiting the only case yet observed of a gaseous refractivity which is lower than that of another element of the same group and of lower atomic weight.

In short, it may be said that the rule of simple integral ratios between their refractivities is probably confined to the elements lying near the centre of the table which are shown enclosed within the heavy rectangular boundary. To these we may possibly add the group potassium, rubidium, caesium, in which the refraction equivalents seem to indicate conformity to the rule. Within the heavily marked enclosure the regularity is very striking, except for the two, or possibly three, elements in the lower left-hand corner.

A general survey of the table, with the new additions, confirms the view already held that, in each group of elements, refractivity increases with atomic weight. But mercury, which stands in a lower horizontal row than the other elements examined, forms a striking exception to this rule, and it remains to be seen whether this is merely an isolated case, or whether it is characteristic of all the heaviest elements. The refraction equivalents of Gladstone lend some colour to the conjecture that there may be a falling off in refractive power when the atomic weight exceeds a certain limit, but, in view of the discrepancies exhibited in Table VII., it would be dangerous to place much reliance on their indications. It is also remarkable that in each horizontal row of Table VIII. refractive power increases as we move to the left, in spite of the decrease in atomic weight; there can be little doubt, therefore, that it is intimately connected with the valency.

We have to express our cordial thanks to Professor Trouton and the staff of the Physical Laboratory at University College, London, for assistance and advice, and to the Royal Society for a grant in aid of the research.

* This arrangement was first suggested by Professor A. W. Porter. It will be observed that it fits in very well with the sequence of the atomic volumes.
IV. On the Discharge of Negative Electricity from Hot Calcium and from Lime.

By Frank Horton, D.Sc., B.A., Fellow of St. John's College, and Clerk-
Maxwell Student of the University, Cambridge.

Communicated by Professor J. J. Thomson, F.R.S.

Received December 10, 1906,—Read January 31, 1907.

INTRODUCTION.

The discharge of electricity from hot metals has been the subject of a great number of researches by different authors. The metal chiefly used in these experiments has been platinum, on account of its high melting-point, its stability in air, and the ease with which it can be obtained in a state of purity. In the present experiments calcium was chosen for investigation because of its strong electropositive character. Since this implies a great attraction for positive electricity, it would be expected that the negative corpuscles would escape more readily from calcium than from platinum. It should, therefore, be possible to obtain a measurable "negative leak" from calcium at a much lower temperature than from platinum or other less electropositive metal.

The first method of experimenting employed consisted in measuring the saturation current from an electrically heated calcium wire to a surrounding electrode, both being placed in a vacuum, but it was found to be impossible to get a clean surface of calcium in this way, for the metal combines with the oxygen, nitrogen, and water vapour in the air, and becomes more or less covered with a coating of calcium compounds before the apparatus can be fitted up. Another difficulty was soon discovered. When the wire was heated to above a dull red heat, the vapour pressure of the metal was sufficient for it to volatilize and condense on the colder walls of the tube. Thus the wire got thinner at its hottest point, and, consequently, the temperature there rose, and the sublimation increased, until in a few seconds the wire had broken through.

It was finally decided to make use of the volatility of calcium in order to obtain a clean surface of the metal. The method of experiment was to fix up a platinum strip as the cathode in a vacuum tube and to ascertain the manner in which the current from this to the other electrode varied with the temperature of the strip, with the difference of potential between the electrodes, and with the gas pressure in the
apparatus. The platinum strip was then covered with a layer of calcium by means of sublimation, and the current between the two electrodes was measured again. It might here be stated that a current between the two electrodes was observed only when the platinum strip was used as the cathode, the positive leak being too small to be detected by the galvanometer used. In what follows, therefore, the platinum strip will be spoken of as the cathode.

When the observations of the negative leak from the calcium-covered cathode had been made, the calcium was oxidised to lime, and the leak measured again. In this way the negative leak from metallic calcium was compared with the negative leak from the same amount of metal in the form of oxide. The full account of the experiments and results is divided for convenience into the following sections:

(1) Description of the apparatus, &c.;
(2) Investigation of the negative leak from platinum;
(3) The negative leak from calcium in helium;
(4) The negative leak from lime in helium and in hydrogen;
(5) Summary of results, and conclusion.

(1) Description of the Apparatus, &c.

The glass apparatus shown in fig. 1 was found to be the most convenient form of discharge tube for these experiments.

A is a platinum strip which can be heated electrically, the current being supplied by means of the thick platinum leads G. The leak from this to the platinum electrodes B, C, which together form the anode, was measured by means of a delicate d'Arsonval galvanometer, giving a deflection of 1 millim. for a current of \(7.19 \times 10^{-10}\) ampère. The calcium wire D, from which the metal is to be sublimed, is beneath the platinum strip, and about two centimetres from it. It can be heated by an electric current led in through the thick copper leads F, which enter the bulb through sealing-wax joints. The apparatus is connected with the mercury pump McLeod gauge and \(\text{P}_2\text{O}_5\) drying bulb by the side tube shown in the figure. The platinum strip was 3.5 centims. long and 2 millims. wide. The calcium wire was about 6 centims. long and 1 millim. in diameter.

Since calcium is readily attacked by all the more common gases, the experiments had to be conducted in an atmosphere of argon or helium. Either of these gases could be admitted into the apparatus through a side tube. For the purpose of purifying the gas a small discharge tube was fitted on to the apparatus. In this the cathode was an alloy of potassium and sodium, made by mixing the metals in atomic proportions. When a discharge from an induction coil is sent through this tube the alloy gradually absorbs any gas that may be present, except argon or helium. The argon or helium in the apparatus could thus be purified by running the discharge
tube until the pressure as indicated on the MacLeod gauge remained constant. In the first experiments the gas employed was argon, while in the later experiments helium gas was used. The helium was purchased out of a grant obtained from the Royal Society.

The arrangement of apparatus used to measure the current from the surface of the platinum is indicated in fig. 2.

One end of the platinum strip C was connected to earth and also, through a fine tin-foil fuse, R, to the negative pole of a battery of small storage cells, B. The positive pole of this battery was connected to the anodes A, through the key K, and the sensitive d'Arsonval galvanometer G, which was well insulated on paraffin blocks and served to measure the current. The difference of potential between the electrodes A and C was determined by means of the electrostatic voltmeter V. H, H, are the leads for heating the platinum strip.

The temperature of the cathode was determined by means of a thermocouple which was welded on to the strip at its middle. The wires forming the thermocouple were
pure platinum, and platinum with 10 per cent. of rhodium. They were of very small diameter (0.0025 centimetre), so that the temperature of the strip was not materially lowered by the heat conducted along them. Each wire was sealed into a fine glass tube, and these tubes were sealed into the bulb vertically above the platinum strip at E (fig. 1). The other ends of the thermocouple wires were some 20 centims. away and were soldered on to wires from a d'Arsonval galvanometer, the junctions being enclosed in a water jacket, through which a stream of water, at a known constant temperature, was kept circulating. The thermocouple was standardised before the platinum strip was placed in the bulb. Very small grains of pure potassium sulphate were placed on the strip near to the junction. The strip was then heated by an electric current, which was increased until the grains of sulphate (observed through a microscope) just melted. The galvanometer deflection corresponding to this temperature was noted. Use was then made of the curve given by Callendar* for transposing the galvanometer readings into degrees Centigrade.

(2) Investigation of the Negative Leak from Platinum.

Professor H. A. Wilson has shown that, in order to get constant values of the negative leak from platinum, great care must be taken to remove all traces of hydrogen, as this gas has a huge effect on the negative leak. For this purpose Professor Wilson recommends boiling the platinum in nitric acid. This method was adopted in the present research. The apparatus shown in fig. 1 consists of two parts, the lower of which, holding the calcium wire and leads, slides into the upper part and is held in position by a sealing-wax joint. When the apparatus had been made, the upper part containing the platinum strip to be used as a cathode was inverted and filled with strong nitric acid. This was boiled for about an hour, and then the acid was replaced by a fresh supply, which was also boiled for some time. After several boilings with strong nitric acid the apparatus was washed out with distilled water and dried by sucking dry air, filtered by passing through cotton wool, through it by means of a water pump. The calcium wire was carefully cleaned with fine emery paper and quickly sealed in position. The whole apparatus was then fixed on to the mercury pump, and the air pumped out until a good vacuum was obtained. The platinum strip was raised to incandescence by means of the current from 10 E.P.S. motor cells. After the platinum strip had been treated with nitric acid there was found to be only a slight increase of gas pressure inside the apparatus when the strip was left at a high temperature for a long time. The slight evolution of gas is probably hydrogen, which had been occluded in the platinum and was not completely eliminated by boiling with nitric acid. The negative leak from the platinum was found to decrease slightly as the gas was evolved, but it soon became fairly constant.

* Callendar, 'Phil. Mag.,' vol. 48, p. 519.
In some cases the attainment of the constant state was hastened by repeatedly washing the apparatus out with dry air and heating the platinum in that gas. When the pressure did not increase on heating the platinum, the apparatus was pumped down to as low a pressure as possible, and helium was let in to a pressure of 3 or 4 millims. The sodium-potassium alloy was then let into the special discharge tube through a well fitting tap, and the helium purified in the manner already described.

The relation between the current and the electromotive force was first investigated. The results obtained were similar to those found by other observers for the negative leak in air, oxygen, or nitrogen. For instance, at a pressure of 0.005 millim. the current was saturated with a potential difference of 30 volts, the distance between the electrodes being about 2 centims. With higher pressures of gas in the apparatus the potential difference required to saturate the current was much greater, on account of the formation of new ions by collisions with the gas molecules. With pressures above about 0.01 millim. the current never became saturated, but increased more and more rapidly with the potential as the latter was raised.

Mention must be made of a curious increase in the negative leak which was obtained whenever the cathode was allowed to remain for some time in a good vacuum. For instance, if the apparatus was left at a low pressure (0.005 millim.) over night, the leak was always found to be much larger when tested on the following day. This increase was sometimes as much as a thousand times the normal current. It gradually died away when the cathode was left at a bright red heat for some time. On investigating this effect it was found that the increased leak was connected with the appearance of a dark substance on the surface of the platinum strip. The amount of this was very small, and it was only visible when the platinum was heated. It disappeared on long continued heating, and its disappearance was always accompanied by a huge decrease in the negative leak. This phenomenon only occurred at low pressures. When the apparatus was left at a pressure of 2 or 3 millims., the negative leak was found to remain practically constant. An effect similar to this seems to have been obtained by Professor H. A. Wilson in his experiments on the discharge of electricity from hot platinum. He says*: "If the wire is simply left standing in air at a low pressure for a long time, the leak is often greater than before on again heating the wire." I think that the black stuff which could be seen on the platinum strip in my apparatus must have been some compound formed by the action of the mercury vapour upon the platinum. Wilson found that mercury vapour increases the negative leak very considerably at high temperatures. This seems to indicate that there is some action between the two metals.

The leak would sometimes increase enormously when the apparatus was left at a low pressure for only a few minutes; sometimes even in the course of an observation it would increase to ten or twenty times the normal value. In one case a platinum

strip gave a leak of $3.76 \times 10^{-9}$ ampere with a potential difference of 40 volts at a temperature of 1480° C. and pressure 0.0042 millim. of mercury. On testing again, two hours later, at the same temperature and pressure, the leak was $5.05 \times 10^{-4}$ ampere!

This increase of the negative leak on standing at low pressures rendered it necessary to have a pressure of several millimetres when comparing the negative leak before and after subliming the calcium on to the cathode. Some observations were therefore made to ascertain the manner in which the leak from the hot platinum varies with the gas pressure in the apparatus over the range of pressures likely to be used in the subsequent experiments. It was found that with 40 volts difference of potential between the electrodes the negative leak at a constant temperature was nearly independent of the gas pressure between 7.5 millims. and 3 millims. If the pressure was reduced below this, the leak decreased gradually until a very low pressure was reached, when it suddenly increased again to many times its former value. This increase is probably due to the cause mentioned above. It did not always occur at exactly the same pressure, but generally at pressures below 0.1 millim. Sometimes it only appeared after allowing the apparatus to remain at a low pressure for several hours.

The conclusion from these experiments is that, for the purpose of comparing the negative leak from platinum with that from calcium or lime, it is best to work with a gas pressure of a few millimetres of mercury and to use a constant voltage of 40 volts, for the current never becomes saturated at this pressure. Working with a constant voltage comes to practically the same thing as measuring the saturation current in each case, for the current passing under a constant electromotive force should be proportional to the number of ions liberated at the surface of the cathode.

The following table contains the values of the negative leak from the platinum strip at different temperatures in helium at a pressure of 3.236 millims. with a potential difference of 40 volts between the electrodes. The series of observations was repeated several times during the course of two or three days, and the values given were found to be practically constant. The numbers in brackets refer to the order in which the measurements were made.

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Negative leak per square centimetre (ampere).</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 1331</td>
<td>$1.95 \times 10^{-9}$</td>
</tr>
<tr>
<td>(2) 1468</td>
<td>$3.96 \times 10^{-8}$</td>
</tr>
<tr>
<td>(3) 1542</td>
<td>$1.75 \times 10^{-7}$</td>
</tr>
<tr>
<td>(4) 1571</td>
<td>$2.99 \times 10^{-7}$</td>
</tr>
<tr>
<td>(5) 1610</td>
<td>$5.91 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

The values given above are slightly smaller than those given by H. A. Wilson for the negative leak per square centimetre from platinum in air at a low pressure.
Professor Wilson gives for the leak at 1545° C. the value $6.38 \times 10^{-7}$ ampère. The smallest value I ever obtained for the negative leak in helium was $6.91 \times 10^{-8}$ ampère per square centimetre of platinum surface at 1540° C. By taking great precautions in cleaning his platinum wires and purifying the air in the apparatus, with a special view to getting rid of all traces of hydrogen evolved by the wire when heated, Professor Wilson was able to reduce the leak to $10^{-8}$ ampère per square centimetre of surface at 1616° C. The values given in Table I. for the negative leaks in helium at different temperatures could be reduced to about one-tenth by reducing the pressure of the gas in the apparatus. Since Professor Wilson's results were obtained in a good vacuum, it seems that the value of the negative leak in helium is practically the same as in air under similar conditions of temperature and pressure.

From the numbers in Table I the curve in fig. 3 was drawn. It is similar to the current-temperature curves obtained by other observers in air.

O. W. Richardson and H. A. Wilson have found that the variation of the negative leak with temperature can be expressed by an equation of the type

$$x = A \theta^b e^{-Q/\theta},$$

where $x$ is the current in ampères, $\theta$ the absolute temperature, and $Q$ and $A$ are constants. $Q$ is a measure of the work done by a corpuscle in escaping from the surface of the metal; it can be obtained from any two values of $x$ by means of the equation

$$Q = 2 \log_\theta x_2/x_1 - \frac{1}{2} \log_\theta \theta_2/\theta_1,$$

$$\theta_1^{-1} - \theta_2^{-1}.$$

By the use of this formula the following values of $Q$ were obtained from the observed currents. The numbers in brackets refer to the observations in Table I., which were used in calculating the value of $Q$.

**Table II.**—Values of the Constant $Q$ calculated from Observations of Table I.

<table>
<thead>
<tr>
<th>From observations</th>
<th>Mean temperature, °C.</th>
<th>$Q$ (calories).</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1, 2)</td>
<td>1400</td>
<td>121,100</td>
</tr>
<tr>
<td>(2, 3)</td>
<td>1505</td>
<td>125,100</td>
</tr>
<tr>
<td>(3, 4)</td>
<td>1557</td>
<td>121,800</td>
</tr>
<tr>
<td>(4, 5)</td>
<td>1591</td>
<td>119,500</td>
</tr>
</tbody>
</table>

Mean = 121,900.
The variations in Q are not greater than can be accounted for by the errors of experiment. The mean value is lower than that given by Wilson (viz., 131,100), but this is probably due to the fact that the present experiments were performed with a gas pressure of several millimetres in the apparatus, whereas Wilson’s result was obtained in a good vacuum.

Taking \( Q = 121,900 \) and the current per square centimetre at 1610° C. as \( 5.91 \times 10^{-7} \) ampère, the value of the constant A in the formula \( x = A \theta e^{-Q/\theta} \) is \( 1.55 \times 10^5 \), so that the equation for the current \( x \) (ampères) at the absolute temperature \( \theta \) becomes

\[
x = 1.55 \times 10^5 \theta e^{-121,900/\theta}.
\]

The following is a comparison of the currents calculated by means of this equation and those found experimentally.

**Table III.**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Negative leak in ampères per square centimetre.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed.</td>
</tr>
<tr>
<td>1331</td>
<td>1.95 \times 10^{-9}</td>
</tr>
<tr>
<td>1468</td>
<td>3.96 \times 10^{-8}</td>
</tr>
<tr>
<td>1542</td>
<td>1.75 \times 10^{-7}</td>
</tr>
<tr>
<td>1671</td>
<td>2.99 \times 10^{-7}</td>
</tr>
<tr>
<td>1610</td>
<td>5.91 \times 10^{-7}</td>
</tr>
<tr>
<td></td>
<td>Calculated.</td>
</tr>
<tr>
<td></td>
<td>1.96 \times 10^{-9}</td>
</tr>
<tr>
<td></td>
<td>4.06 \times 10^{-8}</td>
</tr>
<tr>
<td></td>
<td>1.73 \times 10^{-7}</td>
</tr>
<tr>
<td></td>
<td>2.95 \times 10^{-7}</td>
</tr>
<tr>
<td></td>
<td>5.91 \times 10^{-7}</td>
</tr>
</tbody>
</table>

The observed and calculated values of the current agree very well, showing that the formula expresses the experimental results with considerable accuracy.

(3) The Negative Leak from Calcium in Helium.

Having shown that the negative leak from the platinum strip was of the normal amount, and that it varied with the temperature according to the established law, calcium was sublimed on to it and the alteration of the leak caused thereby was investigated. The sublimation of the calcium was performed by connecting the thick copper leads of the calcium wire (F, fig. 1) to the alternating current from a transformer and gradually decreasing the resistance in the circuit until the calcium became red hot. It then sublimed, and the bulb was covered with a fine metallic mirror, and the electrodes would be similarly covered with calcium. With practice it was possible to regulate the current so that the wire did not fuse through on the first heating. After observations of the negative leak had been taken, more calcium could be sublimed on to the cathode, and the observations repeated. The gas pressure in the apparatus increased during the process on account of the gas evolved by the calcium. The discharge was therefore started in the potassium-sodium tube and kept going until the whole of the evolved gases were absorbed by the alloy and the apparatus contained only helium gas at the same pressure as before. In order to see if the evolved gas increased the leak from the platinum strip, an experiment was
made in which the calcium wire was warmed sufficiently to expel some gas from it, but not to a high enough temperature to cause it to volatilize on to the platinum. The evolved gas was then absorbed in the potassium-sodium alloy, and the leak from the platinum strip in helium gas was again tested. It was found to be the same as before the calcium wire had been heated.

The negative leak from the calcium-covered strip was found at several temperatures. The observed values are given in the following table. The potential difference between the electrodes was 40 volts, and the gas pressure, as before, 3·236 millims.

**Table IV.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Current in ampères per square centimetre.</th>
<th>Q (calories).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed.</td>
<td>Calculated.</td>
</tr>
<tr>
<td>840</td>
<td>$3 \cdot 92 \times 10^{-9}$</td>
<td>$3 \cdot 44 \times 10^{-9}$</td>
</tr>
<tr>
<td>919</td>
<td>$1 \cdot 47 \times 10^{-8}$</td>
<td>$3 \cdot 11 \times 10^{-8}$</td>
</tr>
<tr>
<td>986</td>
<td>$1 \cdot 13 \times 10^{-7}$</td>
<td>$1 \cdot 63 \times 10^{-7}$</td>
</tr>
<tr>
<td>1005</td>
<td>$1 \cdot 53 \times 10^{-7}$</td>
<td>$2 \cdot 52 \times 10^{-7}$</td>
</tr>
<tr>
<td>1050</td>
<td>$4 \cdot 32 \times 10^{-7}$</td>
<td>$6 \cdot 75 \times 10^{-7}$</td>
</tr>
<tr>
<td>1065</td>
<td>$6 \cdot 45 \times 10^{-7}$</td>
<td>$9 \cdot 27 \times 10^{-7}$</td>
</tr>
<tr>
<td>1117</td>
<td>$2 \cdot 35 \times 10^{-6}$</td>
<td>$2 \cdot 61 \times 10^{-6}$</td>
</tr>
<tr>
<td>1142</td>
<td>$4 \cdot 37 \times 10^{-6}$</td>
<td>$4 \cdot 19 \times 10^{-6}$</td>
</tr>
<tr>
<td>1220</td>
<td>$2 \cdot 36 \times 10^{-5}$</td>
<td>$1 \cdot 66 \times 10^{-5}$</td>
</tr>
<tr>
<td>1238</td>
<td>$2 \cdot 95 \times 10^{-5}$</td>
<td>$2 \cdot 23 \times 10^{-5}$</td>
</tr>
<tr>
<td>1310</td>
<td>$9 \cdot 22 \times 10^{-5}$</td>
<td>$1 \cdot 47 \times 10^{-4}$</td>
</tr>
<tr>
<td>1385</td>
<td>$1 \cdot 75 \times 10^{-4}$</td>
<td>$1 \cdot 98 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Mean value of $Q = 7 \cdot 29 \times 10^{-4}$.

The observed currents in the table are plotted against the corresponding temperatures in fig. 4. The unit of current is successively multiplied by ten in passing to the right from one curve to the next.

It will be seen that the curves obtained are exactly similar to those given by platinum.*

The observations of the negative leak from calcium were made as quickly as

* See Richardson, 'Phil. Trans.,' A, vol. 201, p. 497.
possible, because the calcium gradually sublimed off the platinum strip if left heating for a long time. It is somewhat surprising that it remained on long enough for the above readings to be taken. The explanation is, probably, that the calcium melts and combines with the platinum on the surface of the strip, to form an alloy from which the calcium only slowly vapourises away. After long heating the whole of the calcium could be driven off the platinum, and the negative leak was reduced to the value it had before the calcium was sublimed.

From the numbers given it will be seen that the leak from calcium is enormously greater than that from platinum at the same temperature. For example, at 1385°C, the leak from calcium is about 5000 times the leak from platinum, which means that there are 5000 times as many corpuscles liberated per second per square centimetre from calcium as from platinum at this temperature.

The values of the constant Q, deduced from successive pairs of these results, are given in the last column of Table IV.

The large variations in Q are most probably due to the experimental difficulties of measuring the negative leak from calcium. It was generally difficult to get a steady reading of the current at any temperature, for the leak increased and decreased in a capricious manner. Moreover, the series of observations had to be taken very quickly, because the leak gradually decreased with continual heating, owing to the calcium subliming away.

The mean value of the constant A, calculated from the temperatures and currents...
per square centimetre, given in Table IV. is \(1.71 \times 10^4\), so that the equation for the current per square centimetre from calcium at \(T^\circ\) (absolute) becomes

\[
x = 1.71 \times 10^4 T^\circ e^{-72.69x/26}.
\]

The values of the negative leaks calculated from this formula are placed alongside the observed values in Table IV.

The agreement between the observed and calculated currents is not nearly so good as in the case of platinum. This is no doubt due to the difficulties attending the use of calcium. In the course of the experiments a note was made in the laboratory book that the currents recorded at 1050\(^\circ\) C., 1065\(^\circ\) C., and 1310\(^\circ\) C. were steadily increasing during the observations. We see from the table above that the observed currents at these temperatures were considerably too low. If it had been practicable to have left the apparatus for a few minutes before measuring the leak, the values of the currents at these temperatures would, no doubt, have been nearer to the theoretical value. The experiments, however, show in a quite satisfactory manner that at a given temperature the rate of emission of negative corpuscles from calcium is much greater than in the case of platinum; and by applying the results to the formula employed we see that this increased rate of emission is due to a decrease in the value of the constant \(Q\), that is, to a decrease in the energy required to set free the corpuscles from the surface of the platinum; for on any theory of the negative leak \(Q\) is a measure of the work required to produce a gramme molecular weight of corpuscles. The value found for \(Q\) for calcium (7.29 \(\times\) \(10^3\)) lies between the value found for platinum (1.219 \(\times\) \(10^5\)) and that obtained by Richardson for sodium (6.32 \(\times\) \(10^4\)). This is what one would expect, and indicates that the amount of energy required to liberate the corpuscles is less the more electropositive the metal.

(4) The Negative Leak from Lime.

When the series of observations recorded in Table IV. had been made, the calcium on the platinum strip was oxidised to lime by letting into the apparatus some pure dry oxygen. The oxygen was prepared by the electrolysis of water and then passed over sticks of caustic potash and some fused calcium chloride. It was let into the apparatus to a pressure of 3 or 4 millims. On gradually raising the temperature of the cathode the negative leak was at first only slightly greater than before the oxygen was admitted, but soon it increased very rapidly as the calcium oxidised, and a pale glow appeared in the discharge tube. After this luminous discharge had once appeared the negative leak at all temperatures was much greater than before the oxygen had been admitted into the apparatus. The following table gives the negative leaks under a potential difference of 40 volts at various temperatures in helium, the excess of oxygen having been absorbed by sending a discharge for some
time through the tube containing the sodium-potassium alloy. The pressure of the helium was, as in the case of the calcium cathode, 3.236 millims.

**Table V.**

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>Current in ampères per square centimetre.</th>
<th>Calculated.</th>
<th>Q (calories).</th>
</tr>
</thead>
<tbody>
<tr>
<td>730</td>
<td>$5 \times 10^{-8}$</td>
<td>$3 \times 10^{-8}$</td>
<td>$7.25 \times 10^4$</td>
</tr>
<tr>
<td>785</td>
<td>$3.55 \times 10^{-7}$</td>
<td>$4.57 \times 10^{-8}$</td>
<td>$8.82 \times 10^4$</td>
</tr>
<tr>
<td>820</td>
<td>$1.37 \times 10^{-6}$</td>
<td>$1.98 \times 10^{-6}$</td>
<td>$11.19 \times 10^4$</td>
</tr>
<tr>
<td>856</td>
<td>$7.13 \times 10^{-6}$</td>
<td>$8.14 \times 10^{-6}$</td>
<td>$13.76 \times 10^4$</td>
</tr>
<tr>
<td>877</td>
<td>$2.19 \times 10^{-5}$</td>
<td>$1.79 \times 10^{-5}$</td>
<td>$9.55 \times 10^4$</td>
</tr>
<tr>
<td>918</td>
<td>$9.30 \times 10^{-5}$</td>
<td>$7.61 \times 10^{-5}$</td>
<td>$6.59 \times 10^4$</td>
</tr>
<tr>
<td>949</td>
<td>$1.90 \times 10^{-4}$</td>
<td>$2.14 \times 10^{-4}$</td>
<td>$9.91 \times 10^4$</td>
</tr>
<tr>
<td>965</td>
<td>$3.23 \times 10^{-4}$</td>
<td>$3.57 \times 10^{-4}$</td>
<td>$9.58 \times 10^4$</td>
</tr>
</tbody>
</table>

Mean value of $Q = 9.58 \times 10^4$.

The observed currents in the above table are plotted against the corresponding temperatures in fig. 5. The curves obtained are of the usual form for the negative leak from glowing solids.

By comparing Table V. with Table IV. it will be seen that the negative leak from lime is enormously greater than from metallic calcium under the same conditions, the leak from a lime cathode at 950° C. being about the same as the leak from calcium at 1400° C. This is contrary to what we should expect on the supposition that the negative leak is due to the escaping of the corpuscles from the cathode, for the presence of an atom of oxygen in the molecule of lime would hinder, by its attraction for negative electricity, the escape of the corpuscles, and we should expect, in consequence, that the negative leak from lime would be less, under the same conditions of temperature and pressure, than the negative leak from the same amount of calcium in the metallic state.

The values of the constant $Q$, deduced from successive pairs of observations, are given in the last column of Table V.
The variations in the value of Q are very considerable—nearly as large as in the case of the calcium cathode. Several other sets of observations of the negative leak from a lime-covered cathode were made, and in all cases there were considerable variations in the values of the constant Q, calculated from the experimental numbers. It should be mentioned that when the temperature was 877° C. a pale glow was observed in the gas on one side of the cathode. This extended to both sides of the cathode on raising the temperature to 918° C., and became brighter at each subsequent increase of the temperature. The appearance of the glow was not marked by any abnormal increase in the current, as will be seen by the perfect continuity of the curve in fig. 5. The large values of Q obtained at this point seem to be purely accidental. From a large number of experiments with lime cathodes the mean value of Q, calculated from observations made just when the discharge became luminous, was not greater than the average value for the whole series of observations. The appearance of the luminous discharge will be treated of more fully in a later part of this paper.

The negative leak from the lime was tested again a few hours later. It was found to have decreased very considerably, and the luminous discharge did not now appear until the cathode had been raised to a much higher temperature than before. This was found to be a general rule, namely, that long continued heating of the lime diminished the negative leak. In the present case, after heating for about two hours to 1000° C., the negative leak was only of about the same magnitude as in the case of the calcium cathode. This will be seen by comparing the numbers in the following table with those given for calcium in Table IV.:

Table VI.—Negative leak from lime after heating to 1000° C. for two hours in helium gas at a pressure of 3.236 millimetres.

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Negative leak, ampères per square centimetre</th>
<th>Temperature, °C.</th>
<th>Negative leak, ampères per square centimetre</th>
</tr>
</thead>
<tbody>
<tr>
<td>942</td>
<td>6.84 x 10^{-9}</td>
<td>1226</td>
<td>2.24 x 10^{-6}</td>
</tr>
<tr>
<td>1006</td>
<td>1.22 x 10^{-7}</td>
<td>1290</td>
<td>1.81 x 10^{-4}</td>
</tr>
<tr>
<td>1170</td>
<td>1.51 x 10^{-6}</td>
<td>1316</td>
<td>3.42 x 10^{-4}</td>
</tr>
</tbody>
</table>

The mean value of Q obtained from these observations is 1.34 x 10^4—much greater than the mean value given in Table V. The luminous discharge was not observed in these experiments until the temperature was raised to 1316° C.

The mean value of the constant A calculated from the experimental numbers tabulated in Table V. is 6.42 x 10^{11}, so that the equation for the current per square centimetre from lime at the absolute temperature θ is

\[ x = 6.42 \times 10^{11} \theta e^{-0.58 \times 10^4(\theta /300)} \]

The currents calculated by means of this formula are given in the third column of Table V.

From these figures it will be seen that the formula only roughly represents the...
observed results. The discrepancies may be due to the unsteadiness of the negative leak from lime which has been mentioned above. The leak was steadier than with the calcium cathode, but not nearly so steady as with the glowing platinum. The chief alteration of the leak was the gradual decrease as the heating of the cathode was continued. This may have been due to a diminution of the amount of lime by sputtering or by peeling off from the surface of the platinum, although no such phenomena could be observed. It is not due to a decomposition of the lime by electrolysis, for the author has shown* that no signs of electrolysis can be detected when a current is sent through a vacuum tube from a lime cathode, and further experiments with other lime cathodes showed that the negative leak decreased with continual heating of the cathode, whether the discharge was passed or not. The discrepancies between the observed and calculated values in Table V. follow from the discordant values found for the constant Q.

It has already been mentioned that a large series of experiments with lime cathodes all gave similar results. In order to see if these irregularities were peculiar to the present method of experimenting, the values of Q were calculated from WEHNELT's values of the negative leak from lime given in the 'Philosophical Magazine' for July, 1905, p. 87. The variations in the values of Q thus found were considerably greater than those shown in Table V. The mean value was Q = 50,900—considerably less than the value found in the present experiments. It thus seems that the negative leak from lime is subject to irregular variations, and does not obey the Wilson-Richardson law with anything like the accuracy of the leak from platinum.

The fact that the negative leak from calcium is greater than from platinum at the same temperature we have seen to be due to a decrease in the value of the constant Q, that is, to a diminution of the energy required for the liberation of the corpuscles. The value of Q for lime as found in the observations tabulated above is greater than the value for calcium, and the fact that the current is greater in the case of lime than in the case of calcium is due to the enormously greater value of the constant A in the former case.

A theory to account for the negative leak from hot metals has been proposed by Richardson.† He supposes the negative leak to be due to the escape of the corpuscles which, on the ionic theory of metallic conduction, all conductors contain. The corpuscles are supposed to move about freely inside the conductor, and to have a distribution of velocities the same as the molecules of a gas. Corpuscles entering the surface layers of the conductor with a normal velocity component greater than a certain amount are supposed to escape into the surrounding space, and it is these corpuscles which maintain the current forming the negative leak. From these assumptions Richardson has deduced a formula of the type \( x = A \theta e^{-Q/\theta} \), and has

* 'Phil. Mag.,' April, 1906, p. 506.
† O. W. Richardson, 'Phil. Trans.,' A, vol. 201, p. 497.
shown that the constant $A$ is proportional to the number of free corpuscles in a cubic centimetre of the conductor in question.

From experiments on the negative leak from hot platinum in air and in hydrogen H. A. Wilson* has come to the conclusion that the phenomenon cannot be completely explained by such a simple theory, and, moreover, he has shown that in order to obtain the above formula it is not necessary to make any assumption as to the manner of formation of the ions, but only to assume that they are produced in some way at the surface of the hot platinum. In Wilson's view, the constant $Q$ is a measure of the work required to produce a gramme molecular weight of ions at the surface of the hot platinum, but experiments on the negative leak in hydrogen at different pressures have led to the conclusion that the constant $A$ cannot be regarded as proportional to the number of corpuscles in a cubic centimetre of the cathode, and Wilson shows that the number so deduced does not agree with the value found by Patterson† from experiments on the variation of the resistance of platinum in a magnetic field. A comparison of the values of $A$ found for lime and for calcium in the present research appears to support this view of Wilson's, for it does not seem possible that there can be $10^7$ times as many free corpuscles in a cubic centimetre of lime as in a cubic centimetre of calcium. Further, it is well known that the electric conductivity of lime increases rapidly with rise of temperature. The author has shown that this conductivity is mainly, if not entirely, metallic in nature, and, on the ionic theory of metallic conduction, due to a large increase in the number of free corpuscles contained in the substance, for it is improbable that the velocity of the corpuscles increases to this extent. If, then, $A$ is proportional to the number of corpuscles per cubic centimetre, its value should increase with the temperature. In the present experiments with lime, although there were considerable variations in the value of $A$ calculated from the negative leaks at different temperatures, there was no sign of a progressive increase with increasing temperature.

From Wehnelt's work on the discharge of negative ions from glowing lime and other metallic oxides, Richardson has drawn the conclusion that the corpuscles proceed not from the glowing oxide, but from the platinum, and that the oxide merely has the effect of lessening the amount of energy required to set them free. This conclusion is arrived at from the fact that the number of corpuscles per cubic centimetre calculated from the value of the constant $A$, as found from Wehnelt's numbers, is about the same as for platinum. The value of $A$ for lime obtained in the present experiments is much greater than the value obtained for platinum, the former being $6.42 \times 10^{11}$ and the latter $1.55 \times 10^6$. Other experiments with lime-covered cathodes gave values ranging from $A = 1.23 \times 10^6$ to $A = 7.12 \times 10^{13}$, the value given by the observations recorded in Table VI., taken after the cathode had been heated for a long time to a high temperature. The values of $A$, calculated from observations

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† Patterson, 'Phil. Mag.,' 6, III., 655.
with different cathodes, are thus seen to vary very considerably; the values of $Q$, too, were not in very good agreement. It seems likely that this may be due to the platinum being more completely covered with lime in some cases than in others, for it will be readily understood that the cathode could not be quite uniformly covered with calcium at each attempt by the method of sublimation. In order to obtain more accurate knowledge of the values of these constants, experiments must be made with very carefully prepared lime cathodes. Meanwhile, the fact that a large emission of negative corpuscles takes place from a Nernst filament at high temperatures seems to indicate that in experiments with lime-covered cathodes the corpuscles proceed from the oxide, and not from the platinum underneath.

In view of the experiments of Professor Wilson, which have shown that the presence of hydrogen enormously increases the negative leak from platinum, it was thought to be interesting to see if the leak from lime was increased by admitting hydrogen into the apparatus. It was found that this is the case, the leak in hydrogen being many times greater than in helium or oxygen. The effect of introducing a little hydrogen into the apparatus is well shown by some observations taken with a lime cathode which had been used for some days, and the negative leak reduced to even a smaller amount than the values given in Table VI. The following are the values of the negative leak from such a cathode. The gas present was a mixture of helium and oxygen at a pressure of 3.91 millims. The voltage used was $-40$ volts.

**Table VII.**

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Negative leak in amperes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1038</td>
<td>$6 \times 10^{-3}$</td>
</tr>
<tr>
<td>1382</td>
<td>$1.32 \times 10^{-5}$</td>
</tr>
<tr>
<td>1520</td>
<td>$1.13 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

The above numbers are the smallest values of the negative leak at the temperatures given that I ever obtained from a lime cathode. There was no sign of a luminous discharge, even at the highest temperature. After taking these observations, some pure dry hydrogen was let into the apparatus, and the cathode was gently warmed until no further diminution of pressure took place. The resulting gas was a mixture of helium and hydrogen at a pressure of 3.81 millims. A luminous discharge was now noticed when the temperature of the cathode was 1220° C, and the current passing $3.12 \times 10^{-4}$ ampère. The glow in the gas was of a pale blue colour, and appeared only round the edges of the anodes. As the temperature of the cathode was gradually raised and the current passing increased, the glow became more extensive and brighter. At 1465° C. it was very white, and had gathered up into little balls about points on the rim of the anodes. Although the temperature was raised as high as was compatible with the safety of the cathode, and the current passing rose to one-twentith of an ampère, no cathode glow was obtained. The following is a selection from a list of readings obtained in this series of experiments. The readings of the negative leak, at temperatures over 1250° C., were taken with a milliammeter. The
currents measured decreased rapidly as the heating of the cathode was continued, especially at the highest temperatures.

**Table VIII.**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>895</td>
<td>$9.85 \times 10^{-8}$</td>
<td>1380</td>
<td>$4.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>1013</td>
<td>$5.69 \times 10^{-8}$</td>
<td>1465</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>1220</td>
<td>$3.12 \times 10^{-4}$</td>
<td>1535</td>
<td>$2.7 \times 10^{-2}$</td>
</tr>
<tr>
<td>1293</td>
<td>$1.2 \times 10^{-3}$</td>
<td>1620</td>
<td>$4.7 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

It is thus seen that the negative leak from lime is considerably increased by introducing hydrogen gas into the apparatus. H. A. Wilson has shown that hydrogen greatly increases the negative leak from platinum, and has come to the conclusion that the negative leak from platinum in air, or in a vacuum, is almost entirely due to traces of hydrogen in the metal. Wilson reduced the leak to $350,900$ part of that observed by Richardson by taking precautions to remove such traces. It should be mentioned that the currents in the above table are much larger than the negative leaks from platinum in hydrogen obtained by Wilson, and the increase of current cannot be merely due to the effect of the hydrogen upon the platinum.

In another experiment a lime-covered cathode in oxygen at a low pressure (0.002 millim.) with a potential difference of 40 volts gave a negative leak of $4.6 \times 10^{-4}$ ampère at 965°C. On pumping out the oxygen and letting hydrogen into the apparatus and then pumping down to the same pressure as before, the negative leak at temperatures below 900°C was only slightly greater than the leak at the same temperature before the hydrogen was admitted, but at 980°C a faint luminosity was seen in the gas round the cathode, and the negative leak increased without the temperature of the cathode being raised or the difference of potential between the electrodes being altered. This increase was slow for a few minutes, but afterwards became more rapid, and, although the temperature was lowered by putting more resistance in the heating circuit, the negative leak increased to 60 milli-ampères at 885°C. The luminous glow was then quite bright, and filled the whole bulb. It was at first thought that this sudden increase in the negative leak was due to the temperature of the cathode increasing while the discharge was passing, but experiments showed that the temperature of the cathode went up only a few degrees when the electric field was put on, and the leak gradually increased, even though the temperature, as indicated by the thermo-junction, was diminished by putting extra resistance in the heating circuit.

On allowing the cathode to cool down, and then again testing at lower temperatures, it was found that the negative leak at these lower temperatures was now much greater than at the first observations. A measurable leak was obtained at a much lower temperature than before, and the leak at 740°C was $4.6 \times 10^{-4}$ ampère—about $10^4$ times as large as before the glow had been obtained in the discharge tube. On
gradually increasing the temperature the luminous discharge began without any sudden jump in negative leak taking place. I again found that after a certain temperature had been attained and a large current was passing, I could decrease the temperature of the cathode and still get the luminosity to continue and the current to pass.

These experiments show that the negative leak from lime is enormously increased by replacing the gas in the apparatus by hydrogen. With a lime cathode in hydrogen at a pressure of 0.01 millim. I obtained a current of 0.15 ampère per square centimetre at about 900°C, with a difference of potential of 40 volts between the electrodes. This is the largest negative leak I have measured under this potential difference.

The appearance of the luminous discharge is of great interest. Generally the luminosity began round the cathode, and was of a very faint blue colour, getting whiter and more extensive as the temperature of the cathode was increased. When the cathode was unequally covered with lime, the discharge could be seen to radiate out from a few points only. The appearance of the luminosity at any point depends on the current density at that point, and with a very evenly covered cathode large currents could be made to pass through the tube without any signs of a luminous discharge appearing. The appearance of the luminosity also depends on the potential difference between the electrodes. The luminosity could not be obtained with a potential difference of less than 18 volts; and it seems probable that this is the value of the anode fall of potential, for the cathode fall is reduced to a very small amount by the enormous emission of negatively charged corpuscles from the cathode.* As a rule, the luminous discharge gradually became visible, and increased in brightness as the temperature of the cathode was slowly raised. When the luminosity appeared gradually there was no sudden jump in the current passing. This is well illustrated in the curves of fig. 5. On the other hand, when the potential difference between the electrodes was much greater than 40 volts, the luminosity usually appeared quite suddenly and was accompanied by a sudden increase in the negative leak.

The current density obtained with a calcium-covered cathode was, generally, not sufficient to produce a luminous discharge, but on one occasion, on heating the cathode to a much higher temperature than usual, a faint luminosity was observed. This was at about 1520°C, and the current passing through the tube was 4 milliampères. Some interesting experiments were made with this cathode. The temperature was kept constant, and the potential difference between the electrodes was increased from zero by two volts at a time. No luminosity was obtained until a potential difference of 20 volts was reached. With this voltage a pale glow was seen round the anode. This glow increased in brightness as the voltage was increased. With 28 volts the glow left the anode and a pale luminosity appeared round the cathode. At the same time the current passing increased from being too small to

NEGATIVE ELECTRICITY FROM HOT CALCIUM AND FROM LIME.

measure on a milliammeter to 2-8 milli-ampères. These experiments were performed in helium at a pressure of 3-28 millins. Similar results were obtained with lime cathodes. For instance, during the observations recorded in Table VIII, a faint luminosity was noticed round the edges of the anode when the cathode was at 1220° C. This luminosity increased in brightness as the temperature was raised, but with a potential difference of 40 volts the glow was always on the anode only. It was found that at 1410° C, it required a potential difference of 74 volts to give a luminosity round the cathode. With 72 volts there was a very bright anode glow, and the current passing was 4-5 milli-ampères. With 74 volts a brilliant cathode glow was obtained, and the current suddenly increased to 0-5 ampère. Further experiments showed that the difference of potential required to give the cathode glow was less the higher the temperature of the cathode.

The appearance of the luminosity round the cathode has been studied by Professor J. J. Thomson,* who worked in a slightly different manner from that described above. By keeping the temperature of the cathode constant, and very gradually increasing the potential difference by means of a potential divider, Professor Thomson found that the luminosity always appeared quite abruptly and was accompanied by a very rapid increase in the negative leak. In one case, at 1400° C., an increase in the potential difference of \( \frac{1}{100} \) of a volt caused a bright luminosity to appear and increased the current forty-fold. A result similar to this was obtained in the experiments now recorded, when the cathode was at a high temperature and the voltage gradually increased; but if the temperature of the cathode was not too high, a luminosity round the anode was first obtained, and this at a certain potential difference appeared to leave the anodes and surrounded the cathode. This inversion of the appearance of the discharge was accompanied by a large increase in the current.

In the present experiments, when a difference of potential of 40 volts was used and the temperature of the cathode gradually increased, the luminosity appeared sometimes round the anodes and sometimes round the cathode, but always quite gradually, except when a cathode newly covered with lime was used. In this case the luminosity did not appear until a temperature higher than usual had been reached. Under these circumstances it generally appeared quite suddenly and then increased in brightness, although the temperature was kept constant or, in some cases, actually lowered.

Professor Thomson has concluded from his experiments that the gas becomes luminous in consequence of the internal energy of the atoms increasing, under the bombardment of the corpuscles shot out by the cathode, to such an extent that the equilibrium of the atomic system becomes unstable and an explosion occurs. This explosion results in an expulsion of corpuscles and such a shaking up of those left in the atom that they vibrate so vigorously that the energy radiated is sufficient to produce luminosity. When the luminosity appears abruptly, we must imagine that

* Royal Institution Lecture, Friday, January 19, 1906.
just before it occurs the atoms are in such a state that a small change in the electrical conditions is sufficient to cause them to pass from a condition in which they are giving out no light to one in which they are brightly luminous. Now the current passing through the tube increases with the potential difference between the electrodes at a rate which increases rapidly with the temperature of the cathode. The higher the temperature of the cathode, therefore, the greater will be the effect of a given increase in the potential difference, and whereas at low temperatures the appearance of the luminosity may be quite gradual, the same increment in the potential difference may, at high temperatures, make all the difference between no glow and a very bright one, so that the luminosity appears quite suddenly. In the present experiments the gas pressure was so great that the current was never saturated, but increased at an ever increasing rate with the potential difference. Under these circumstances a similar argument will apply to the case of the potential being kept steady and the temperature being gradually increased. With a low potential difference between the electrodes the luminosity would be expected to appear gradually, and with a large potential difference to appear more abruptly. It has already been stated that this is what was observed.

The conditions which decide whether the luminosity appears round the anode or the cathode need further investigation and will form the subject of future research.

(5) Summary of Results, and Conclusion.

The results contained in this paper may be summarised as follows:

1. The experiments with a platinum cathode show that the negative leak from platinum in helium or argon at low pressures is practically the same as in air or oxygen. The variation of the negative leak per square centimetre with the temperature can be expressed by an equation of the form used by H. A. Wilson and by O. W. Richardson, viz., \( x = A \theta e^{-Q/\theta} \), where \( x \) is the current in amperes, \( \theta \) the absolute temperature, and \( Q \) and \( A \) are constants. The values of these constants for a cathode well cleaned with nitric acid in helium at a pressure of 3.236 millims. with a potential difference of 40 volts between the electrodes are \( Q = 1.22 \times 10^8 \), \( A = 1.55 \times 10^6 \).

2. Attention has been drawn to a curious increase in the negative leak caused by allowing the cathode to stand for some time with a very low gas pressure in the apparatus. This increase seems to be caused by the appearance of a dark substance on the surface of the platinum cathode. The substance is probably produced by the action of the mercury vapour on the platinum. It could be driven away by long continued heating of the cathode.

3. The negative leak from calcium is enormously greater than from platinum at the same temperature. As with platinum, the variation of the leak with the temperature can be expressed by the equation \( x = A \theta e^{-Q/\theta} \), but the observed values of the negative leaks from calcium at different temperatures do not so closely agree
NEGATIVE ELECTRICITY FROM HOT CALCIUM AND FROM LIME.

with the values calculated from the equation as is the case with platinum. This is probably due to the greater experimental difficulties attending the use of calcium.

4. On oxidising the calcium on the cathode to lime there is an enormous increase in the negative leak, the leak from a lime cathode at 950° C. being about the same as the leak from calcium at 1400° C. The variation of the negative leak from lime with the temperature roughly obeys the Wilson-Richardson law, but the leak at any fixed temperature is not constant, but gradually decreases with continued heating. This diminution is not due to the same cause as the diminution of the leak from a new platinum wire. In the case of platinum the decrease is caused by the gradual evolution of gas—probably hydrogen—occluded in the metal. With lime it seems to be due either to a spluttering away of the lime from the surface of the platinum or to a change in the nature of the lime itself. In this connection it is interesting to note that a piece of lime subjected to a strong heat glows very brightly at first, but gradually loses this property of glowing when kept continuously at a high temperature. It is not improbable that there is some connection between these two phenomena. Experiments are at present being made with this idea in view.

5. The following are the values of the constants Q and A for platinum, calcium, and lime respectively, obtained from observations of the negative leaks under a potential difference of 40 volts in helium at a pressure of 3·236 millims. :

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Q (calories)</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>$1.22 \times 10^6$</td>
<td>$1.6 \times 10^6$</td>
</tr>
<tr>
<td>Calcium</td>
<td>$7.29 \times 10^4$</td>
<td>$1.7 \times 10^4$</td>
</tr>
<tr>
<td>Lime</td>
<td>$9.58 \times 10^4$</td>
<td>$6.4 \times 10^{11}$</td>
</tr>
</tbody>
</table>

The constant Q represents the work done by a gramme molecular weight of corpuscles in escaping from the surface of the cathode. We see from the numbers given above that this is least in the case of calcium, but owing to the great variations in the different values of Q obtained for lime and for calcium we cannot lay much stress on the difference between the mean values for these two cathodes given above. It would, of course, be expected that the corpuscles would escape more easily from the metal than from the oxide, for we should expect the presence of the electro-negative atom of oxygen in the molecule to act as an attracting force tending to retain the escaping corpuscle.

6. The greatly increased leak obtained by oxidising the calcium cathode into lime is due to an enormous increase in the value of the constant A. Reasons have been given for thinking that this constant cannot be proportional to the number of free corpuscles per cubic centimetre of the cathode as follows from RICHARDSON's theory of the negative leak.

7. The negative leak from lime in hydrogen is much greater than that in air or helium.

8. When the current density through the discharge tube reaches a certain value (only obtained with a calcium or lime cathode) the gas becomes luminous. This
luminosity appears abruptly if the temperature of the cathode is high and the potential difference between the electrodes is gradually increased, or if a large potential difference is used and the temperature of the cathode is gradually raised. The abrupt appearance is accompanied by a large increase of the current passing through the tube. The luminosity cannot be obtained with a potential difference of less than 18 volts, which is probably the value of the anode fall of potential. With small differences of potential (between 18 and 40 volts) the luminosity appears quite gradually as the temperature of the cathode is raised, and without any sudden increase in the current passing.

With low potential differences the luminosity appears sometimes round the anode and sometimes round the cathode. In the former case it may be caused to leave the anode and to appear round the cathode by increasing the potential difference. This inversion of the appearance of the discharge is always accompanied by a large increase in the current.

In conclusion, I wish to say that my best thanks are due to Professor J. J. Thomson for his advice and interest in these experiments, which were carried out at the Cavendish Laboratory.
V. The Gravitational Stability of the Earth.

By A. E. H. Love, F.R.S., Sedleian Professor of Natural Philosophy in the University of Oxford.

Received February 16,—Read March 14, 1907.

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PART I.

INTRODUCTION.

1. If in a gravitating body there occurs a displacement which involves alteration of density, there must be a tendency for the material to move towards the places where the density is increased, and away from the places where the density is diminished. The effect of this tendency, if it were not held in check, would be to accentuate local
alterations of density. In any body the tendency is partially held in check by the
elasticity of the body, and, in particular, by the elastic resistance which the body
offers to compression. If this resistance is sufficiently great, the body is stable, in
spite of the tendency to instability which arises from gravitation. It is important to
determine the conditions of stability for bodies of various forms and constitutions,
with various distributions of density. The problem of the stability of spherically
symmetrical configurations of a quantity of gravitating gas has been investigated by
J. H. Jeans,* and he has drawn from his investigations some interesting conclusions
in regard to the course of evolution of stellar and planetary systems. In a subse-
quent memoir† he proceeded to investigate a similar problem in regard to gravitating
bodies of a more coherent character. A gravitating solid body, such as a planet may
be conceived to be, might exist in a spherical shape with a spherically symmetrical
distribution of density. In the absence of gravitation there could be no question of
instability. The effect of any local condensation would be to set up vibrations, and
the frequency of the vibration of any spherical harmonic type would depend upon the
elasticity of the material. If the resistance of the material to compression is suffi-
ciently high the stability persists in spite of gravitation. There are thus two
competing agencies: gravitation, tending to instability, and the elasticity of the
material, tending to stability. In a general way it is clear that, as the elasticity
diminishes, the frequency of vibration of any type also diminishes; and, if the
frequency can vanish for sufficiently small elasticity, the planetary body possessing
such elasticity cannot continue to exist in the spherically symmetrical configuration.
The problem is to determine the conditions as regards elasticity in which the
instability occurs.

A grave difficulty presents itself at the outset. In the equilibrium configuration
the gravitating planet is in a state of stress; and, in a body of such dimensions as the
Earth, this stress is so great that the total stress existing in the body when it vibrates
cannot be calculated by the ordinary methods of the theory of elasticity. In that
theory it is ordinarily assumed that the body under investigation is in a state so little
removed from one of zero stress that the strain, measured from this state as a zero or
reckoning, is proportional to the stress existing at any instant. In order that this
assumption may be valid, it is necessary that the strain which is calculated by means
of it should be so small that its square may be neglected. Now if we apply the
equations of the ordinary theory to the problem of a solid sphere strained by its own
gravitation, and if we take the sphere to be of the same size and mass as the Earth,
and the material of which it is composed to possess moduluses of elasticity as great as
those of ordinary steel, we find that the strains may be as great as \( \frac{1}{3} \), and thus the
strains are much too great for the assumption to be valid. The initial stress existing

Soc.,' A, vol. 201 (1903), p. 157. Quoted below as "JEANS (1903)."
in the gravitating planet, the stress by which the self-attraction of the body is equilibrated, is much too great to permit of the application of the ordinary theory. The same difficulty presents itself in every problem concerning the elasticity of a gravitating planet, for example, in the problem of tidal deformation or of the stress produced in the interior by the weight of continents. In these problems the difficulty was turned by Lord KELVIN* and Sir G. H. DARWIN† by taking the modulus of compression to be much greater than that of any known material, in other words, by taking the material to be incompressible. Their object was to determine the degree of rigidity which must be assigned to the Earth, and for that object it is permissible to turn the difficulty in this way. When the problem is that of gravitational instability this artifice cannot be adopted, because the whole question is that of the degree of compressibility which is admissible if the gravitating planet is to be stable in a spherically symmetrical configuration. The artifice adopted by JEANS (1903) consisted in annulling the initial stress by introducing an imagined external field of force to equilibrate the self-attraction of the planet.

The problem thus posed is an artificial one, which may, nevertheless, throw light on the actual problem. When the initial configuration is taken to be one of uniform density, the analysis of the problem is of the same kind as that which presents itself in the problem of the vibrations of an elastic sphere, a problem which has been worked out very completely by H. LAMB.‡ The determination of the effect produced by gravitation in lowering the frequencies of the various modes of vibration is reduced to a question of troublesome analytical computation. JEANS worked out the problem on the basis of the ordinary theory of elasticity, using the elastic constants $\lambda$ and $\mu$ of LAME. The constant $\mu$ is the modulus of rigidity, and the constant $\lambda$ is such that $\lambda + \frac{2}{3}\mu$ is the modulus of compression. In the case of the Earth the values of these constants can be inferred from the observed rates of propagation of the various types of disturbance which are perceived as earthquake shocks. He concluded that, when the proper values are attributed to these constants, the Earth must be held to be in a state far removed from one of gravitational instability; but he suggested that, if the resistance to compression was at one time considerably smaller than it is now, the spherically symmetrical configuration would then have been unstable; and he held that there are traces of the instability in the distribution of land and water on the surface of the globe.

The actual problem differs from this artificial problem in the mode of balancing of the internal gravitation. Lord RAYLEIGH§ has proposed a method of meeting the difficulty as to initial stress. He proposed to consider the stress in the vibrating

* See, in particular, KELVIN and TAIT's 'Natural Philosophy,' Part II., §§ 833–846, Cambridge, 1883.
gravitating sphere as compounded of two stress-systems: a hydrostatic pressure by which gravitation would be balanced if the sphere were in equilibrium, and an additional stress. He proposed to measure the strain, not from the unattainable state of zero stress, but from the equilibrium state; and he proposed to take the additional stress to be determined in terms of the strain by those equations which are commonly used in the theory of elasticity. To simplify the problem he proposed to take the material in the equilibrium state to be homogeneous and the elasticity to be isotropic, so that the equations connecting the additional stress and the strain are of the same form as the ordinary stress-strain relations of isotropic elasticity. In justification of the proposed procedure he brought forward theoretical considerations founded upon the general theory of energy, and other evidence drawn from an interpretation of the experimental results in regard to the behaviour of elastic solid bodies. It is not too much to say that all the evidence there is, is just as strong in favour of Lord Rayleigh’s proposed method as it is in favour of Hooke’s law, in the sense in which that law is applied in the ordinary theory. The only objection which can be raised against the method, an objection mentioned by Lord Rayleigh himself, is that the body to be treated is certainly not homogeneous, and possibly not isotropic. When the proposed method is adopted, the density and the moduluses of elasticity must be taken to have their mean values. The justification for treating the values of these quantities at any point as equal to the mean values, is that it is advisable in the first instance to work out the simplest case.*

In the first part of this paper the mathematical problem proposed by Lord Rayleigh is worked out; and the conclusion is drawn that the effective moduluses of elasticity of the Earth, in its present state, are sufficiently great for a homogeneous spherical configuration to be thoroughly stable. The second part of the paper is devoted to developing the consequences of supposing that the elasticity of the material of the Earth was once much less than it is at present.

Statement of the Mathematical Problem.

2. We have before us a perfectly definite mathematical problem, which may be stated as follows:—A sphere of radius \( a \), and of uniform density \( \rho_0 \), is in equilibrium under its own gravitation, and the stress within it is hydrostatic pressure of amount \( p_0 \) at a distance \( r \) from the centre. When any small disturbance takes place, so that

* It may be observed that the method advocated by Lord Rayleigh is the same, except for a slight modification, as that which was used in the second edition of my "Treatise on the Mathematical Theory of Elasticity," Cambridge, 1906, in the discussion of the statical problem of a gravitating sphere held strained by external disturbing forces. The modification consists in the assumption, which was there made, that the material might be treated as incompressible. If this assumption is not made, the analysis becomes much more difficult. An earlier indication of the method will be found in a paper by J. Larmor, Cambridge, 'Proc. Phil. Soc.,' 9, 1898, p. 183.
the particle which was initially at \((x, y, z)\) is displaced to \((x+u, y+v, z+w)\), the stress is specified by six stress-components \(X_x, Y_y, Z_z, Y_z, Z_z, X_x\), and these are connected with the initial pressure \(p_0\) and the displacement \((u, v, w)\) by the formulae

\[
\begin{align*}
X_x &= -p_0 + \lambda \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) + 2\mu \frac{\partial u}{\partial x}, \\
Y_y &= -p_0 + \lambda \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) + 2\mu \frac{\partial v}{\partial y}, \\
Z_z &= -p_0 + \lambda \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) + 2\mu \frac{\partial w}{\partial z}, \\
Y_z &= \mu \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right), \\
Z_x &= \mu \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right), \\
X_y &= \mu \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right), \\
\end{align*}
\]

where \(\lambda\) and \(\mu\) are constants. It is required to form the equations of vibration, and to solve them, so as to determine the character of the modes of vibration and the equation for the frequencies, and, in particular, to ascertain the relations which must hold among the quantities \(\lambda, \mu, p_0, \alpha\) in order that any frequency may be reduced to zero. We proceed to express this problem in terms of a system of differential equations which hold at all points of the body, and a system of special conditions which hold at all points of the undisturbed surface.

3. In the equilibrium state the potential \(V_0\) at any point is given by the equation

\[
V_0 = \frac{2}{3} \pi \gamma r_0 (3a^2 - r^2),
\]

where \(\gamma\) is the constant of gravitation. The equation of equilibrium is

\[
-\frac{1}{\rho_0} \frac{\partial p_0}{\partial r} + \frac{\partial V_0}{\partial r} = 0,
\]

or

\[
\frac{\partial p_0}{\partial r} = -\frac{2}{3} \pi \gamma p_0 r.
\]

Since \(p_0 = 0\) at the surface \(r = a\), the value of \(p_0\) at any point is given by the equation

\[
p_0 = \frac{2}{3} \pi \gamma p_0^2 (a^2 - r^2).
\]

When the sphere vibrates, the equations of motion are three equations of the type

\[
\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = \rho \frac{\partial V}{\partial x} + \frac{\partial X_x}{\partial x} + \frac{\partial X_x}{\partial y} + \frac{\partial Z_z}{\partial z},
\]

where \(\rho\) is the density, and \(V\) the potential, in the disturbed state. In the left-hand members of these equations we may ignore the distinction between \(\rho\) and \(\rho_0\). In the right-hand members we may put

\[
\rho = \rho_0 (1 - \Delta),
\]

where \(\Delta\) is a small quantity.
where \( \Delta \) is the dilatation expressed by the formula
\[
\Delta = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}.
\] (8)
Further, we may put
\[
V = V_0 + W,
\] (9)
where \( W \) is the additional potential due to concentration of density at internal points, and to displacement of mass across the initial bounding surface. We may neglect terms of the type \( \rho_0 \Delta \partial W/\partial x \). When we substitute for \( X \), . . . from equations (1), and make these simplifications, the equation (6) becomes
\[
\rho_0 \frac{\partial^2 u}{\partial t^2} = \rho_0 (1 - \Delta) \frac{\partial V_0}{\partial x} + \rho_0 \frac{\partial W}{\partial x} - \frac{\partial \rho_0}{\partial x} + (\lambda + \mu) \frac{\partial \Delta}{\partial x} + \mu \nabla^2 u.
\]
On omitting the terms which cancel each other in virtue of equation (3), we have the first of the three equations (10) below. The remaining two of these equations are obtained in the same way. Thus we have the equations of vibratory motion in the forms
\[
\begin{align*}
\rho_0 \frac{\partial^2 u}{\partial t^2} &= (\lambda + \mu) \frac{\partial \Delta}{\partial x} + \mu \nabla^2 u + \frac{4}{3} \pi \gamma \rho_0^2 x \Delta + \rho_0 \frac{\partial W}{\partial x}, \\
\rho_0 \frac{\partial^2 v}{\partial t^2} &= (\lambda + \mu) \frac{\partial \Delta}{\partial y} + \mu \nabla^2 v + \frac{4}{3} \pi \gamma \rho_0^2 y \Delta + \rho_0 \frac{\partial W}{\partial y}, \\
\rho_0 \frac{\partial^2 w}{\partial t^2} &= (\lambda + \mu) \frac{\partial \Delta}{\partial z} + \mu \nabla^2 w + \frac{4}{3} \pi \gamma \rho_0^2 z \Delta + \rho_0 \frac{\partial W}{\partial z}.
\end{align*}
\] (10)
In addition to these equations we have the equation connecting the potential with the density in the form
\[
\nabla^2 W = 4 \pi \gamma \rho_0 \Delta.
\] (11)
The system of equations (10) and (11) are the differential equations of the problem.*

4. Besides satisfying the differential equations (10) and (11), the additional potential \( W \) and the components of displacement \( u, v, w \) must also satisfy certain conditions at the surface \( r = a \). Let \( U \) denote the radial component of displacement, so that
\[
Ur = xu + yv + zw,
\] (12)
and let \( U_a \) denote the value of \( U \) at \( r = a \). The potential \( W \) is that due to a volume distribution of density \(-\rho_0 \Delta\), together with that due to a superficial distribution \( \rho_0 U_a \)

* In the problem as formulated by Jeans, when the self-attraction of the body is balanced by an external field of force, the equations of vibratory motion differ from those which are obtained here by the omission of the terms such as \( \frac{4}{3} \pi \gamma \rho_0^2 x \Delta \). In Lord Rayleigh's paper already cited, the equations given by Jeans are discussed in accordance with the analysis which was developed by Lamb in the paper on the vibrations of a sphere.
on the surface \( r = a \). By the method of spherical harmonics we can, when \( W \) is known, write down the expression for the function \( W^{(0)} \) which is the potential at external points of the same distribution. The surface characteristic equation gives

\[
\left( \frac{\partial W^{(0)}}{\partial r} \right)_{r=a} - \left( \frac{\partial W}{\partial r} \right)_{r=a} = -4\pi \gamma \rho_a U_a. \quad (13)
\]

This is one of the conditions which must be satisfied at the surface \( r = a \). To obtain the other conditions which must be satisfied at this surface, we observe that the disturbed surface \( r = a + U_a \) is free from traction. If \( l, m, n \) denote the direction cosines of the outward drawn normal to this surface we have three equations of the type

\[
lX_x + mX_y + nZ_z = 0,
\]

which hold at the surface \( r = a + U_a \). If in this equation we substitute for \( X, \ldots \) from equations (1), we see that in the terms containing \( u, \ldots \) we may replace \( l, \ldots \) by the approximate values \( x/r, y/r, z/r \). The only term which does not contain \( u, \ldots \) is the term \(-lp_0\) arising from \(-lX_x\). Now \( p_0 \) vanishes at \( r = a \), and therefore at \( r = a + U_a \) we have

\[
p_0 = U_a \left( \frac{\partial p_0}{\partial r} \right)_{r=a}
\]

to the first order in \( u, v, w \). Hence in this term also we may replace \( l \) by \( x/r \). On substituting for \( p_0 \) from (5) we find that the equation

\[
\frac{4}{3} \pi \gamma \rho_a^2 x U + \frac{x}{r} \left( \frac{\lambda \Delta + 2\mu}{\partial x} \frac{\partial u}{\partial x} + \frac{\mu}{\partial y} \frac{\partial v}{\partial y} + \frac{\mu}{\partial z} \frac{\partial w}{\partial z} \right) = 0
\]

must hold at the surface \( r = a \). By an easy transformation this equation becomes the first of the three equations written in (14) below. The remaining two of these equations are obtained in the same way. The equations which must hold at the surface \( r = a \) are therefore equation (13) and the equations

\[
\begin{align*}
\frac{\lambda}{\mu} & \frac{x \Delta + \frac{\partial}{\partial x} (U r) + r \frac{\partial u}{\partial r}}{-u + \frac{4}{3} \pi \gamma \rho_a^2 x U r} = 0, \\
\frac{\lambda}{\mu} & \frac{y \Delta + \frac{\partial}{\partial y} (U r) + r \frac{\partial v}{\partial r}}{-v + \frac{4}{3} \pi \gamma \rho_a^2 y U r} = 0, \\
\frac{\lambda}{\mu} & \frac{z \Delta + \frac{\partial}{\partial z} (U r) + r \frac{\partial w}{\partial r}}{-w + \frac{4}{3} \pi \gamma \rho_a^2 z U r} = 0.
\end{align*}
\quad (14)
\]

These equations can be interpreted in the statement that the traction on the mean sphere is a pressure equal to the weight per unit of area of the material heaped up to form the inequality \( U_a \).
5. We shall now suppose that the system executes a normal, or principal, vibration of frequency \( p/2\pi \), or, in other words, that every component of displacement is proportional to the same simple harmonic function of \( pt \). The equations of vibratory motion become three equations of the type

\[
(\lambda + \mu) \frac{\partial^2 \Delta}{\partial x^2} + \mu \nabla^2 u + \rho_0 p^2 u + \frac{4}{3} \pi \gamma \rho_0^2 x \Delta + \rho_0 \frac{\partial W}{\partial x} = 0, \quad \ldots \quad (15)
\]

where \( W \) satisfies the equation (11). The solutions of this system of equations (11) and (15) must be adjusted to satisfy the conditions (13) and (14) at \( r = \alpha \). These conditions can be satisfied only if \( p \) has one or other of a certain infinite set of values, which are the roots of the frequency equation. The problem of gravitational instability is solved when we find the conditions that one of the values of \( p \) may be zero.

**Solution of the Differential Equations by Means of Spherical Harmonics.**

6. We introduce the notation

\[
\frac{\rho_0^2}{\lambda + 2\mu} = h^2, \quad \frac{\rho_0^2}{\mu} = k^2, \quad \frac{4}{3} \pi \gamma \rho_0^2 = s^2, \quad W = 4\pi \gamma \rho_0 E. \quad \ldots \quad (16)
\]

The equations of motion (15) become three equations of the type

\[
(\nabla^2 + h^2) u + \left( \frac{k^2}{h^2} - 1 \right) \frac{\partial \Delta}{\partial x} + \frac{k^2}{h^2} s^2 \left( x \Delta + 3 \frac{\partial E}{\partial x} \right) = 0, \quad \ldots \quad (17)
\]

and the equation \( \nabla^2 W = 4\pi \gamma \rho_0 \Delta \) becomes

\[
\nabla^2 E = \Delta; \quad \ldots \quad \ldots \quad (18)
\]

in these equations \( \Delta \) stands for

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}.
\]

By differentiating the left-hand members of the equations of type (17) with respect to \( x, y, z \), respectively, adding the results, and simplifying by means of (18), we obtain the equation

\[
(\nabla^2 + h^2) \Delta + 6s^2 \Delta + s^2 r \frac{\partial \Delta}{\partial r} = 0. \quad \ldots \quad \ldots \quad (19)
\]

The method of solution of the problem is this:—We seek first a solution of the equation (19) in which \( \Delta \) has the form

\[
\Delta = \Sigma f_n(r) \omega_n, \quad \ldots \quad \ldots \quad (20)
\]

where \( \omega_n \) is a spherical solid harmonic of positive integral degree \( n \), and \( f_n \) is a
function of \( r \) which is such that \( r^p f_n \) is finite at all points within \( r = \alpha \), including the origin \( r = 0 \). We seek next to determine \( E \) in the form

\[
E = \Sigma [E_n(r) \omega_n + F_n], \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (21)
\]

where \( E_n(r) \) is a certain function of \( r \) which is such that \( r^p E_n \) is finite at all points within \( r = \alpha \), including the origin \( r = 0 \), and \( F_n \) is a spherical solid harmonic of degree \( n \). The equations of motion of type (15) then become three equations of the type

\[
(\nabla^2 + k^2) u + \left(\frac{k^2}{\lambda^2} - 1\right) \Sigma \left\{ \frac{\partial}{\partial x} (f_n \cdot \omega_n) \right\} + \frac{k^2}{\lambda^2} s^2 x \Sigma (f_n \cdot \omega_n)
\]

\[
+ \frac{3k^2}{\lambda^2} s^2 \Sigma \left\{ \frac{\partial}{\partial x} (E_n \cdot \omega_n) \right\} + \frac{3k^2}{\lambda^2} s^2 \Sigma \left( \frac{\partial F_n}{\partial x} \right) = 0, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (22)
\]

in which we must have

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = \Sigma (f_n \cdot \omega_n). \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (23)
\]

It appears on trial that we can obtain a solution in which

\[
u = u_1 + u_2 + u_3, \quad v = v_1 + v_2 + v_3, \quad w = w_1 + w_2 + w_3, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (24)
\]

where \( u_1, v_1, w_1 \) satisfy the system of equations

\[
(\nabla^2 + k^2) u_1 \left(\frac{k^2}{\lambda^2} - 1\right) \Sigma \left\{ \frac{\partial}{\partial x} (f_n \cdot \omega_n) \right\} + \frac{k^2}{\lambda^2} s^2 x \Sigma (f_n \cdot \omega_n)
\]

\[
+ \frac{3k^2}{\lambda^2} s^2 \Sigma \left\{ \frac{\partial}{\partial x} (E_n \cdot \omega_n) \right\} = 0, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (25)
\]

also \( u_2, v_2, w_2 \) satisfy the system of equations

\[
(\nabla^2 + k^2) u_2 + \frac{3k^2}{\lambda^2} s^2 \Sigma \left( \frac{\partial F_n}{\partial x} \right) = 0, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (26)
\]

\[
\frac{\partial u_2}{\partial x} + \frac{\partial v_2}{\partial y} + \frac{\partial w_2}{\partial z} = 0;
\]

and \( u_3, v_3, w_3 \) are a complementary solution of the system of equations

\[
(\nabla^2 + k^2) u_3 = 0, \quad (\nabla^2 + k^2) v_3 = 0, \quad (\nabla^2 + k^2) w_3 = 0,
\]

\[
\frac{\partial u_3}{\partial x} + \frac{\partial v_3}{\partial y} + \frac{\partial w_3}{\partial z} = 0.
\]

7. The sets of functions \( u_1, v_1, w_1 \) and \( u_2, v_2, w_2 \) can be any particular solutions.
of the systems of equations (25) and (26). It appears on trial that \( u_1, v_1, w_1 \) can have the forms

\[
\begin{align*}
u_1 & = \Sigma \left[ P_n(r) \frac{\partial \omega_n}{\partial x} + Q_n(r) y^{2n+3} \frac{\partial}{\partial x} \left( \frac{\omega_n}{y^{2n+1}} \right) \right], \\
v_1 & = \Sigma \left[ P_n(r) \frac{\partial \omega_n}{\partial y} + Q_n(r) x^{2n+3} \frac{\partial}{\partial y} \left( \frac{\omega_n}{x^{2n+1}} \right) \right], \\
w_1 & = \Sigma \left[ P_n(r) \frac{\partial \omega_n}{\partial z} + Q_n(r) z^{2n+3} \frac{\partial}{\partial z} \left( \frac{\omega_n}{z^{2n+1}} \right) \right],
\end{align*}
\]  

(28)

where \( P_n(r) \) and \( Q_n(r) \) are certain functions of \( r \). Also it is clear that \( u_2, v_2, w_2 \) can have the forms

\[
\begin{align*}
u_2 & = - \frac{3s^2}{h^2} \Sigma \left( \frac{\partial F_n}{\partial x} \right), \\
v_2 & = - \frac{3s^2}{h^2} \Sigma \left( \frac{\partial F_n}{\partial y} \right), \\
w_2 & = - \frac{3s^2}{h^2} \Sigma \left( \frac{\partial F_n}{\partial z} \right).
\end{align*}
\]  

(29)

Further, the forms of \( u_3, v_3, w_3 \) are known from the analysis of the problem of the vibrating sphere which is free from gravitation. We have

\[
\begin{align*}u_3 & = \Sigma \left[ \psi_n(kr) \left( y \frac{\partial \chi_n}{\partial z} - z \frac{\partial \chi_n}{\partial y} \right) + \psi_{n-1}(kr) \frac{\partial \phi_n}{\partial x} - \frac{n}{n+1} \psi_{n+1}(kr) k^2 r^{2n+3} \frac{\partial}{\partial x} \left( \frac{\phi_n}{r^{2n+1}} \right) \right], \\
\phi_n(kr) & = \left( \frac{1}{kr} \right)^n \left( \sin kr \right),
\end{align*}
\]  

(30)

where \( \chi_n \) and \( \phi_n \) are spherical solid harmonics of degree \( n \), and the expressions for \( v_3, w_3 \) are to be obtained from the expression for \( u_3 \) by cyclical interchanges of the letters \( x, y, z \). It appears that to a single term \( f_n \omega_n \) in the expression for \( \Delta \) there corresponds a definite term \( F_n \) in the expression for \( E \). Further, when we form the boundary conditions, it appears that the terms of \( u_3, v_3, w_3 \) which contain \( \chi_n \) represent a free vibration, and the frequency of this vibration is determined by the same equation as if the sphere were free from gravitation. Also it appears that to any term \( f_n \omega_n \) in the expression for \( \Delta \) there corresponds a definite function \( \phi_n \) in the expression for \( u_3, v_3, w_3 \). The solution expressed by a single term \( f_n \omega_n \) of \( \Delta \) and the corresponding terms of \( (u_1, v_1, w_1), (u_2, v_2, w_2) \) and \( (u_3, v_3, w_3) \) determines a normal mode of vibration. We shall therefore omit \( \chi_n \), and reduce all the summations to typical terms.

8. If in the equation

\[
(\nabla^2 + h^2) \Delta + 6s^2 \Delta + s^2 r \frac{\partial \Delta}{\partial r} = 0
\]  

(19 bis)

we put \( f_n(r) \omega_n \) for \( \Delta \), we find that \( f_n(r) \) must satisfy the equation

\[
\begin{align*}\frac{d^2 f_n}{dr^2} + \frac{2}{r} \frac{df_n}{dr} + 2n \frac{df_n}{dr} + s^2 \left( \frac{d^2 f_n}{dr^2} + n f_n \right) + (h^2 + 6s^2) f_n & = 0, \\
\frac{d^2 f_n}{dr^2} + \left\{ \frac{2(n+1)}{r} + s^2 r \right\} \frac{df_n}{dr} + (h^2 + (n+6) s^2) f_n & = 0.
\end{align*}
\]  

(32)
This equation is a linear differential equation of the second order; and the forms of the coefficients show that the point \( r = 0 \) is a critical point, and that there is no other critical point at any finite value of \( r \). If we seek a solution in series of the form

\[
f_n = a_0 r^m + a_1 r^{m+1} + a_2 r^{m+2} + \ldots,
\]

we find the "indicial equation"

\[
m(m-1) + 2(n+1)m = 0,
\]

from which either \( m = 0 \), or \( m = -(2n+1) \). We must take the series for which \( m = 0 \), because \( r^m f_n \) must be finite at \( r = 0 \). Further, the form of the equation shows that this series contains even powers of \( r \) only. We assume, therefore, for \( f_n \) the form

\[
f_n = A[1 + a_2 r^2 + a_4 r^4 + \ldots + a_{2k} r^{2k} + \ldots],
\]

where \( A \) is an arbitrary constant, and then we find the sequence equation

\[
a_{2k+2} (2\kappa+2) (2\kappa+1+2n+2) + a_{2k} \{ h^2 + (n+6) s^2 + 2\kappa s^2 \} r^4 = 0,
\]

or

\[
a_{2k+2} = -a_{2k} \frac{h^2 + (n+6+2\kappa) s^2}{(2\kappa+2) (2\kappa+2n+3)}.
\]

Hence we have

\[
f_n = A \left[ 1 - \frac{h^2 + (n+6) s^2}{2 \cdot (2n+3)} r^4 + \frac{\{ h^2 + (n+6) s^2 \} \{ h^2 + (n+8) s^2 \} r^6 \ldots}{2 \cdot 4 \cdot (2n+3) (2n+5)} \right]
\]

\[
\left( -r^2 \left[ \frac{h^2 + (n+6) s^2}{2 \cdot 4 \cdot 6 (2n+3) (2n+5)} \left\{ h^2 + (n+8) s^2 \right\} \ldots \left\{ h^2 + (n+2\kappa+4) s^2 \right\} r^6 \ldots \right] \right) .
\]

The series is convergent and represents the function \( f_n \) for all finite values of \( r \).

9. We must next determine the function \( E_n (r) \) from the equation

\[
\nabla^2 (E_n \omega_n) = f_n \omega_n,
\]

or

\[
\frac{d^2 E_n}{dr^2} + \frac{2(n+1)}{r} \frac{dE_n}{dr} = f_n,
\]

or

\[
\frac{d}{dr} \left[ r \frac{dE_n}{dr} + (2n+1) E_n \right] = rf_n.
\]

We introduce an intermediate function \( \theta_n (r) \) by the equation

\[
\theta_n = r \frac{dE_n}{dr} + (2n+1) E_n.
\]

Then

\[
\theta_n = \int rf_n dr
\]

\[
= C + A \left[ \frac{1}{2} r^2 - \frac{h^2 + (n+6) s^2}{2 \cdot 4 \cdot (2n+3)} r^4 + \frac{\{ h^2 + (n+6) s^2 \} \{ h^2 + (n+8) s^2 \} r^6 \ldots}{2 \cdot 4 \cdot 6 (2n+3) (2n+5)} \right],
\]
where $C$ is constant of integration. Then we have
\[
\frac{d}{dr} \left( r^{2n+1}E_n \right) = r^{2n} \theta_n,
\]
and therefore
\[
E_n = \frac{C'}{r^{2n+1}} + \frac{C}{2n+1} + A \left[ \frac{r^2}{2 \cdot (2n+3)} - \frac{(h^2 + (n+6) s^2) r^4}{2 \cdot 4 \cdot (2n+3) (2n+5)} + \ldots \right],
\]
where $C'$ is a constant of integration. Since $r^n E_n$ is finite at $r = 0$, the constant $C'$ must be zero; but the constant $C$ is in our power, and we may choose it in any way that is convenient. The term contributed to $E$ by $C$ is $(2n+1)^{-1} C \omega_n$, which satisfies Laplace's equation, and therefore any change in the chosen value of $C$ is equivalent to borrowing a term of $F_n$ to make up a term of $E_n \omega_n$.

Now the series
\[
1 - \frac{h^2 + (n+4) s^2}{2 \cdot (2n+1)} r^2 + \frac{(h^2 + (n+4) s^2) (h^2 + (n+6) s^2)}{2 \cdot 4 \cdot (2n+1) (2n+3)} r^4 - \ldots
\]
satisfies the equation
\[
\left[ \frac{d^2}{dr^2} + \left( \frac{2n}{r} + s^2 r \right) \frac{d}{dr} + \{h^2 + (n+4) s^2\} \right] \left( \frac{1 - \frac{h^2 + (n+4) s^2}{2 (2n+1)} r^2 + \ldots}{2 \cdot 4 \cdot (2n+1)} \right) = 0;
\]
and therefore, if we take for $C$ the value
\[
C = -\frac{2n+1}{h^2 + (n+4) s^2} A,
\]
the function $\theta_n$ satisfies the equation
\[
\frac{d^2 \theta_n}{dr^2} + \left( \frac{2n}{r} + s^2 r \right) \frac{d \theta_n}{dr} + \{h^2 + (n+4) s^2\} \theta_n = 0. \ldots \ldots (36)
\]

We shall choose this value for $C$, and thus we shall have
\[
\theta_n = A \left[ -\frac{2n+1}{h^2 + (n+4) s^2} \right] + \frac{1}{2} r^2 - \frac{h^2 + (n+6) s^2}{2 \cdot 4 \cdot (2n+3)} r^4 + \ldots
\]
\[
(\ldots) + \frac{(h^2 + (n+6) s^2) (h^2 + (n+8) s^2) (h^2 + (n+2\kappa+2) s^2)}{2 \cdot 4 \cdot 2\kappa (2n+3) (2n+5) \ldots (2n+2\kappa-1)} r^{2\kappa} \ldots\ldots (37)
\]
and
\[
E_n = A \left[ -\frac{1}{h^2 + (n+4) s^2} \right] + \frac{r^2}{2 \cdot (2n+3)} - \frac{(h^2 + (n+6) s^2) r^4}{2 \cdot 4 \cdot 2\kappa (2n+3) (2n+5) \ldots (2n+2\kappa+1)} + \ldots
\]
\[
(\ldots) + \frac{(h^2 + (n+6) s^2) (h^2 + (n+8) s^2) (h^2 + (n+2\kappa+2) s^2)}{2 \cdot 4 \cdot 2\kappa (2n+3) (2n+5) \ldots (2n+2\kappa+1)} r^{2\kappa} \ldots\ldots (38)
\]
The function $E_n$ satisfies the equation
\[
\frac{d^2 E_n}{dr^2} + \left( \frac{2 \cdot (n+1) r^2}{r} + s^2 r \right) \frac{dE_n}{dr} + \{h^2 + (n+4) s^2\} E_n = 0. \ldots \ldots (39)
\]
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It will be convenient presently to have observed that the equation derived from this one by differentiating the left-hand member with respect to \( r \) can be written

\[
\left[ \frac{d^2}{dr^2} + \left( \frac{2(n+2)}{r} + s^2 r \right) \frac{d}{dr} + \left[ k^2 + (n+6) s^2 \right] \right] \left( \frac{1}{r} \frac{dE_n}{dr} \right) = 0. \quad (40)
\]

10. The forms of \( u_2, v_2, w_2 \) and \( u_3, v_3, w_3 \) have been put down and it remains to determine \( u_1, v_1, w_1 \). We have a system of three equations of the type

\[
\left( \nabla^2 + k^2 \right) u_1 + \left( \frac{k^2}{h^2} - 1 \right) \left( f_n + \frac{r}{2n+1} \frac{df_n}{dr} \right) + \frac{k^2}{h^2} s^2 \left( \frac{1}{r} \frac{dE_n}{dr} \right) + \frac{3k^2}{h^2} s^2 \left( \frac{1}{r} \frac{dE_n}{dr} \right) = 0. \quad (41)
\]

We express \( x\omega_n \) in the form

\[
x\omega_n = \frac{r^2}{2n+1} \left\{ \frac{\partial \omega_n}{\partial x} - \left( \frac{\omega_n}{(2n+1)} \right) \right\}, \quad \ldots \ldots \quad (42)
\]

and then the above equation becomes

\[
\left( \nabla^2 + k^2 \right) u_1 = -\frac{\partial \omega_n}{\partial x} \left[ \left( \frac{k^2}{h^2} - 1 \right) \left( f_n + \frac{r}{2n+1} \frac{df_n}{dr} \right) + \frac{k^2}{h^2} s^2 \left( \frac{1}{r} \frac{dE_n}{dr} \right) \right] + \frac{1}{2n+1} \frac{r^{2n+3}}{h^2} \frac{\partial}{\partial x} \left[ \left( \frac{k^2}{h^2} - 1 \right) \frac{1}{r} \frac{df_n}{dr} + \frac{k^2}{h^2} s^2 \left( \frac{1}{r} \frac{dE_n}{dr} \right) \right]. \quad (43)
\]

We seek solutions of the system of three equations of this type in the forms of the type

\[
u_1 = P_n \frac{\partial \omega_n}{\partial x} + Q_n r^{2n+3} \frac{\partial}{\partial x} \left( \frac{\omega_n}{(2n+1)} \right), \quad \ldots \ldots \quad (44)
\]

in which \( P_n \) and \( Q_n \) are functions of \( r \). We find

\[
\left( \nabla^2 + k^2 \right) u_1 = \left[ \frac{d^2 P_n}{dr^2} + \frac{2n}{r} \frac{dP_n}{dr} + k^2 P_n \right] \frac{\partial \omega_n}{\partial x} + \left[ \frac{d^2 Q_n}{dr^2} + \frac{2(n+2)}{r} \frac{dQ_n}{dr} + k^2 Q_n \right] r^{2n+3} \frac{\partial}{\partial x} \left( \frac{\omega_n}{(2n+1)} \right).
\]

Hence the assumed forms can be adjusted to satisfy the equations if \( P_n \) and \( Q_n \) satisfy the linear equations

\[
\frac{d^2 P_n}{dr^2} + \frac{2n}{r} \frac{dP_n}{dr} + k^2 P_n = -\left( \frac{k^2}{h^2} - 1 \right) \left( f_n + \frac{r}{2n+1} \frac{df_n}{dr} \right) - \frac{k^2}{h^2} s^2 \left( \frac{r^3}{2n+1} f_n + 3E_n + \frac{3r}{2n+1} \frac{dE_n}{dr} \right), \quad \ldots \ldots \quad (45)
\]

\[
\frac{d^2 Q_n}{dr^2} + \frac{2(n+2)}{r} \frac{dQ_n}{dr} + k^2 Q_n = \frac{1}{2n+1} \left\{ \left( \frac{k^2}{h^2} - 1 \right) \frac{1}{r} \frac{df_n}{dr} + \frac{k^2}{h^2} s^2 \left( f_n + \frac{3}{r} \frac{dE_n}{dr} \right) \right\}. \quad (46)
\]
The right-hand members of these equations can be simplified by introducing the functions \( \theta_n \) and \( r^{-1} dE_n/dr \). We have

\[
f_n + \frac{r}{2n+1} \frac{df_n}{dr} = \frac{1}{r} \frac{d \theta_n}{dr} + \frac{r}{2n+1} \frac{d}{dr} \left( \frac{1}{r} \frac{d \theta_n}{dr} \right)
\]

and

\[
\frac{r^2}{2n+1} f_n + 3E_n + \frac{3r}{2n+1} \frac{dE_n}{dr} = \frac{1}{2n+1} \left( r \frac{d \theta_n}{dr} + 3 \theta_n \right);
\]

and thus the equation for \( P_n \) becomes

\[
\frac{d^2 P_n}{dr^2} + \frac{2n}{r} \frac{dP_n}{dr} + k^2 P_n
\]

\[
= \frac{1}{2n+1} \left( \frac{d^2 \theta_n}{dr^2} + \frac{2n}{r} \frac{d \theta_n}{dr} \right) - \frac{1}{2n+1} \frac{k^2}{h^2} \left( \frac{d^2 \theta_n}{dr^2} + \frac{2n}{r} \frac{d \theta_n}{dr} + s^2 r \frac{d \theta_n}{dr} + 3s^2 \theta_n \right)
\]

\[
= \frac{1}{2n+1} \left( \frac{d^2 \theta_n}{dr^2} + \frac{2n}{r} \frac{d \theta_n}{dr} + k^2 \theta_n \right) - \frac{1}{2n+1} \left[ \frac{k^2 \theta_n}{h^2} - \frac{k^2}{h^2} \right] \left( \frac{h^2 + (n+4)s^2}{\theta_n} + 3 \frac{k^2}{h^2} s^2 \theta_n \right)
\]

by the equation (36). Hence we have

\[
P_n = \frac{\theta_n}{2n+1} + P'_n,
\]

where \( P'_n \) satisfies the equation

\[
\frac{d^2 P'_n}{dr^2} + \frac{2n}{r} \frac{dP'_n}{dr} + k^2 P'_n = \frac{n+1}{2n+1} \frac{k^2}{h^2} s^2 \theta_n
\]

(48)

Again, we have

\[
\frac{1}{r} \frac{d}{dr} \left( \frac{df_n}{dr} \right) = \frac{1}{r} \frac{d}{dr} \left[ \frac{d^2 E_n}{dr^2} + \frac{2(n+1)}{r} \frac{dE_n}{dr} \right]
\]

\[
= \frac{1}{r} \frac{d}{dr} \left[ \frac{d}{dr} \left( \frac{1}{r} \frac{dE_n}{dr} \right) + \frac{2(n+1)}{r} \frac{dE_n}{dr} \right]
\]

\[
= \frac{d^2}{dr^2} \left( \frac{1}{r} \frac{dE_n}{dr} \right) + \frac{2(n+2)}{r} \frac{d}{dr} \left( \frac{1}{r} \frac{dE_n}{dr} \right)
\]

and

\[
f_n + \frac{3}{r} \frac{dE_n}{dr} = \frac{d^2 E_n}{dr^2} + \frac{2(n+1)}{r} \frac{dE_n}{dr} + \frac{3}{r} \frac{dE_n}{dr}
\]

\[
= r \frac{d}{dr} \left( \frac{1}{r} \frac{dE_n}{dr} \right) + \frac{2(n+3)}{r} \frac{dE_n}{dr}.
\]
and thus the equation for $Q_n$ becomes

$$\frac{d^2 Q_n}{dr^2} + \frac{2(n+2)}{r} \frac{d Q_n}{dr} + k^2 Q_n$$

$$= - \frac{1}{2n+1} \left[ \frac{d^2}{dr^2} \left( \frac{1}{r} \frac{d E_n}{dr} \right) + \frac{2(n+2)}{r} \frac{d}{dr} \left( \frac{1}{r} \frac{d E_n}{dr} \right) \right]$$

$$+ \frac{1}{2n+1} \left[ \frac{d^2}{dr^2} \left( \frac{1}{r} \frac{d E_n}{dr} \right) + \frac{2(n+2)}{r} \frac{d}{dr} \left( \frac{1}{r} \frac{d E_n}{dr} \right) + s^2 r \frac{d}{dr} \left( \frac{1}{r} \frac{d E_n}{dr} \right) \right]$$

$$+ 2(n+3) s^2 \left( \frac{1}{r} \frac{d E_n}{dr} \right)$$

by the equation (40). Hence we have

$$Q_n = - \frac{1}{2n+1} \frac{1}{r} \frac{d E_n}{dr} + Q'_n . . . . . . . . . . (49)$$

where $Q'_n$ satisfies the equation

$$\frac{d^2 Q'_n}{dr^2} + \frac{2(n+2)}{r} \frac{d Q'_n}{dr} + k^2 Q'_n = \frac{n}{2n+1} \frac{k^2}{h^2} \frac{1}{s^2} \frac{d E_n}{dr} . . . . . . (50)$$

11. To find the form of $P'_n$, we assume

$$P'_n = \frac{n+1}{2n+1} \frac{k^2}{h^2} s^2 A (p_0 + p_2 r^2 + p_4 r^4 + ...) . . . . . . . (51)$$

Then equations (48) and (37) give

$$k^2 p_0 + 2(n+1) p_2 = - \frac{2n+1}{h^2 + (n+4) s^2} ;$$

$$k^2 p_2 + 4(n+3) p_4 = \frac{1}{2} ;$$

$$k^2 p_4 + 6(n+5) p_6 = - \frac{h^2 + (n+6) s^2}{2.4.(2n+3)} ;$$

$$k^2 p_6 + 8(2n+7) p_8 = \frac{h^2 + (n+6) s^2 \{h^2 + (n+8) s^2\}}{2.4.6(2n+3)(2n+5)} ;$$

$$\ldots$$

$$k^2 p_{2k} + (2\kappa+2)(2n+2\kappa+1) p_{2k+2}$$

$$= (-1)^{n+1} \frac{\{h^2 + (n+6) s^2\} \{h^2 + (n+8) s^2\} \ldots \{h^2 + (n+2\kappa+2) s^2\}}{2.4\ldots 2\kappa(2n+3)(2n+5)\ldots(2n+2\kappa-1)} ,$$

$$\ldots$$
By these equations \( p_0 \) is left arbitrary, and \( p_2, p_4, \ldots \) are determined when \( p_0 \) is chosen. As we need a particular integral only of the equation for \( P'_n \), we may choose \( p_0 \) in any way that may be convenient. We shall put \( p_0 = 0 \). Then

\[
p_2 = - \frac{1}{2\left(h^2 + (n + 4)s^2\right)}, \quad p_4 = \frac{1}{2.4\left(2n + 3\right)} + \frac{1}{2.4.\left(2n + 3\right)h^2 + (n + 4)s^2},
\]

\[
p_6 = - \frac{1}{2.4.6\left(2n + 3\right)\left(2n + 5\right)}\left\{h^2 + (n + 6)s^2 + k^2 + \frac{k^4}{h^2 + (n + 4)s^2}\right\},
\]

\[
p_8 = \frac{1}{2.4.6.8\left(2n + 3\right)\left(2n + 5\right)\left(2n + 7\right)}\left\{\left\{h^2 + (n + 6)s^2\right\}\left\{h^2 + (n + 8)s^2\right\} + k^2\left\{h^2 + (n + 6)s^2\right\} + k^4 + \frac{k^8}{h^2 + (n + 4)s^2}\right\},
\]

\[
\text{(52)}
\]

\[
\text{...}
\]

To find the form of \( Q'_n \), we assume

\[
Q'_n = \frac{n}{2n + 1} \frac{k^2}{h^2} s^2 A \left(q_0 + q_2 r^2 + q_4 r^4 + \ldots \right). \quad \ldots \quad \ldots \quad (53)
\]

Then equations (50) and (38) give

\[
k^2 q_0 + 2\left(2n + 5\right) q_2 = \frac{1}{2n + 3},
\]

\[
k^2 q_2 + 4\left(2n + 7\right) q_4 = -\frac{h^2 + (n + 6)s^2}{2.\left(2n + 3\right)\left(2n + 5\right)},
\]

\[
k^2 q_4 + 6\left(2n + 9\right) q_6 = \frac{\left\{h^2 + (n + 6)s^2\right\}\left(h^2 + (n + 8)s^2\right)}{2.4\left(2n + 3\right)\left(2n + 5\right)\left(2n + 7\right)},
\]

\[
k^2 q_{2k} + (2\kappa + 2)\left(2n + 2\kappa + 5\right) q_{2k + 2} = \left(-\right)^k\frac{\left\{h^2 + (n + 6)s^2\right\}\left(h^2 + (n + 8)s^2\right)\ldots\left\{h^2 + (n + 2\kappa + 4)s^2\right\}}{2.4\ldots\left(2\kappa + 2\right)\left(2n + 3\right)\left(2n + 5\right)\ldots\left(2n + 2\kappa + 3\right)},
\]

\[
\text{...}
\]

As before, \( q_0 \) can be chosen arbitrarily, and then \( q_2, q_4, \ldots \) are known. We observe that if we put

\[
q_0 = \frac{2p_2}{2n + 3}, \quad q_2 = \frac{4p_4}{2n + 5}, \quad \ldots, \quad q_{2k} = \frac{\left(2\kappa + 2\right)p_{2k + 2}}{2n + 2\kappa + 3}, \quad \ldots
\]

the sequence equations for the \( q' \)s are transformed into the sequence equations for the \( p' \)s, beginning with the equation containing \( p_2, p_4 \). We shall therefore choose \( q_0 \) to be \((2n + 3)^{-1}2p_2\), and then

\[
Q'_n = \frac{n}{2n + 1} \frac{k^2}{h^2} s^2 A \left\{ \frac{2p_2}{2n + 3} + \frac{4p_4}{2n + 5} r^2 + \frac{6p_6}{2n + 7} r^4 + \ldots \right\}. \quad \ldots \quad (54)
\]
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This choice of the q's amounts to subjecting the functions \( P'_n \) and \( Q'_n \) to the equation

\[
\frac{d}{dr} \left( r^{2n+3} Q'_n \right) = \frac{n}{n+1} r^{2n+1} \frac{dP'_n}{dr} .
\] (55)

To see that this equation is compatible with the differential equations (48) and (50) for \( P'_n \) and \( Q'_n \), we observe that

\[
\frac{d\theta_n}{dr} = \frac{1}{r^{2n+1}} \frac{d}{dr} \left( r^{2n+3} \frac{1}{r} \right) ,
\]

and that from the equation (48) we can form the equation

\[
\left\{ \frac{d^2}{dr^2} - \frac{2(n+1)}{r} \frac{d}{dr} + k^2 + \frac{2(n+1)}{r^2} \right\} \left( r^{2n+1} \frac{dP'_n}{dr} \right) = \frac{n+1}{2n+1} \frac{k^2}{h^2} s^2 \frac{d}{dr} \left( r^{2n+3} \frac{1}{r} \right) ,
\]

while from (50) we can form the equation

\[
\left\{ \frac{d^2}{dr^2} - \frac{2(n+1)}{r} \frac{d}{dr} + k^2 + \frac{2(n+1)}{r^2} \right\} \left\{ \frac{d}{dr} \left( r^{2n+3} Q'_n \right) \right\} = \frac{n}{2n+1} \frac{k^2}{h^2} s^2 \frac{d}{dr} \left( r^{2n+3} \frac{1}{r} \right) .
\]

12. We have still to satisfy the condition

\[
\frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} = f_n \omega_n .
\] (56)

If we form the expression in the left-hand member from the expressions of the type (44) for \( u_1, v_1, w_1 \), we have

\[
\frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} = \left( n \frac{dP_n}{dr} - \frac{n+1}{r} \frac{d}{dr} \left( r^{2n+3} Q_n \right) \right) \omega_n .
\]

By means of the formulae (47) and (49) for \( P_n \) and \( Q_n \), the coefficient of \( \omega_n \) in the right-hand member of this equation is transformed into

\[
\frac{1}{2n+1} \left[ n \frac{d\theta_n}{dr} + \frac{n+1}{r} \frac{d}{dr} \left( r^{2n+3} \frac{1}{r} \right) \right] + \frac{n+1}{2n+1} \left[ \frac{n}{n+1} \frac{dP_n}{dr} - \frac{d}{dr} \left( r^{2n+3} Q'_n \right) \right] .
\]

The first term is equal to

\[
\frac{1}{2n+1} [nf_n + (n+1)f'_n] \text{ or } f_n ,
\]

and the second term vanishes identically in virtue of equation (55). It follows that, with our choice of \( p_0 \) and \( q_n \), the equation (56) is satisfied identically.

13. We have now completed the determination of the forms of \( u, v, w \) in terms of the spherical solid harmonics \( \omega_n, F_n, \phi_n \), and of certain functions of \( r \), viz.: \( f_n, \theta_n, E_n \), 2 B 2
Various relations between these functions have been noted incidentally. It will be convenient hereafter to have noted the following properties of \( \psi_n (kr) \):

\[
\psi_n (kr) = \frac{(-1)^n}{1.3.5...(2n+1)} \left\{ 1 - \frac{k^2 r^2}{2(2n+3)} + \frac{k^4 r^4}{2.4(2n+3)(2n+5)} - \ldots \right\},
\]

\[
\left\{ \frac{d^2}{d (kr)^2} + \frac{2(n+1)}{kr} \frac{d}{d (kr)} + 1 \right\} \psi_n (kr) = 0, \ldots \ldots \ldots (58)
\]

\[
k r \frac{d\psi_n (kr)}{d (kr)} = k^2 r^2 \psi_{n+1} (kr) = -\{\psi_{n-1} (kr) + (2n+1) \psi_n (kr)\}. \ldots \ldots (59)
\]

**Adjustment of the Harmonics to Satisfy the Boundary Conditions.**

14. In order to express \( F_n \) in terms of \( \omega_n \) and \( \phi_n \) we use the condition that \( 4\pi\gamma \rho_0 (E_n \omega_n + F_n) \) is the potential at points within the sphere \( r = \alpha \) of a distribution of volume density within the sphere and of surface density on the sphere. The corresponding external potential is

\[
4\pi\gamma \rho_0 \left( \frac{\alpha}{r} \right)^{2n+1} \{E_n (\alpha) \omega_n + F_n\},
\]

where \( E_n (\alpha) \) is the value of \( E_n \) at \( r = \alpha \). The surface density is \( \rho_0 U_a \), where \( U_a \) is the value at \( r = \alpha \) of the radial displacement \( U \). Hence we have the equation

\[
\frac{\partial}{\partial r} \left[ \left( \frac{\alpha}{r} \right)^{2n+1} \{E_n (\alpha) \omega_n + F_n\} \right] - \frac{\partial}{\partial r} (E_n \omega_n + F_n) = -U,
\]

which holds at the surface \( r = \alpha \); it gives

\[
\left[ \left( \frac{2n+1}{r} E_n + \frac{dE_n}{d \alpha} \right) \omega_n + \frac{2n+1}{r} F_n \right]_{r=\alpha} = U_a.
\]

Now

\[
U = \left\{ \frac{n}{r} P_n - (n+1)r Q_n \right\} \omega_n - \frac{3n^2}{\alpha h^2} F_n + \frac{n}{r} \{\psi_{n-1} (kr) + k^2 r^2 \psi_{n+1} (kr)\} \phi_n.
\]

It follows that the equation

\[
\left\{ \frac{2n+1}{\alpha} + \frac{3n^2}{\alpha h^2} \right\} F_n = \omega_n \left\{ \frac{n}{r} P_n - (n+1)r Q_n - \frac{dE_n}{d \alpha} - \frac{2n+1}{r} E_n \right\}_{r=\alpha} + \phi_n \frac{n}{\alpha} \{\psi_{n-1} (ka) + k^2 \alpha^2 \psi_{n+1} (ka)\}
\]

holds at the surface \( r = \alpha \). Since this equation connects the values at \( r = \alpha \) of three spherical solid harmonics of the same degree \( n \), it holds for all values of \( r \), and gives
a generally valid expression of $F_n$ in terms of $\omega_n$ and $\phi_n$. By means of equations (35) and (59) the equation becomes

$$F_n = \tau \frac{h^2}{3ns^2 + (2n + 1)h^2} \left[ \{ \theta_n - nP_n + (n + 1)\alpha^2Q_n \}_{r = a} \omega_n + n(2n + 1)\psi_n(k\alpha)\phi_n \right]. \quad (60)$$

15. The three remaining conditions which hold at the surface $r = \alpha$ are expressed by equations of the type

$$\left( \frac{k^2}{h^2} - 2 \right) x\Delta + \frac{\partial}{\partial x} (rU) + r \frac{\partial u}{\partial r} - u + \frac{k^2}{h^2} s^2 xrU = 0. \quad \ldots \quad (61)$$

Every term of the left-hand member can be expressed in terms of the spherical solid harmonics

$$\frac{\partial \omega_n}{\partial x}, \quad r^{2n+3} \frac{\partial}{\partial x} \left( \frac{\omega_n}{r^{2n+1}} \right), \quad \frac{\partial \phi_n}{\partial x}, \quad r^{2n+3} \frac{\partial}{\partial x} \left( \frac{\phi_n}{r^{2n+1}} \right).$$

We have

$$x\Delta = x\omega_n \cdot f_n = \frac{\varphi^2}{2n + 1} \int_0^\alpha \frac{\partial \omega_n}{\partial x} \left( \frac{\omega_n}{r^{2n+1}} \right) + \frac{\varphi^{2n+3}}{2n + 1} \int_0^\alpha \frac{\partial \phi_n}{\partial x} \left( \frac{\phi_n}{r^{2n+1}} \right).$$

Also

$$rU = \{ nP_n - (n + 1)r^2Q_n \} \omega_n - n(2n + 1)\psi_n(k\alpha)\phi_n$$

$$+ \frac{3ns^2}{3ns^2 + (2n + 1)h^2} \left[ \{ \theta_n - nP_n + (n + 1)\alpha^2Q_n \}_{r = a} \omega_n + n(2n + 1)\psi_n(k\alpha)\phi_n \right],$$

and therefore

$$\frac{\partial}{\partial x} (rU) = \left[ nP_n - (n + 1)r^2Q_n + \frac{3ns^2}{3ns^2 + (2n + 1)h^2} \left( \{ \theta_n - nP_n + (n + 1)\alpha^2Q_n \}_{r = a} \right) \frac{\partial \omega_n}{\partial x} \right.$$}

$$- \left[ n(2n + 1)\psi_n(k\alpha) - \frac{3ns^2}{3ns^2 + (2n + 1)h^2} \psi_n(k\alpha) \right] \frac{\partial \phi_n}{\partial x}$$

$$+ \frac{d}{dr} \left( nP_n - (n + 1)r^2Q_n \right) \frac{r}{2n + 1} \left[ \frac{\partial \omega_n}{\partial x} - r^{2n+1} \frac{\partial}{\partial x} \left( \frac{\omega_n}{r^{2n+1}} \right) \right]$$

$$- nkr \frac{d\psi_n(k\alpha)}{dr} \left[ \frac{\partial \phi_n}{\partial x} - r^{2n+1} \frac{\partial}{\partial x} \left( \frac{\phi_n}{r^{2n+1}} \right) \right].$$

Again,

$$r \frac{\partial u}{\partial r} - u = \left\{ r \frac{dP_n}{dr} + (n - 2)P_n \right\} \frac{\partial \omega_n}{\partial x} + \left\{ r \frac{d}{dr} \left( r^{2n+3}Q_n \right) - (n + 3)r^{2n+3}Q_n \right\} \frac{\partial}{\partial x} \left( \frac{\omega_n}{r^{2n+1}} \right)$$

$$+ \frac{3(n - 2)s^2}{3ns^2 + (2n + 1)h^2} \left[ \{ \theta_n - nP_n + (n + 1)\alpha^2Q_n \}_{r = a} \frac{\partial \omega_n}{\partial x} + n(2n + 1)\psi_n(k\alpha) \frac{\partial \phi_n}{\partial x} \right]$$

$$+ \left\{ r \frac{d\psi_{n-1}(kr)}{dr} + (n - 2)\psi_{n-1}(kr) \right\} \frac{\partial \phi_n}{\partial x}$$

$$- \frac{n}{n + 1} k^2 \left[ r \frac{d}{dr} \left( r^{2n+3}\psi_{n+1}(kr) \right) - (n + 3)r^{2n+3}\psi_{n+1}(kr) \right] \frac{\partial}{\partial x} \left( \frac{\phi_n}{r^{2n+1}} \right).$$
Further,

\[ x r U = \left[ n P_n - (n+1) r^2 Q_n \right] + \frac{3 n^2}{3 n^2 + (2n+1) h^2} \left\{ \theta_n - n P_n + (n+1) \alpha^2 Q_n \right\} + \frac{r^2}{2n+1} \left\{ \frac{\partial \omega_n}{\partial x} - r^{2n+1} \frac{\partial}{\partial x} \left( \frac{\omega_n}{r^{2n+1}} \right) \right\} - n (2n+1) \left\{ \psi_n(kr) - \frac{3 n^2}{3 n^2 + (2n+1) h^2} \psi_n(k \alpha) \right\} + \frac{r^2}{2n+1} \left\{ \frac{\partial \phi_n}{\partial x} - r^{2n+1} \frac{\partial}{\partial x} \left( \frac{\phi_n}{r^{2n+1}} \right) \right\} . \]

16. The equations which hold at the surface \( r = \alpha \) can be arranged in such forms as

\[ A_n \frac{\partial \omega_n}{\partial x} + B_n r^{2n+3} \frac{\partial}{\partial x} \left( \frac{\omega_n}{r^{2n+1}} \right) + C_n \frac{\partial \phi_n}{\partial x} + D_n r^{2n+3} \frac{\partial}{\partial x} \left( \frac{\phi_n}{r^{2n+1}} \right) = 0 , \ldots (62) \]

in which \( A_n, B_n, C_n, D_n \) are certain functions of \( \alpha \), viz:

\[ A_n = \left( \frac{k}{h} - 2 \right) \frac{\alpha^2}{2n+1} f_n + \frac{3 n^2}{3 n^2 + (2n+1) h^2} \theta_n + \frac{(2n+1) h^2}{3 n^2 + (2n+1) h^2} \left\{ n P_n - (n+1) \alpha^2 Q_n \right\} + \frac{3(n-2) x^2}{3 n^2 + (2n+1) h^2} \left[ \theta_n - n P_n + (n+1) \alpha^2 Q_n \right] + \frac{s^2 k^2 \alpha^2}{(2n+1) h^2} \left[ \frac{3 n^2}{3 n^2 + (2n+1) h^2} \theta_n + \frac{(2n+1) h^2}{3 n^2 + (2n+1) h^2} \left( n P_n - (n+1) \alpha^2 Q_n \right) \right] , (63) \]

\[ B_n = - \left( \frac{k}{h^2} - 2 \right) \frac{1}{2n+1} f_n - \frac{1}{2n+1} \frac{1}{\alpha} \frac{d}{d \alpha} \left( n P_n - (n+1) \alpha^2 Q_n \right) + \frac{d Q_n}{d \alpha} + n Q_n - \frac{s^2 k^2}{(2n+1) h^2} \left[ \frac{3 n^2}{3 n^2 + (2n+1) h^2} \theta_n + \frac{(2n+1) h^2}{3 n^2 + (2n+1) h^2} \left( n P_n - (n+1) \alpha^2 Q_n \right) \right] , (64) \]

\[ C_n = - n \left[ (2n+1) \psi_n(k \alpha) + \alpha \frac{d}{d \alpha} \psi_n(k \alpha) - \frac{3 n^2(2n+1)}{3 n^2 + (2n+1) h^2} \psi_n(k \alpha) \right] + \frac{3(n-2) s^2 n (2n+1)}{3 n^2 + (2n+1) h^2} \psi_n(k \alpha) \right\} + \frac{\partial}{\partial \alpha} \psi_{n-1}(k \alpha) + (n-2) \psi_{n-1}(k \alpha) + \frac{n (2n+1) s^2 k^2 \alpha^2}{3 n^2 + (2n+1) h^2} \psi_n(k \alpha) . \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (65) \]

\[ D_n = \frac{n}{\alpha} \frac{d}{d \alpha} \psi_n(k \alpha) - \frac{n}{n+1} k^2 \left\{ \alpha \frac{d}{d \alpha} \psi_{n+1}(k \alpha) + n \psi_{n+1}(k \alpha) \right\} + \frac{n (2n+1) s^2 k^2}{3 n^2 + (2n+1) h^2} \psi_n(k \alpha) . \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (66) \]

In these formulæ \( \alpha \) is supposed to be written instead of \( r \) in the expressions for \( f_n, \theta_n, P_n, Q_n \).
17. We may express $A_n$ and $B_n$ in more convenient forms by the use of the identities

$$nP_n-(n+1)\alpha^2Q_n = \theta_n-(n+1)E_n + nP'_n-(n+1)\alpha^2Q'_n,$$

$$\frac{d\theta_n}{d\alpha} = \alpha f_n,$$

$$\frac{d^2E_n}{d\alpha^2} + \frac{2(n+1)}{\alpha} \frac{dE_n}{d\alpha} = f_n,$$

$$\alpha \frac{dE_n}{d\alpha} = \theta_n-(2n+1)E_n,$$

$$\alpha \frac{dQ'_n}{d\alpha} + (2n+3)Q'_n = \frac{n}{n+1} \frac{dP'_n}{d\alpha}.$$

We find

$$A_n = \frac{k^2}{2n+1} \left[ f_n + s^2\theta_n \right] + \alpha \frac{dP'_n}{d\alpha} + 2(n-1) \left( \frac{\theta_n}{2n+1} + P'_n \right)$$

$$+ \frac{6(n-1)s^2 - k^2s^2\alpha^2}{3ns^2 + (2n+1)h^2} \left\{ (n+1)E_n - nP'_n + (n+1)\alpha^2Q'_n \right\}, \quad \ldots \quad (67)$$

$$B_n = -\frac{k^2}{2n+1} \left[ f_n + s^2\theta_n \right] + \frac{2n+4}{2n+1} \frac{dE_n}{d\alpha} + \alpha \frac{dQ'_n}{d\alpha} - Q'_n$$

$$+ \frac{k^3s^2}{3ns^2 + (2n+1)h^2} \left\{ (n+1)E_n - nP'_n + (n+1)\alpha^2Q'_n \right\}, \quad \ldots \quad (68)$$

We may also express $C_n$ and $D_n$ in simpler forms by the use of the equations connecting the $\psi$ functions. We find

$$C_n = -2(n-1)k^2\alpha^2 \left[ \psi_{n+1}(k\alpha) + \frac{(2n+1)^2}{3ns^2 + (2n+1)h^2} \frac{h^2}{k^2} \psi_n(k\alpha) + \frac{ns^2}{3ns^2 + (2n+1)h^2} \psi_n(k\alpha) \right]$$

$$+ \frac{(2n+1)k^2s^2}{3ns^2 + (2n+1)h^2} \psi_n(k\alpha), \quad \ldots \quad \ldots \quad \ldots \quad (69)$$

$$D_n = k^2 \left[ \frac{n}{n+1} \left( \psi_n(k\alpha) + (2n+4)\psi_{n+1}(k\alpha) \right) + \frac{(2n+1)ns^2}{3ns^2 + (2n+1)h^2} \psi_n(k\alpha) \right], \quad \ldots \quad \ldots \quad (70)$$

The Frequency Equation and the Condition of Gravitational Instability.

18. Exactly as in the problem of the vibrating sphere which is free from gravitation, it follows from the equations of type (62) that we must have at once

$$A_n\omega_n + C_n\phi_n = 0, \quad \text{and} \quad B_n\omega_n + D_n\phi_n = 0, \quad \ldots \quad \ldots \quad (71)$$

and the frequency equation is of the form

$$A_nD_n - B_nC_n = 0. \quad \ldots \quad \ldots \quad \ldots \quad (72)$$

The forms of all the functions which enter into the expressions of $A_n$, $B_n$, $C_n$, $D_n$ have been determined.

To investigate gravitational instability, we have to determine the conditions which
must hold in order that the frequency equation may be satisfied by \( p^2 = 0 \). When \( p^2 \) vanishes, \( h^2 \) and \( k^2 \) also vanish, but the quantity \( k^2/h^2 \), which is \( (\lambda + 2\mu)/\mu \), has a determinate value. We may not, however, obtain the result which we seek by first replacing \( k^2/h^2 \), wherever it occurs, by \( (\lambda + 2\mu)/\mu \), and then putting \( h^2 \) and \( k^2 \) equal to zero wherever they occur, otherwise than in the ratio \( k^2/h^2 \). This precautionary statement is necessary because it appears from the formulae (69) and (70) of § 17 that \( C_n \) and \( D_n \) both vanish if \( h^2 \) and \( k^2 \) vanish. Thus we ought to regard the equations (71) as being equivalent to the equations

\[
A_n\omega_n + (C_nk^{-2})k^2\phi_n = 0, \quad B_n\omega_n + (D_nk^{-2})k^2\phi_n = 0;
\]

in other words, we ought to remove a factor \( k^2 \) from the equation \( A_nD_n - B_nC_n = 0 \) before putting \( h^2 = 0 \) and \( k^2 = 0 \). An exceptional case occurs when \( n = 1 \). In this case \( C_1k^{-2} \) vanishes when \( h^2 \) vanishes, and it will appear that \( A_1 \) also vanishes with \( h^2 \), and the equations (71) ought to be regarded as equivalent to

\[
(A_1h^{-2})\omega_1 + (C_1h^{-2}k^{-2})k^2\phi_1 = 0, \quad B_1\omega_1 + D_1k^{-2}k^2\phi_1 = 0,
\]

and we must remove a factor \( h^2k^2 \) from the equation \( A_1D_1 - B_1C_1 = 0 \) before putting \( h^2 = 0 \) and \( k^2 = 0 \). When we proceed in this way, the equation \( A_nD_n - B_nC_n = 0 \), with the appropriate factors removed, and with \( h^2 \) and \( k^2 \) put equal to zero after their removal, becomes an equation to determine \( s^2a^2 \), or \( \frac{4}{3}\pi\gamma_{p_0}s^2a^2/(\lambda + 2\mu) \). If the equation has a real root, the value so determined for \( s^2a^2 \) gives a value of \( \lambda + 2\mu \) for which instability can occur. Since \( k^2\phi_n \) is a finite multiple of \( \omega_n \) when \( \lambda + 2\mu \) has any such value, it is certain that the homogeneous spherical configuration really is unstable for such values of \( \lambda + 2\mu \). If the value of \( \lambda + 2\mu \) belonging to the body is but little greater than the critical value, the equilibrium is practically unstable; for a large displacement takes place if the sphere begins to vibrate according to the type specified by the degree \( n \) of the corresponding spherical harmonic function. For practical stability it is necessary that the value of \( \lambda + 2\mu \) should be well above any critical value. The equation which yields the critical values contains the constant \( (\lambda + 2\mu)/\mu \) as well as \( s^2a^2 \). It will be convenient to write

\[
\nu = \frac{\mu}{\lambda + 2\mu} = \frac{h^2}{k^2},
\]

(73)

The value of \( \nu \) cannot be negative, nor can it be greater than \( \frac{3}{4} \). If the Poisson's ratio \( \{\lambda/2(\lambda + \mu)\} \) of the material is positive, \( \nu \) cannot exceed \( \frac{1}{2} \). If the modulus of rigidity \( \mu \) were very small in comparison with the modulus of compression \( \lambda + \frac{2}{3}\mu \), \( \nu \) would be very small. If the velocity of propagation of waves of dilatation were twice that of waves of distortion, \( \nu \) would be \( \frac{1}{4} \). This appears to be the most appropriate value to assume in the case of the Earth (see § 40 below). Since it is improbable that the ratio of the rigidity to the modulus of compression of the Earth has diminished since the date of consolidation, it will be sufficient for our purpose to
examine the two cases in which \( \nu = 0 \) and \( \nu = \frac{1}{2} \). We have now to discuss the conditions of gravitational instability in respect of the values 0, 1, 2, ... of the number \( n \) which specifies the type of vibration.

**Instability in Respect of Radial Displacements.**

19. The case in which \( n = 0 \) is the case of a sphere vibrating radially. This case is not very easily included in the foregoing analysis, and it is very easy to investigate it independently. Let \( U \) denote the radial displacement. Then \( U \) is a function of \( r \), and we have

\[
u = \frac{x}{r} U, \quad v = \frac{y}{r} U, \quad w = \frac{z}{r} U, \quad \Delta = \frac{dU}{dr} + \frac{2U}{r}.
\]

We go back to the equations (15) of the type

\[
(\lambda + \mu) \frac{\partial \Delta}{\partial x} + \mu \nabla^2 u + \rho_0 x^2 u + \frac{4}{3} \pi \gamma \rho_0 x \Delta + \rho_0 \frac{\partial W}{\partial x} = 0,
\]

where \( W \), the additional potential, is a function of \( r \). This equation is

\[
(\lambda + \mu) \frac{x}{r} \frac{d}{dr} \left( \frac{dU}{dr} + \frac{2U}{r} \right) + \mu \left\{ x \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) \left( \frac{U}{r} \right) + \frac{2x}{r} \frac{d}{dr} \left( \frac{U}{r} \right) \right\} + \rho_0 x^2 \frac{r}{r} U
\]

\[
+ s^2 (\lambda + 2\mu) x \left( \frac{dU}{dr} + \frac{2U}{r} \right) + \rho_0 x \frac{dW}{dr} = 0. \quad (74)
\]

Now

\[
\frac{d^2 W}{dr^2} + 2 \frac{dW}{dr} = 4\pi \gamma \rho_0 \left( \frac{dU}{dr} + \frac{2U}{r} \right),
\]

and therefore we may write

\[
\frac{dW}{dr} = 4\pi \gamma \rho_0 U + R,
\]

where

\[
\frac{dR}{dr} + \frac{2}{r} R = 0, \quad \text{or} \quad Rr^2 = \text{const}.
\]

Since \( dW/dr \) is finite at \( r = 0 \), we must have \( R = 0 \), and thus equation (74) becomes after division by \( (\lambda + 2\mu) x/r \)

\[
\frac{d^2 U}{dr^2} + 2 \frac{dU}{dr} - \frac{2U}{r^2} + s^2 \left( \frac{dU}{dr} + 2U \right) + 3s^2 U + h^2 U = 0, \quad . . . \quad (75)
\]

where \( s^2 = \frac{4}{3} \pi \gamma \rho_0^2 / (\lambda + 2\mu) \) and \( h^2 = p^2 \rho_0 / (\lambda + 2\mu) \). This equation can be solved by means of a series, which is convergent for all finite values of \( r \), in the form

\[
U = A \left[ \frac{r}{3} - \frac{h^2 + 6s^2}{2} \frac{r^3}{2.3.5} + \frac{(h^2 + 6s^2)(h^2 + 8s^2)}{2} \frac{r^5}{2.4.3.5.7} \right. \]

\[
\left. - \frac{(h^2 + 6s^2)(h^2 + 8s^2)}{2} \frac{r^7}{2.4.3.5.7} \right] \frac{r^2}{2 \cdot 4 \cdot 2 \cdot 3 \cdot 5 \cdot (2k + 3)}, \quad \cdot (76)
\]
where \( A \) is an arbitrary constant. The second solution of the differential equation for \( U \) becomes infinite at \( r = 0 \), and thus the above is the most general form for \( U \).

20. The condition that the surface \( r = \alpha + U_a \) is free from traction can easily be shown to be the condition that

\[
\frac{4}{3} \pi \gamma R^2 \nu U + (\lambda + 2\mu) \frac{dU}{dr} + 2\lambda \frac{U}{r} = 0
\]

at \( r = \alpha \). Hence we have

\[
\left( \frac{dU}{dr} \right)_a + (2 - 4\nu + 8\alpha^2) \frac{U_a}{\alpha} = 0, \ldots \ldots \ldots \ldots (77)
\]

where \( \nu = \mu/(\lambda + 2\mu) \), so that \( 2\lambda/(\lambda + 2\mu) = 2 - 4\nu \). The frequency equation is therefore

\[
\frac{1}{3} \left[ 1 + 2 - 4\nu + 8\alpha^2 \right] - \frac{h^2 + 6s^2}{2.3.5} \alpha^2 (3 + 2 - 4\nu + 8\alpha^2) + \ldots
\]

\[
(-)^k \left[ \frac{h^2 + 6s^2}{2.4 \ldots 2k.3.5} \ldots \{ h^2 + (2k+4) s^2 \} \alpha^2 (2k+1 + 2 - 4\nu + 8\alpha^2) \ldots = 0. \quad (78)
\]

The condition of gravitational instability is obtained by putting \( h^2 = 0 \). It is

\[
\frac{1}{3} (3 - 4\nu + 8\alpha^2) - \frac{6s^2\alpha^2}{2.3.5} (5 - 4\nu + 8\alpha^2) + \ldots
\]

\[
(-)^k \left[ \frac{6.8 \ldots (2k+4) s^2\alpha^2}{2.4 \ldots 2k.3.5 \ldots (2k+3)} (2k+3 - 4\nu + 8\alpha^2) \ldots = 0. \quad (79)
\]

21. The coefficient of \( s^2\alpha^2 \) in the left-hand member of (79) is

\[
(-)^k \left[ \frac{(2k+2) (2k+4)}{3.5 \ldots (2k+3)} (2k+3 - 4\nu) - \frac{2k (2k+2)}{3.5 \ldots (2k+1)} \right],
\]

or

\[
\frac{(-)^k}{2} \left[ \frac{1}{3.5 \ldots (2k-1)} + \frac{1}{3.5 \ldots (2k+1)} \right]
\]

\[
-\nu \left[ \frac{1}{3.5 \ldots (2k-1)} + \frac{2}{3.5 \ldots (2k+1)} - \frac{1}{3.5 \ldots (2k+3)} \right],
\]

and the equation (79) can be written

\[
\frac{1}{2} \left[ (1-x^3 + \frac{x^4}{3} - \frac{x^5}{3.5} + \ldots) + (1-x^3 + \frac{x^4}{3} - \frac{x^5}{3.5} - \ldots) \right]
\]

\[
-\nu \left[ (1-x^3 + \frac{x^4}{3} - \ldots) + 2 \left( 1-x^3 + \frac{x^4}{3} - \ldots \right) - \left( \frac{1}{3} - \frac{x^3}{3.5} + \frac{x^4}{3.5} \ldots \right) \right] = 0,
\]

where \( x \) is written for \( s\nu \). Now we have

\[
\int_0^\infty e^{ix} dx = e^{ix} \left( x - \frac{x^3}{3} + \frac{x^5}{3.5} - \ldots \right),
\]

and therefore

\[
1 - \frac{x^3}{3} + \frac{x^5}{3.5} - \ldots = x^{-1} e^{-ix} \int_0^\infty e^{ix} dx;
\]
and the equation may be written

\[ 1 - \nu \left( 1 - \frac{1}{x^3} \right) - \left[ \left( 1 - \frac{1}{x^3} \right) - \nu \left( 1 - \frac{2}{x^3} - \frac{1}{x^6} \right) \right] xe^{-i\nu x} \int_0^x e^{i\nu x} \, dx = 0. \quad \cdots \quad (80) \]

22. The left-hand member of equation (80), being equal to

\[ 2 \left( 1 - \frac{3}{4} \nu \right) + 2 \left( \frac{3}{4} \nu - \frac{3}{8} \right) x^3 + \ldots, \]

is positive when \( x = 0 \). To determine its sign for large values of \( x \) we observe that

\[
\int_0^x e^{i\nu x} \, dx = \int_0^1 e^{i\nu x} \, dx + \int_1^x e^{-x^{-1} \nu x} \, dx
\]

\[
= \int_0^1 e^{i\nu x} \, dx + x^{-1} e^{i\nu x} - e^i + \int_1^x x^{-2} e^{i\nu x} \, dx
\]

\[
= \int_0^1 e^{i\nu x} \, dx + x^{-1} e^{i\nu x} - e^i + x^{-3} e^{i\nu x} - e^i + 3 \int_1^x x^{-4} e^{i\nu x} \, dx
\]

\[
\ldots,
\]

and therefore there is an asymptotic expansion* for \( xe^{-i\nu x} \int_0^x e^{i\nu x} \, dx \) when \( x \) is large in the form

\[ 1 + x^{-2} + 3x^{-4} + 3 \cdot 5x^{-6} + 3 \cdot 5 \cdot 7 x^{-8} + \ldots. \]

Hence the expression in the left-hand member of (80) is asymptotically equal to

\[ 1 - \nu \left( 1 - \frac{1}{x^3} \right) - \left\{ 1 - \frac{1}{x^3} - \nu \left( 1 - \frac{2}{x^3} - \frac{1}{x^6} \right) \right\} \left[ 1 + \frac{1}{x^3} + \frac{3}{x^4} + \frac{3 \cdot 5}{x^5} + \ldots \right]. \]

The term of highest degree independent of \( \nu \) is \(-2x^{-4}\); the term of highest degree containing \( \nu \) is \( 8\nu x^{-6} \). It follows that the expression is always negative when \( x \) is sufficiently great. The expression therefore changes sign for some positive value of \( x \), and the equation (80) has at least one positive root.

23. When \( \nu = 0 \) the equation (80) becomes

\[ 1 - \frac{x^3 - 1}{x} e^{-i\nu x} \int_0^x e^{i\nu x} \, dx = 0. \]

If \( x^3 < 1 \) the left-hand member is necessarily positive. We shall take \( x^3 > 1 \) and write the equation

\[ \frac{x}{x^3 - 1} e^{i\nu x} - \int_0^x e^{i\nu x} \, dx = 0. \]

Let \( y \) denote the left-hand member of this equation. Then we have

\[ \frac{dy}{dx} = e^{i\nu x} \left[ \frac{1}{x^2 - 1} + \frac{x^3}{x^2 - 1} - \frac{2x^3}{(x^2 - 1)^2} \right] = -\frac{2}{(x^2 - 1)^2} e^{i\nu x}. \]

Since this expression cannot vanish, the equation cannot have more than one positive root.

* For the suggestion that this step might prove useful in demonstrating the existence of a root of equation (80) I am indebted to Mr. G. H. HARDY, Fellow of Trinity College, Cambridge.
Again, when \( \nu = \frac{1}{4} \), the equation can be written
\[
3 + \frac{1}{x^2} - \left(3 - \frac{2}{x^2} + \frac{1}{x^4}\right) \int_0^x x^3 e^{3s^2} ds = 0,
\]
or
\[
\frac{(5-3x^3)x^3}{3x^4 - 2x^2 + 1} e^{3s^2} + \int_0^x x^3 e^{3s^2} ds = 0,
\]
where the left-hand member is certainly positive when \( x^3 < 1 \); also the differential coefficient of the left-hand member with respect to \( x \) is
\[
\frac{-8x^2 (3x^2 - 2)}{(3x^4 - 2x^2 + 1)^{3/2}} e^{3x^2},
\]
and this expression cannot vanish for any value of \( x \) which is greater than unity. Hence the equation (80) cannot have more than one positive root.

24. Now take \( \nu = 0 \), and write the equation (80)
\[
\frac{1}{x^3 - 1} - \left(1 - \frac{x^2}{3} + \frac{x^4}{3.5} - ...\right) = 0.
\]
When \( x^3 = 4 \), we have
\[
1 - \frac{x^2}{3} + \frac{x^4}{3.5} - ... = \left(1 - \frac{4}{3} + \frac{4^2}{3.5} - ...\right)
\]
\[
= \frac{44123}{3.5...13} - \frac{4^7}{3.5...15} \left(1 - \frac{4}{17}\right) - \frac{4^9}{3.5...19} \left(1 - \frac{4}{21}\right) - ...,
\]
and
\[
\frac{1}{x^3 - 1} = \frac{1}{3} = \frac{45045}{3.5...13}.
\]
Hence, when \( x^3 = 4 \), the sign of the left-hand member of the equation (81) is plus.

When \( x^3 = 5 \), we have
\[
1 - \frac{x^2}{3} + \frac{x^4}{3.5} - ... = 1 - \frac{5}{3} + \frac{5^2}{3.5} - ...
\]
\[
= \frac{20056}{3.7.9.11.13.3} + \frac{15625}{3.7.9.11.13.3.17} \left(1 - \frac{5}{19}\right)
\]
\[
+ \frac{5^8}{3.7.9.11.13.3.17.19.21} \left(1 - \frac{5}{23}\right) + ...,
\]
Also
\[
\frac{15625}{3.7.9.11.13.3} > \frac{19}{17},
\]
and therefore
\[
1 - \frac{5}{3} + \frac{5^2}{3.5} - ... > \frac{20733}{3.7...13.3},
\]
but
\[
\frac{1}{4} (3.7...13.3) = 20270 + \frac{1}{4} < 20733.
\]
Hence, when \( x^3 = 5 \), the sign of the left-hand member of equation (81) is minus. It follows that the value of \( x^3 \), or \( s^2 \), which satisfies the equation is between 4 and 5.
25. Again, when \( \nu = \frac{1}{1} \), equation (80) can be written
\[
\frac{3x^2+1}{3x^2-2x^2+1} - \left(1 - \frac{x^3}{3} + \frac{x^4}{3.5} - \cdots \right) = 0. \ldots \ldots \ (82)
\]
If we put \( x^2 = 4 \), the left-hand member becomes
\[
\frac{13}{41} - \left(1 - \frac{4}{3} + \frac{4^2}{3.5} - \cdots \right).
\]
Now
\[
1 - \frac{4}{3} + \frac{4^2}{3.5} - \cdots = \frac{645461}{3.5...15} + \frac{4^8}{3.5...17} \left(1 - \frac{4}{19}\right) + \cdots,
\]
and
\[
\frac{13}{41} (3.5...15) = 642715 + \frac{10}{41}.
\]
Hence \( 1 - \frac{4}{3} + \frac{4^2}{3.5} - \cdots > \frac{13}{41} \), and the sign of the left-hand member of (82) is minus when \( x^2 = 4 \). When we put \( x^2 = 3 \), the left-hand member of (82) becomes
\[
\frac{5}{11} - \left(1 - \frac{3}{3} + \frac{3^2}{3.5} - \cdots \right);
\]
but
\[
1 - \frac{3}{3} + \frac{3^2}{3.5} - \cdots = \frac{3}{5} - \frac{9}{5} \cdot \frac{5.7}{5.7} + \frac{5.7}{5.7} \cdot \frac{9}{11} \left(1 - \frac{3}{13}\right) + \cdots
\]
\[
= \frac{3}{7} - \frac{9}{5.7} \cdot \frac{11}{13} \left(1 - \frac{3}{13}\right) + \cdots,
\]
and
\[
\frac{5}{11} > \frac{3}{7} - \left(1 - \frac{3}{3} + \frac{3^2}{3.5} - \cdots \right),
\]
or the sign of the left-hand member of (82) is plus when \( x^2 = 3 \). It follows that the root of the equation (82) for \( x^2 \) lies between 3 and 4.

**Instability in respect of Displacements specified by Harmonics of the First Degree.**

26. When \( n > 0 \), we have to calculate expressions for \( A_n, B_n, C_n, D_n \) from the formulæ of § 17. If \( n = 1 \), we have
\[
A_n = A_1 = \frac{1}{\nu} \frac{\alpha^2}{3} \left( f_1 + s^2 \theta_1 \right) + \alpha \frac{dP'}{da} - k^2 \frac{s^2 \alpha^2}{3s^2 + k^2} (2E_n - P'_1 + 2\alpha^2 Q'_1). \ldots \ (83)
\]
Now if we put \( h^2 = 0 \) and \( k^2 = 0 \), we find
\[
f_1 = A \left[1 - \frac{7s^2 \alpha^2}{2.5} + \frac{9s^4 \alpha^4}{2.4.5} - \cdots \left(-\right) \left(\frac{2k+5}{2.4\ldots2k.5}\right) \right],
\]
\[
s^2 \theta_1 = A \left[-\frac{3}{5} + \frac{s^2 \alpha^2}{2} - \frac{7s^4 \alpha^4}{2.4.5} + \cdots \left(-\right)^{+1} \left(\frac{2k+3}{2.4\ldots2k.5}\right) \right],
\]
\[
P'_1 = \frac{2}{3\nu} A \left[1 - \frac{\alpha^2}{2.5} + \frac{s^2 \alpha^4}{2.4.5} - \cdots \left(-\right)^{+1} \left(\frac{s^2 - 2\alpha^2}{2.4\ldots2k.5}\right) \right],
\]
and therefore, if we put \( h^2 = 0 \) and \( k^2 = 0 \) in \( A_1 \), we get

\[
A_1 = \frac{\alpha^2}{3\nu} \frac{2A}{5} \left[ 1 - \frac{s^2 \alpha^2}{2} + \frac{s^4 \alpha^4}{2.4} - \ldots \left(-\right)^{s^x \alpha^{2x}} \frac{s^{2x-2} \alpha^{2x}}{2.4 \ldots 2k \ldots} \right] + \frac{2A}{3\nu} \left[ -\alpha^2 + \frac{s^2 \alpha^4}{2} - \ldots \left(-\right)^{s^x \alpha^{2x}} \frac{s^{2x-2} \alpha^{2x}}{2.4 \ldots 2(2k-2) \ldots} \right] = 0.
\]

It follows that \( A_1 \) vanishes to the first order in \( h^2 \) and \( k^2 \), and therefore, as has been explained, we must evaluate the limit of \( A_e h^{-2} \) when \( h^2 \) and \( k^2 \) vanish. We have to expand the terms of \( f_1 \), \( s^2 \theta_1 \) and \( \alpha dP_1/da \) correctly as far as \( h^2 \); in calculating the remaining terms of \( A_1 \), we may put \( h^2 \) and \( k^2 \) equal to zero in \( E_1 \), \( P_1' \) and \( Q_1' \).

The terms of \( f_1 \) which are of the first order in \( h^2 \) are

\[
Ah^2 \left[ \frac{-\alpha^2}{2.5} + \frac{7.9 s^2 \alpha^4}{2.4.5} \left(\frac{1}{9} + \frac{1}{7}\right) - \ldots \left(-\right)^{s^x \alpha^{2x}} \frac{7.9 \ldots (2k+5) s^{2x-2} \alpha^{2x}}{2.4 \ldots 2k \ldots} \right] .
\]

The terms of \( s^2 \theta_1 \) which are of the first order in \( h^2 \) are

\[
Ah^2 \left[ \frac{3}{5} \frac{1}{5s^3} - \frac{s^2 \alpha^4}{2.4.5} - \ldots \left(-\right)^{s^x \alpha^{2x}} \frac{s^{2x-2} \alpha^{2x}}{2.4 \ldots 2k} \left(\frac{1}{7} + \frac{1}{9} + \ldots + \frac{1}{2k+3}\right) \right].
\]

Hence the terms of \((f_1 + s^2 \theta_1) \alpha^2 / 3\nu \) which are of first order in \( h^2 \) are

\[
Ah^2 \left[ \frac{3}{5} \frac{1}{5s^3} - \frac{s^2 \alpha^4}{2.4.5} + \ldots \left(-\right)^{s^x \alpha^{2x}} \frac{s^{2x-2} \alpha^{2x}}{2.4 \ldots 2k} \right] \left(\frac{1}{7} + \frac{1}{9} + \ldots + \frac{1}{2k+3}\right)^{-1}.
\]

Again, when we keep those terms only which are of the first order in \( h^2 \) and \( k^2 \), we find from (52) of \$ 11,

\[
p_2 = \frac{1}{2.5s^3} h^2 ,
\]

\[
p_4 = \frac{1}{2.4.5} k^2 ,
\]

\[
p_5 = -\frac{1}{2.4.6.5.7} (h^2 + k^2) ,
\]

\[
p_6 = \frac{1}{2.4.6.8.5.7} \left( 7.9 s^2 h^2 \left(\frac{1}{7} + \frac{1}{9}\right) + k^2 7s^3 \right) ,
\]

\[
p_7 = -\frac{1}{2.4.6.8.10.5.7.9} 11s^4 h^2 \left(\frac{1}{7} + \frac{1}{9} + \frac{1}{11}\right) + k^2 7.9. s^2 \right) ,
\]

\[
\ldots ,
\]

\[
p_{2x} = (-)^x \frac{1}{2.4 \ldots 2k.5.7 \ldots (2k+1)} \left( 7.9 \ldots (2k+1) s^{2x-e} h^2 \left(\frac{1}{7} + \frac{1}{9} + \ldots + \frac{1}{2k+1}\right) + k^2 7.9 \ldots (2k-1) s^2 \right) ;
\]

\[
\ldots.
\]
and therefore the terms of \( \alpha dP' / da \) which are of the first order in \( h^2 \) and \( k^2 \) are

\[
\frac{2}{3\nu} s^2 A \left[ 2p_2 \alpha^2 + 4p_4 \alpha^4 + \ldots + 2\kappa p_2 \alpha^2 \right],
\]

where \( p_2, \ldots \) have the above values, that is to say, these terms are

\[
\frac{2Ah^2}{15\nu} \left[ \frac{\alpha^2}{5s^2} - \frac{s^2 \alpha^4}{2.4.7} + \ldots (\cdots \frac{s^2 \alpha^{2k+1}}{2.4 \ldots (2k-2)} \right] \frac{1}{(2k-2)^2} + \frac{1}{2k+1} \cdots \frac{1}{2} + \frac{1}{9} + \ldots \right]
\]

\[
+ \frac{2Ak^2}{15\nu} \left[ \frac{\alpha^4}{2.5} - \frac{s^2 \alpha^6}{2.4.7} + \ldots (\cdots \frac{s^2 \alpha^{2k}}{2.4 \ldots (2k-2)} \right] \frac{1}{(2k-2)^2} + \frac{1}{2k+1} \cdots \frac{1}{2} + \frac{1}{9} + \ldots \right].
\]

It follows that the terms of the first order in \( h^2 \) and \( k^2 \) in

\[
\frac{\alpha^2}{3\nu} (f + s^2 \theta) + \alpha \frac{dP'}{da}
\]

are

\[
\frac{Ah^2 \alpha^2}{15\nu} \left[ \frac{1}{s^2} \frac{\alpha^2}{2} + \frac{s^2 \alpha^4}{2.4} + \ldots (\cdots \frac{s^2 \alpha^{2k}}{2.4 \ldots (2k-2)} \right] \frac{1}{(2k-2)^2} + \frac{1}{2k+1} \cdots \frac{1}{2} + \frac{1}{9} + \ldots \right]
\]

\[
+ \frac{2Ak^2 \alpha^2}{15\nu} \left[ \frac{1}{5} \frac{\alpha^4}{2.5} + \frac{1}{7} \frac{s^2 \alpha^6}{2.4.7} + \ldots (\cdots \frac{s^2 \alpha^{2k}}{2.4 \ldots (2k-2)} \right] \frac{1}{(2k-2)^2} + \frac{1}{2k+1} \cdots \frac{1}{2} + \frac{1}{9} + \ldots \right],
\]

or they are

\[
\frac{Ak^2 \alpha^2}{15s^2} e^{-4\phi a} + \frac{2Ak^2 \alpha^2}{15s^2 \nu} \left( \frac{1}{5} \frac{s^2 \alpha^2}{2} - \frac{1}{7} \frac{s^2 \alpha^4}{2.4} + \ldots \right).
\]

Again, when we put \( h^2 \) and \( k^2 \) equal to zero, we find

\[
2E_1 = \frac{2A}{5s^2} \left[ -1 + \frac{s^2 \alpha^2}{2} - \frac{s^2 \alpha^4}{2.4} + \ldots (\cdots \frac{s^2 \alpha^{2k}}{2.4 \ldots (2k-2)} \right] ,
\]

\[
- P' = \frac{2As^2}{15\nu} \left[ -1 + \frac{s^2 \alpha^4}{2} + \frac{s^2 \alpha^6}{2.4.6} - \ldots (\cdots \frac{s^2 \alpha^{2k}}{2.4 \ldots (2k-2)} \right] ,
\]

\[
2\alpha^2 Q'_1 = \frac{2As^2}{15\nu} \left[ - \frac{1}{5s^2} + \frac{1}{7} \frac{s^2 \alpha^4}{2} - \frac{1}{9} \frac{s^2 \alpha^6}{2.4} - \ldots (\cdots \frac{s^2 \alpha^{2k}}{2.4 \ldots (2k-2)} \right] ,
\]

and therefore the terms of the first order in \( h^2 \) and \( k^2 \) in

\[
- \frac{k^2 \alpha^2}{3s^2 + h^2} (2E_1 - P' + 2\alpha^2 Q'_1)
\]

are

\[
- \frac{1}{3} k^2 \alpha^2 \left[ - \frac{2A}{5s^2} e^{-4\phi a} + \frac{2A}{5s^2 \nu} \left( \frac{s^2 \alpha^2}{2.5} - \frac{s^2 \alpha^4}{2.4.7} + \ldots (\cdots \frac{s^2 \alpha^{2k}}{2.4 \ldots (2k-2)} \right) \right] .
\]

Hence the terms of \( A_1 \) which are of the first order in \( h^2 \) and \( k^2 \) are

\[
\frac{1}{5} \frac{Ak^2 \alpha^2}{s^2} e^{-4\phi a},
\]

and

\[
\lim_{h \to 0} \frac{A_1}{h^2} = \frac{A}{5s^2 \nu} \alpha^2 e^{-4\phi a} . . . . . . . . . . (84)
\]
27. Again, when we put \( h^2 = 0 \) and \( k^2 = 0 \), we find that

\[
B_1 = -\frac{1}{3 \nu} (f_1 + s^2 \theta_1) + \frac{2}{\alpha} \frac{dE_1}{d\alpha} + \alpha \frac{dQ_1'}{d\alpha} - Q_1',
\]

where

\[
-\frac{1}{3 \nu} (f_1 + s^2 \theta_1) = -\frac{2A}{15 \nu} \left[ 1 - \frac{s^2 \alpha^2}{2} + \frac{s^4 \alpha^4}{2 \cdot 4} - \frac{s^6 \alpha^{2\kappa}}{2 \cdot 4 \cdot 6 \cdot 8} - \ldots \right],
\]

\[
\frac{2}{\alpha} \frac{dE_1}{d\alpha} = \frac{2A}{5} \left[ 1 - \frac{s^2 \alpha^2}{2} + \frac{s^4 \alpha^4}{2 \cdot 4} - \frac{s^6 \alpha^{2\kappa}}{2 \cdot 4 \cdot 6 \cdot 8} - \ldots \right],
\]

\[
\alpha \frac{dQ_1'}{d\alpha} - Q_1' = \frac{A}{15 \nu} \left[ \frac{1}{5} - \frac{s^2 \alpha^2}{2} \frac{6}{7 - 1} + \frac{s^4 \alpha^4}{2} \frac{6}{7 - 1} - \frac{s^6 \alpha^{2\kappa}}{2 \cdot 4 \cdot 6 \cdot 8} - \ldots \right].
\]

Hence we have, when \( h^2 = 0 \) and \( k^2 = 0 \),

\[
B_1 = \frac{2A}{5} \left( 1 - \frac{1}{2 \nu} \right) e^{-q \alpha} + \frac{2A}{5 \nu} \left[ \frac{1}{5} - \frac{1}{7} \frac{s^2 \alpha^2}{2} + \frac{1}{9} \frac{s^4 \alpha^4}{2 \cdot 4} - \ldots \right],
\]

\[
= -\frac{A}{5} \left( 2 - \frac{1}{\nu} \right) e^{-q \alpha} + \frac{2A}{5 \nu} (s \alpha)^{-2} \int_0^{\infty} x^4 e^{-q x} dx \quad \ldots \ldots \quad (85)
\]

Also when \( n = 1 \) we have

\[
C_n = C_1 = \frac{h^3 k^2 \alpha^2}{s^3} \psi_n(k \alpha),
\]

and therefore

\[
\lim_{n \to 0} \frac{C_1}{h^3 k^2} = -\frac{\alpha^2}{3 s^2}; \quad \ldots \ldots \quad (86)
\]

and we have also

\[
D_n = D_1 = k^3 \left[ \frac{1}{2} \psi_1(k \alpha) + 3 \psi_2(k \alpha) + (1 + h^2/s^3)^{-1} \psi_1(k \alpha) \right],
\]

and therefore

\[
\lim_{n \to 0} \frac{D_1}{k^2} = \frac{3}{2} \left( -\frac{1}{3} \right) + 3 \frac{1}{3} \frac{1}{5} = -\frac{3}{10}; \quad \ldots \ldots \quad (87)
\]
28. In the case where \( n = 1 \) the condition of gravitational instability, viz.,
\[
\lim_{k \to 0} \left( A_j \kappa^{-2} D_j \kappa^{-2} - B_j \kappa^{-2} \right) = 0,
\]
becomes
\[
- \frac{3}{10} \frac{A \alpha^2}{5 \pi \nu} e^{-v_{\omega}} + \frac{\alpha^2}{3 \pi^2} \left( \frac{1}{5} \left( 2 - \frac{1}{\nu} \right) e^{-v_{\omega}} + \frac{2 A}{5 \nu} (s \alpha)^{-1} \int_0^{s \alpha} x^4 e^{-v_{\omega}} dx \right) = 0. \quad (88)
\]

But we have
\[
\int_0^{s \alpha} x^4 e^{-v_{\omega}} dx = - (s^3 \alpha^3 + 3s \alpha) e^{-v_{\omega}} + \int_0^{s \alpha} 3 e^{-v_{\omega}} dx,
\]
and therefore the condition of gravitational instability becomes
\[
3 \left[ \int_0^{s \alpha} e^{-v_{\omega}} dx - e^{-v_{\omega}} \left( 3s \alpha + (s \alpha)^3 + \left( \frac{19}{20} - \nu \right) (s \alpha)^5 \right) \right] = 0.
\]

If now we put
\[
s^3 \alpha^3 = x^3 = 2z^3,
\]
the equation becomes
\[
\frac{3}{2} \int_0^{s \alpha} e^{-v_{\omega}} dx = e^{-v_{\omega}} \left[ 3z + 2x^3 + \left( \frac{19}{5} - 4\nu \right) z^5 \right] = 0, \quad . . . \quad (89)
\]
where the factor \( 2\pi^{-1} \) has been inserted because the expression in the square brackets is tabulated in many easily accessible books.

Let \( y \) denote the left-hand member of the equation (89). When \( z \) is small, \( y \) is small of order \( z^5 \). In fact, we have
\[
\int_0^{s \alpha} e^{-v_{\omega}} dt = e^{-v_{\omega}} \left[ z + \frac{2x^3}{3} + \frac{4z^5}{3.5} + \ldots + \frac{2x^2z^{2k+1}}{3.5 \ldots (2k+1)} + \ldots \right];
\]
and when \( z \) is small, the first approximation to \( y \) is \(- (3 - 4\nu)z^5 \). When \( z \) is great, \( \int_0^{s \alpha} e^{-v_{\omega}} dt \) is approximately equal to \( \frac{3}{2} \sqrt{\pi} \); and thus \( y \) is positive when \( z \) is great. The equation (89) has a root zero and at least one positive root. The zero root is irrelevant to our problem; it is introduced in transforming equation (88) into equation (89). Now we have
\[
\frac{dy}{dz} = - z^5 e^{-v_{\omega}} \left\{ (15 - 20\nu) - \frac{2}{5} (19 - 20\nu) z^2 \right\};
\]
and, since \( 15 - 20\nu \) and \( 19 - 20\nu \) are positive when \( \nu < \frac{3}{4} \), the expression last written vanishes for one positive value of \( z \). Hence it follows that the equation (89) has only one positive root, and there is one and only one positive value of \( s^3 \alpha^3 \) which satisfies equation (88).

By means of the tables it can be shown that, when \( \nu = 0 \), the root \( z \) lies between 1.9 and 2, so that \( s^3 \alpha^3 \) lies between 7.22 and 8. When \( \nu = \frac{1}{3} \), the root \( z \) lies between 1.8 and 1.9, so that \( s^3 \alpha^3 \) lies between 6.48 and 7.22.
Stability in Respect of Displacements Specified by Harmonics of the Second and Third Degrees.

29. When \( n = 2 \) and \( h^2 = 0, k^2 = 0 \), we have

\[
A_n = A_2 = \frac{\alpha^2}{5\nu} \left( f_2 + s^2\theta_2 \right) + \alpha \frac{dP'}{d\alpha} + \frac{2}{5} \theta_2 + 3E_2 + 3\alpha^2Q'_2,
\]

where

\[
f_2 = A \left[ 1 - \frac{8}{2.7} s^3\alpha^2 + \frac{8}{2.4} \left( \frac{8}{7} \right) \left( \frac{8}{4} \right) \left( \frac{8}{1} \right) \alpha^4 - \ldots \right],
\]

\[
\theta_2 = A \left[ -\frac{5}{6s^3} + \frac{1}{2}s^2\alpha^2 - \frac{8}{2.7} \alpha^4 - \ldots \right],
\]

\[
E_2 = A \left[ -\frac{1}{6s^3} + \frac{\alpha^2}{2.7} - \frac{8}{2.4} \alpha^4 - \ldots \right],
\]

\[
P'_2 = \frac{3s^2A}{5\nu} \left[ -\frac{\alpha^2}{12s^3} + \frac{\alpha^4}{2.4} - \frac{8}{2.4} \alpha^6 - \ldots \right],
\]

\[
Q'_2 = \frac{2As^2}{5\nu} \left[ -\frac{1}{6s^3} + \frac{\alpha^2}{2.7} - \frac{8}{2.4} \alpha^4 - \ldots \right],
\]

From these we find

\[
A_2 = -\frac{2A\alpha^2}{5\nu} \left[ \frac{1}{6} - \frac{s^3\alpha^2}{2.7} + \frac{8s^4\alpha^4}{2.4} - \ldots \right],
\]

\[
-\frac{6A\alpha^2}{5\nu} \left[ \frac{1}{6.7} - \frac{s^3\alpha^2}{2.7} + \frac{8s^4\alpha^4}{2.4} - \ldots \right],
\]

\[
-\frac{15A}{s^3} \left[ \frac{1}{6} - \frac{s^3\alpha^2}{2.7} + \frac{8s^4\alpha^4}{2.4} - \ldots \right],
\]

\[
-\frac{2A}{s^3} \left[ \frac{1}{6} - \frac{s^3\alpha^2}{2.5} + \frac{8s^4\alpha^4}{2.4} - \ldots \right].
\]

By means of the identities

\[
\frac{(2\kappa+2)(2\kappa+4)}{(2\kappa+3)(2\kappa+5)} = 1 - \frac{2}{2\kappa+3} + \frac{3}{(2\kappa+3)(2\kappa+5)},
\]

\[
\frac{(2\kappa+2)(2\kappa+4)}{(2\kappa+5)(2\kappa+7)} = 1 - \frac{6}{2\kappa+5} + \frac{15}{(2\kappa+5)(2\kappa+7)},
\]

\[
\frac{(2\kappa+2)(2\kappa+4)}{(2\kappa+1)(2\kappa+3)} = 1 + \frac{2}{2\kappa+1} - \frac{1}{(2\kappa+1)(2\kappa+3)},
\]
we transform the series

\[
\frac{1}{5} \left[ \frac{1}{6} - \frac{x^2}{2.7} + \frac{8x^4}{2.4.7.9} - \cdots \right] (2\kappa + 2) (2\kappa + 4) x^{2\kappa + 6} \cdot \frac{1}{2.4.6.7.9} \cdots (2\kappa + 5) \cdots
\]

\[
\frac{1}{5} \left[ \frac{1}{6.7} - \frac{x^2}{2.7.9} + \frac{8x^4}{2.4.7.9.11} - \cdots \right] (2\kappa + 2) (2\kappa + 4) x^{2\kappa + 6} \cdot \frac{1}{2.4.6.7.9} \cdots (2\kappa + 7) \cdots
\]

\[
\left[ \frac{1}{6} - \frac{x^2}{2.5} + \frac{8x^4}{2.4.5.7} - \cdots \right] (2\kappa + 2) (2\kappa + 4) x^{2\kappa + 6} \cdot \frac{1}{2.4.6.5.7} \cdots (2\kappa + 3) \cdots
\]

respectively, into the forms

\[
\frac{1}{16} \left[ \left( \frac{1}{3} - \frac{2}{3.5} \right) - \frac{2}{3} \left( \frac{1}{3} - \frac{2}{3.5} + \frac{3}{3.5.7} \right) + \frac{3}{3} \left( \frac{1}{3} - \frac{2}{3.5} + \frac{3}{3.5.7} - \frac{3}{3.5.7} \right) - \cdots \right],
\]

\[
\frac{1}{16} \left[ \left( \frac{1}{3} - \frac{6}{3.5} + \frac{15}{3.5.7} \right) - x^2 \left( \frac{1}{3} - \frac{6}{3.5} + \frac{15}{3.5.7} \right) + x^4 \left( \frac{1}{3} - \frac{6}{3.5} + \frac{15}{3.5.7} \right) \right. \ldots, \]

\[
\frac{1}{16} \left[ \left( 1 + \frac{2}{3} - \frac{3}{3.5} \right) - x^2 \left( 1 + \frac{2}{3} - \frac{3}{3.5} \right) + x^4 \left( 1 + \frac{2}{3} - \frac{3}{3.5} \right) - \cdots \right],
\]

or

\[
\frac{1}{16} \left[ \left( \frac{1}{3} - \frac{x^2}{3.5} \right) - x^2 \left( \frac{1}{3} - \frac{x^2}{3.5} + \frac{x^4}{3.5.7} \right) + \frac{3}{3} \left( \frac{1}{3} - \frac{x^2}{3.5} + \frac{x^4}{3.5.7} \right) - \cdots \right],
\]

\[
\frac{1}{16} \left[ \left( \frac{1}{3} - \frac{x^2}{3.5} + \frac{x^4}{3.5.7} \right) - x^2 \left( \frac{1}{3} - \frac{x^2}{3.5} + \frac{x^4}{3.5.7} \right) + \frac{3}{3} \left( \frac{1}{3} - \frac{x^2}{3.5} + \frac{x^4}{3.5.7} \right) - \cdots \right]
\]

\[
\frac{1}{16} \left[ \left( 1 - \frac{x^2}{3} + \frac{x^4}{3.5} + \cdots \right) + 2 \left( \frac{1}{3} - \frac{x^2}{3.5} \right) - \left( \frac{1}{3} - \frac{x^2}{3.5} \right) - \cdots \right].
\]

Now we have

\[
1 - \frac{x^2}{3} + \frac{x^4}{3.5} = \cdots = x^{-1} e^{-t \omega} \int_0^\infty e^{t \omega} dx,
\]

\[
1 - \frac{x^2}{3} + \frac{x^4}{3.5} = \frac{1}{x^2} - x^{-2} e^{-t \omega} \int_0^\infty e^{t \omega} dx,
\]

\[
\cdots,
\]

and therefore the three series are respectively equal to

\[
\frac{1}{16} \left[ \left( 1 + \frac{2}{x^2} + \frac{3}{x^4} \right) x^{-1} e^{-t \omega} \int_0^\infty e^{t \omega} dx - \left( \frac{1}{x^2} + \frac{3}{x^4} \right) \right],
\]

\[
\frac{1}{16} \left[ \frac{1}{x^4} + \frac{15}{x^6} - \left( \frac{1}{x^2} + \frac{6}{x^4} + \frac{15}{x^6} \right) x^{-1} e^{-t \omega} \int_0^\infty e^{t \omega} dx \right],
\]

\[
\frac{1}{16} \left[ 1 - \frac{1}{x^2} - \left( x^2 - \frac{2}{x^2} \right) x^{-1} e^{-t \omega} \int_0^\infty e^{t \omega} dx \right].
\]
On substituting for the three series in the expression for $A_2$ we find

$$A_2 = \frac{a^2}{8v} \left[ \frac{1}{s^3a^2} - \frac{45}{s^4a} - \left( \frac{1}{s^3a^2} - \frac{15}{s^4a^4} - \frac{45}{s^4a^6} \right) \right] e^{-i\omega} \int_0^\infty e^{i\omega x} dx - \frac{A}{16s^2} \left[ 2 + \frac{17}{s^3a^2} - \frac{45}{s^4a^4} - \left( \frac{32}{s^4a^5} - \frac{45}{s^4a^6} \right) \right] e^{-i\omega} \int_0^\infty e^{i\omega x} dx \right].$$

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30. Again we have, when $h^2 = 0$ and $k^2 = 0$,

$$B_2 = -\frac{1}{5\nu} \left( f_2 + s^2\theta_2 \right) + \frac{8}{5a} \frac{dE_2}{da} + a \frac{dQ'_2}{da} - Q'_2,$$

and with the values already used for $f_2$... this gives

$$B_2 = -\frac{A}{5\nu} \left[ \frac{1}{6} \left( \frac{s^2a^2}{2.7} + \frac{8s^4\alpha}{2.47.9} \right) - \left( \frac{(2k+2)(2k+4)}{2.4.6.7.9} \right) \right]$$

$$+ \frac{8A}{5} \left[ \frac{1}{7} \left( \frac{8s^2a^2}{2.7.9} + \frac{8.10s^4\alpha}{2.47.9.11} \right) - \left( \frac{(2k+2)(2k+4)(2k+6)}{2.4.6.7.9...(2k+7)} \right) \right]$$

$$- \frac{2A}{5\nu} \left[ \frac{1}{6.7} \left( \frac{s^2a^2}{2.7.9} + \frac{3.8s^4\alpha}{2.47.9.11} \right) - \left( \frac{(2k-1)(2k+2)(2k+4)}{2.4.6.7.9...(2k+7)} \right) \right].$$

The first of these series has already been transformed into

$$-\frac{A}{16\nu} \left[ \left( 1 + \frac{2}{s^2a^2} + \frac{3}{s^4a^4} \right) e^{-i\omega} \int_0^\infty e^{i\omega x} dx - \left( \frac{x^3}{s^3a^2} + \frac{3}{s^4a^4} \right) \right].$$

By means of the identity

$$\frac{(2k+2)(2k+4)(2k+6)}{(2k+3)(2k+5)(2k+7)} = 1 - \frac{3}{2k+3} + \frac{9}{(2k+3)(2k+5)} - \frac{15}{(2k+3)(2k+5)(2k+7)}$$

we transform the series

$$\frac{1}{5} \left[ \frac{1}{7} \left( \frac{8x^2}{2.7.9} + \ldots \right) - \left( \frac{(2k+2)(2k+4)x^{2k}}{2.4.6.7.9...(2k+7)} \right) \right]$$

into

$$\frac{1}{16} \left[ \left( 1 - \frac{3x^3}{3.5} \right) - 9 \left( \frac{x^3}{3.5} + \frac{x^4}{3.5.7} \right) \right] + 9 \left( \frac{x^3}{3.5} + \frac{x^4}{3.5.7} \right) + 9 \left( \frac{x^3}{3.5.7} + \frac{x^4}{3.5.7.9} \right)$$

$$- 15 \left( \frac{x^3}{3.5.7} + \frac{x^4}{3.5.7.9} \right) \right],$$

which is the same as

$$\frac{1}{16} \left[ \left( 1 + \frac{3}{x^3} + \frac{9}{x^4} \right) x^{-1} e^{-i\omega} \int_0^\infty e^{i\omega x} dx - \left( \frac{1}{x^3} + \frac{4}{x^4} + \frac{15}{x^5} \right) \right],$$
and by means of the identity
\[
\frac{(2\kappa-1)(2\kappa+2)(2\kappa+4)}{(2\kappa+3)(2\kappa+5)(2\kappa+7)} = 1 - \frac{10}{2\kappa+3} + \frac{51}{(2\kappa+3)(2\kappa+5)} - \frac{120}{(2\kappa+3)(2\kappa+5)(2\kappa+7)}
\]
we transform the series
\[
\frac{1}{5} \left[ \frac{-1}{6.7} - \frac{x^2}{2.7.9} + \frac{3.8x^4}{2.4.7.9.11} - \ldots \right] (\frac{2\kappa-1}{2\kappa+3})(\frac{2\kappa+2}{2\kappa+5})(\frac{2\kappa+4}{2\kappa+7}) x^n \ldots
\]
into
\[
\frac{1}{16} \left[ \left(1 - \frac{x^2}{3} + \frac{x^4}{3.5} \ldots \right) - 10 \left( \frac{1}{3} - \frac{x^2}{3.5} + \frac{x^4}{3.5.7} \ldots \right) + 51 \left( \frac{1}{3.5} - \frac{x^2}{3.5.7} + \frac{x^4}{3.5.7.9} \ldots \right) - 120 \left( \frac{1}{3.5.7} - \frac{x^2}{3.5.7.9} + \frac{x^4}{3.5.7.9.11} \ldots \right) \right],
\]
which is the same as
\[
\frac{1}{16} \left[ (1 + \frac{10}{x^2} + \frac{51}{x^4} + \frac{120}{x^6}) x^{-1} e^{-ix} \int_0^{\pi} e^{ix} dx - (\frac{1}{x^2} + \frac{11}{x^4} + \frac{120}{x^6}) \right].
\]
Hence we have
\[
B_2 = \frac{A}{16} \left[ \frac{3}{x^2} + \frac{25}{s^4} + \frac{240}{s^8} \left( \frac{3}{s^2} + \frac{22}{s^4} + \frac{105}{s^6} + \frac{240}{s^8} \right) (s\alpha)^{-1} x^{-1} e^{-ix} \int_0^{\pi} e^{ix} dx \right]
\]
\[
- \frac{A}{2} \left[ \frac{1}{s^2} + \frac{4}{s^4} + \frac{15}{s^6} \left( \frac{1}{s^2} + \frac{3}{s^4} + \frac{9}{s^6} + \frac{15}{s^8} \right) (s\alpha)^{-1} x^{-1} e^{-ix} \int_0^{\pi} e^{ix} dx \right].
\]
Again we find
\[
\lim_{s^2 = 0} C_2 = \frac{1}{5.7.9} (8s^2a^2 + 175\nu), \quad \ldots \quad (92)
\]
and
\[
\lim_{s^2 = 0} D_2 = \frac{33}{5.7.9}, \quad \ldots \quad (93)
\]
Hence the equation \(\lim_{s^2 = 0} (A_2D_2k^2 - B_2C_2k^2) = 0\) is
\[
(8x^2 + 175\nu) \left[ \frac{3}{x^2} + \frac{25}{x^4} + \frac{240}{x^6} \right] - \left( \frac{3}{x^2} + \frac{22}{x^4} + \frac{105}{x^6} + \frac{240}{x^8} \right) x^{-1} e^{-ix} \int_0^{\pi} e^{ix} dx
\]
\[
- 8\nu \left[ \left( \frac{1}{x^2} + \frac{4}{x^4} + \frac{15}{x^6} \right) - \left( \frac{1}{x^2} + \frac{3}{x^4} + \frac{9}{x^6} + \frac{15}{x^8} \right) x^{-1} e^{-ix} \int_0^{\pi} e^{ix} dx \right]
\]
\[
+ 33 \left[ \left( \frac{2}{x^2} - \frac{90}{x^4} \right) - \left( 2x^2 - \frac{2}{x^2} - \frac{30}{x^4} - \frac{90}{x^6} \right) x^{-1} e^{-ix} \int_0^{\pi} e^{ix} dx \right]
\]
\[
- \nu \left[ \left( \frac{2}{x^2} - \frac{17}{x^4} - \frac{45}{x^6} \right) - \left( 2x^2 - \frac{19}{x^2} - \frac{32}{x^4} - \frac{45}{x^6} \right) x^{-1} e^{-ix} \int_0^{\pi} e^{ix} dx \right] \right] = 0, \quad (94)
\]
where \(x\) is written for \(sa\). A factor \(\nu^{-1}s^{-2}\) has been omitted in forming the equation, as neither \(\nu\) nor \(s\) is supposed to vanish. The terms of lowest degree in the left-hand
member of the equation (94) will be found to be \( \frac{1}{3} 80\nu (24\nu -19) \), which is negative when \( \frac{2}{3} > \nu > 0 \). Hence the left-hand member of this equation is negative when \( x = 0 \). Also it will be found by the method of asymptotic expansion (cf. § 22 above) that, when \( x \) is great, the left-hand member is approximately equal to \(-1280x^{-4}\) for all values of \( \nu \). After the previous cases, in which the corresponding equations have a single root, we are led to expect that in this case there is no root, for it is unlikely that there is more than one. We proceed to verify this expectation in the cases where \( \nu = 0 \) and \( \nu = \frac{1}{3} \).

31. Multiply the left-hand member of (94) by \( x^4 \) and put \( \nu = 0 \). We get

\[
8 \left[ (3x^6 + 25x^2 + 240) - (3x^6 + 22x^4 + 105x^2 + 240) x^{-1} e^{-12z} \int_{0}^{z} e^{12z} \, dx \right]
+ 33 \left[ (2x^4 - 90) - (2x^4 - 2x^4 - 30x^2 - 90) x^{-1} e^{-12z} \int_{0}^{z} e^{12z} \, dx \right] = 0,
\]

or, since 10 is a factor,

\[
9x^6 + 20x^2 - 105 - (9x^6 + 11x^4 - 15x^2 - 105) x^{-1} e^{-12z} \int_{0}^{z} e^{12z} \, dx = 0.
\]

The term of lowest degree in the left-hand member, when expanded in powers of \( x \), is \(-\frac{1}{3} 8x^6\); when \( x \) is great, the left-hand member approximates to \(-128\). Now multiply by \( xe^{12z} \), and put

\[
y = (9x^6 + 20x^2 - 105x) e^{12z} - (9x^6 + 11x^4 - 15x^2 - 105) \int_{0}^{z} e^{12z} \, dx.
\]

We know that when \( x \) is small \( y \) is small and negative of the order \(-\frac{1}{3} 8x^6\), and that when \( x \) is great \( y \) is great and negative of the order \(-128xe^{12z}\). Now

\[
\frac{dy}{dx} = (54x^6 - 30x^2) e^{12z} - (54x^6 + 44x^2 - 30x) \int_{0}^{z} e^{12z} \, dx,
\]

and, if we put \( z \) for \( x^{-1} dy/dx \),

\[
z = (54x^6 - 30x) e^{12z} - (54x^6 + 44x^2 - 30) \int_{0}^{z} e^{12z} \, dx,
\]

where \( z \) is negative both when \( x \) is small and when \( x \) is great; also

\[
\frac{dz}{dx} = 88x^2 e^{12z} - (216x^2 + 88x) \int_{0}^{z} e^{12z} \, dx,
\]

and if we put \( w \) for \( x^{-1} dz/dx \),

\[
w = 88xe^{12z} - (216x^2 + 88) \int_{0}^{z} e^{12z} \, dx,
\]

where \( w \) is negative both when \( x \) is small and when \( x \) is great; and now

\[
\frac{dw}{dx} = -128x^2 e^{12z} - 432x \int_{0}^{z} e^{12z} \, dx,
\]
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which is always negative. Hence \( u \) is always negative, and therefore \( dz/dx \) is always negative, therefore also \( z \) is always negative and \( dy/dx \) is always negative, and therefore \( y \) is always negative. Thus the equation \( y = 0 \) has no real root other than the irrelevant root \( x = 0 \), which was introduced in the process of forming the equation.

Again, when \( \nu = \frac{1}{4} \), we multiply the left-hand member of (94) by \( x^{6} \) and obtain the equation

\[
(23x^{6} + 128x^{4} - 70x^{2} + 3675) - (23x^{8} + 105x^{6} + 268x^{4} + 1155x^{2} + 3675) x^{-1} e^{-4z} \int_{0}^{z} e^{4z} dx = 0,
\]

of which the left-hand member is of the order \( -x^{6} \) when \( x \) is small and \( -x^{2} \) when \( x \) is great. We put

\[
y = (23x^{7} + 128x^{5} - 70x^{3} + 3675x) e^{4z} - (23x^{8} + 105x^{6} + 268x^{4} + 1155x^{2} + 3675) \int_{0}^{z} e^{4z} dx,
\]

and then we put

\[
z = \frac{1}{x} \frac{dy}{dx}, \quad w = \frac{1}{x} \frac{dz}{dx}, \quad u = \frac{1}{x} \frac{dw}{dx},
\]

and find

\[
\frac{du}{dx} = -(512x^{4} + 4552x^{2} + 3640)e^{4z} - 8832 \int_{0}^{z} e^{4z} dx,
\]

which is always negative. Just as before, we deduce that \( y \) is always negative. It is therefore proved that the equation

\[
\lim_{A \to 0} (A_{2} D_{2} k^{-2} - B_{2} C_{2} k^{-2}) = 0
\]

has no real root.

32. When \( n = 3 \), and \( h^{3} = 0 \) and \( k^{3} = 0 \), we have

\[
A_{3} = \frac{\alpha^{2}}{7\nu} \left( f_{3} + s^{2} \theta_{3} \right) + \frac{4}{7} \theta_{3} + \alpha \frac{d\bar{P}_{3}}{d\alpha} + \frac{4}{8} \left( 4E_{3} + 4\alpha^{2}Q'_{3} \right),
\]

where

\[
f_{3} = A \left( 1 - \frac{s^{2} \alpha^{2}}{2} + \frac{s^{4} \alpha^{4}}{2.4} - \ldots \right) \left( - \frac{s^{2} \alpha^{2}}{2.4 \ldots 2k} \right),
\]

\[
\theta_{3} = -\frac{A}{s^{3}} \left( 1 - \frac{s^{2} \alpha^{2}}{2} + \frac{s^{4} \alpha^{4}}{2.4} - \ldots \right) \left( - \frac{s^{2} \alpha^{2}}{2.4 \ldots 2k} \right),
\]

\[
\bar{P}_{3} = \frac{4A}{7\nu} \left( - \frac{\alpha^{2}}{7} + \frac{s^{2} \alpha^{4}}{2.9} - \frac{s^{4} \alpha^{6}}{2.4.11} + \ldots \right) \left( - \frac{s^{2} \alpha^{2}}{2.4 \ldots 2k} \right),
\]

\[
E_{3} = \frac{A}{s^{3}} \left( - \frac{1}{7} + \frac{s^{2} \alpha^{2}}{2.9} - \frac{s^{4} \alpha^{4}}{2.4.11} + \ldots \right) \left( - \frac{s^{2} \alpha^{2}}{2.4 \ldots 2k} \right),
\]

\[
Q'_{3} = \frac{3A}{7\nu} \left( - \frac{1}{7} \cdot \frac{s^{2} \alpha^{2}}{2.9.11} - \frac{s^{4} \alpha^{4}}{2.4.11.13} + \ldots \right) \left( - \frac{s^{2} \alpha^{2}}{2.4 \ldots 2k} \right),
\]
We use the identity
\[
\frac{4}{(2\kappa + 5)(2\kappa + 7)} = \frac{2}{2\kappa + 5} - \frac{2}{2\kappa + 7}
\]
to transform \( Q'_3 \) and then we use the results
\[
1 - \frac{s^2 \alpha^2}{2} \frac{s' \alpha^4}{2} - ... = e^{-s' \alpha} \nu,
\]
\[
\frac{1}{7} \frac{s^2 \alpha^2}{2} \frac{s' \alpha^4}{2} + ... = (s\alpha)^{-7} \int_0^{sa} x^8 e^{-x^8} dx,
\]
\[
\frac{1}{9} \frac{s^2 \alpha^2}{2} \frac{s' \alpha^4}{2} + ... = (s\alpha)^{-9} \int_0^{sa} x^8 e^{-x^8} dx.
\]

We thus find
\[
A_3 = -\frac{4A}{7\nu s^2} \left[ 3(s\alpha)^{-5} \int_0^{sa} x^8 e^{-x^8} dx - 2(s\alpha)^{-7} \int_0^{sa} x^8 e^{-x^8} dx \right. + \nu e^{-s' \alpha} + \frac{28}{3} \nu(s\alpha)^{-1} \int_0^{sa} x^8 e^{-x^8} dx \]. \quad (95)
\]

Again we have, when \( k^3 = 0 \) and \( k^2 = 0 \),
\[
B_3 = -\frac{1}{7\nu} (f_3 + s^2 \theta_3) + \frac{10}{7} \frac{dE_3}{da} + \alpha \frac{dQ'_3}{da} - Q'_3,
\]
and here we have
\[
\alpha \frac{dQ'_3}{da} - Q'_3 = -\frac{3A}{7\nu} \left[ -\frac{1}{7} \frac{s^2 \alpha^2}{2} \frac{s' \alpha^4}{2} + ... \right. \left. + \frac{3s' \alpha^4}{2} \frac{s^2 \alpha^2}{2} - ... \right] \left[ \frac{(2k-1)s^2 \alpha^2}{2} \ldots \right.
\]
\[
while the other series can be obtained from those written above. We use the identity
\[
\frac{2k-1}{(2k+7)(2k+9)} = -\frac{4}{2k+7} + \frac{5}{2k+9}
\]
to transform the series last written, and we use also the results which we used in obtaining the expression (95) for \( A_3 \), and find
\[
B_3 = A \left[ 12(s\alpha)^{-1} \int_0^{sa} x^8 e^{-x^8} dx - 15(s\alpha)^{-2} \int_0^{sa} x^8 e^{-x^8} dx + 10\nu(s\alpha)^{-2} \int_0^{sa} x^8 e^{-x^8} dx \right]. \quad (96)
\]

We find also the results
\[
\lim_{k^3 \to 0} \frac{C_3}{k^3} = \frac{4}{3.5.7.9.9} (2s^2 \alpha^2 + 49\nu), \quad \ldots \ldots \ldots \quad (97)
\]
\[
\lim_{k^3 \to 0} \frac{D_3}{k^3} = -\frac{3}{4.5.7} \quad \ldots \ldots \ldots \quad (98)
\]
Hence the equation
\[ \lim_{\nu \to 0} (A_3D_4k^{-2} - B_3C_3k^{-2}) = 0 \]
becomes
\[
3 \left[ \left( 3x^2 + \frac{28}{3} \nu \right) x^{-7} \int_0^x x^6 e^{-i\theta} dx + \nu e^{-i\theta} - 2x^{-7} \int_0^x x^6 e^{-i\theta} dx \right]
- \frac{4}{27} (2x^3 + 49\nu) \left[ 12x^{-7} \int_0^x x^6 e^{-i\theta} dx - (15 - 10\nu)x^{-9} \int_0^x x^6 e^{-i\theta} dx \right] = 0, \quad (99)
\]
where \( x \) is written for \( sa \).

33. An irrelevant factor \( \nu \) has been introduced into the left-hand member of (99). We find that when \( x = 0 \) this expression becomes
\[
\frac{\nu}{81} \left( 539 - \frac{1960}{3} \nu \right),
\]
which is positive for all admissible values of \( \nu \). We find also, by the method of asymptotic expansion, that the expression is positive, when \( x \) is great, for all values of \( \nu \). We proceed to show that, in the important cases \( \nu = 0 \) and \( \nu = \frac{1}{4} \), the equation has no real root. The left-hand member of (99) being an even function of \( x \), we may treat \( x \) as positive.

When \( \nu = 0 \), the left-hand member of equation (99) is
\[
\frac{7}{9} x^{-7} \left[ 7x^3 \int_0^x x^6 e^{-i\theta} dx - 2 \int_0^x x^6 e^{-i\theta} dx \right],
\]
which is positive for small values of \( x \). The differential coefficient of the expression within the square brackets is
\[ 14x \int_0^x x^6 e^{-i\theta} dx + 5x^5 e^{-i\theta}, \]
which is positive for all real values of \( x \). Hence the left-hand member of equation (99) cannot be negative if \( x \) is positive, or the equation has no real root.

When \( \nu = \frac{1}{4} \), the left-hand member of equation (99) becomes
\[
x^{-9} \left[ \left( \frac{49}{9} x^4 - \frac{133}{9} x^3 \right) \int_0^x x^6 e^{-i\theta} dx - \left( \frac{62}{27} x^2 - \frac{1225}{54} \right) \int_0^x x^6 e^{-i\theta} dx \right] + \frac{3}{4} e^{-i\theta} = 0. \quad (100)
\]
The expression within the square brackets is greater than
\[
5 (x^4 - 3x^3) \int_0^x x^6 e^{-i\theta} dx - (3x^2 - 22) \int_0^x x^5 e^{-i\theta} dx, \quad \ldots \quad \ldots \quad (101)
\]
where this expression is obtained from the other by replacing every positive coefficient by the next smaller integer and every negative coefficient by the next greater integer.
Since
\[ \int_0^x x^a e^{- bx} \, dx = - x^b e^{- bx} + 7 \int_0^x x^a e^{- bx} \, dx, \]
the expression (101), when multiplied by 7, is
\[ (5x^4 - 36x^2 + 154) \int_0^x x^a e^{- bx} \, dx + 5 (x^2 - 3)x^a e^{- bx}. \quad \ldots \quad (102) \]
Also we have
\[ \int_0^x x^a e^{- bx} \, dx = x^a e^{- bx} \left( \frac{1}{9} + \frac{x^2}{9 \cdot 11} + \frac{x^4}{9 \cdot 11 \cdot 13} + \ldots \right); \]
and therefore the coefficient of \( x^a e^{- bx} \) in the expansion of (102) is \( \frac{1}{9} (154 - 9 \times 15) \), the coefficient of \( x^{a+2} e^{- bx} \) is \( \frac{1}{9} (154 - 36 \times 11 + 5 \times 99) \), and the coefficient of \( x^{a+2k} e^{- bx} \) for all values of \( k \) which are greater than 1 is
\[ \frac{1}{9 \cdot 11 \ldots (2\kappa + 5)} \left( \frac{154}{(2\kappa + 7)(2\kappa + 9)} - \frac{36}{2\kappa + 7} + 5 \right), \]
or
\[ \frac{20\kappa^2 + 88\kappa + 145}{9 \cdot 11 \ldots (2\kappa + 5)}. \]
Hence all the coefficients are positive, the expression (102) is positive, and the left-hand member of (100) is positive for all positive values of \( x \). Thus, in this case also, the equation (99) has no real root.

**Summary of the Solution of the Mathematical Problem.**

34. We have now solved in essentials the mathematical problem of the vibrations of a gravitating sphere, initially homogeneous and in a state of hydrostatic pressure, and have found the conditions of gravitational instability. We have shown that, when any normal, or principal, vibration is taking place, the dilatation at a distance \( r \) from the centre is specified by the product of a certain function of \( r \) and a spherical harmonic of positive integral degree. We have shown further that, in each such mode of vibration, the components of displacement can be expressed in terms of the same spherical harmonic, and that the radial displacement at a point distant \( r \) from the centre is the product of a function of \( r \) and the same harmonic. We obtained the form of the frequency equation, and the forms of all the functions which enter into its expression.

We proceeded to investigate the conditions which must hold in order that the frequency equation may be satisfied by a zero value of the frequency. We showed that, when such a value is not introduced irrelevantly in the process of forming the equation, its occurrence points to genuine gravitational instability. We found that the condition of such instability is the condition that a certain equation, containing the variable quantity \( s^2 a^2 \), or \( \frac{4\pi \gamma \rho \beta^2}{(\lambda + 2\mu)} \), may be satisfied by a real positive value.
of this quantity. The constant $\mu$ denotes the rigidity and $\lambda + \frac{3}{2}\mu$ the modulus of compression. When the harmonic specifying the vibrations is of zero degree, that is to say, when the vibrations are radial, we found that the critical value of $s^2a^2$ lies between 4 and 5 if $v$, or $\mu/(\lambda + 2\mu)$, is zero, and that it lies between 3 and 4 if $v$ is $\frac{1}{4}$. In the case of vibrations specified by spherical harmonics of the first degree, we found that the critical value of $s^2a^2$ lies between 7.22 and 8 if $v = 0$, and it lies between 6.48 and 7.22 if $v = \frac{1}{4}$. In the cases of vibrations specified by spherical harmonics of the second and third degrees we found that there is no critical value of $s^2a^2$, or that the sphere is stable, in respect of the corresponding types of displacement, for all values of $\lambda + 2\mu$. It was to be expected that the critical values of $s^2a^2$ would increase rapidly as the complexity of the type of vibration, specified by the degree of the appropriate harmonic, increases; and we appear to be justified in concluding that instability cannot occur in respect of displacements specified by spherical harmonics of any degree higher than the first.

35. The result that the critical values of $s^2a^2$ are lower when $v = \frac{1}{4}$ than when $v = 0$ means that a higher value of the constant $\lambda + 2\mu$ is required, to secure stability, when there is considerable rigidity than when there is very little rigidity. This result accords with general dynamical principles; for it is a known result, and one which has been shown to be in accordance with such principles, that the frequency of any mode of vibration, involving compression, of a sphere free from gravitation diminishes as $(\lambda + 2\mu)/\mu$ diminishes, that is, as $v$ increases.* Consequently, for a given value of $\gamma\rho_0^2a^2$, the value of $\gamma\rho_0^2a^2/(\lambda + 2\mu)$ which would be required, in order to reduce the frequency to zero, diminishes as $v$ increases, or the critical value of $\lambda + 2\mu$ increases as $v$ increases.

36. The result that the critical value of $s^2a^2$ is lower when $n = 0$ than when $n = 1$ means that a higher value of $\lambda + 2\mu$ would be required, to secure stability, in the case of radial displacements than in the case of displacements specified by spherical harmonics of the first degree. The spherical body of uniform density could be stable in respect of all types of displacement except radial displacements. If the value of $s^2a^2$ were intermediate between the critical values corresponding to $n = 0$ and $n = 1$, this would be the case; and the body would tend to take up a different configuration, in which the density would be more concentrated towards the centre. The result that, in the case where $n = 1$ also, there exists a critical value of $s^2a^2$, which is not more than twice as great as the value associated with $n = 0$, the initial state in both cases being one of uniform density, suggests very strongly that there would be a critical value of $\lambda + 2\mu$, in respect of the case $n = 1$, even if the configuration were such that the body was stable as regards radial displacements. We should then have a body with a spherically symmetrical distribution of density, but with elasticity too small for this configuration to be stable in respect of displacements specified by spherical harmonics of the first degree; and it may be inferred that the critical mean

value of $\lambda + 2\mu$ for such a body would not be very different from the critical value obtained for $\lambda + 2\mu$ by treating the body as homogeneous, and paying attention to those types of displacement only which are specified by spherical harmonics of the first degree.

37. If this conclusion is admitted, as I think it must be, it would follow that a spherical planet with a spherically symmetrical distribution of density, and stable as regards radial displacements, might be unstable as regards displacements of the type in question; and then it would tend to be displaced in such a way that the boundary, or any concentric sphere, moves to a position in which its centre no longer coincides with the centre of gravity, while the matter in a thin spherical layer becomes condensed in one hemisphere and rarefied in the other. The density being in excess in one hemisphere and in defect in the other, and the excess or defect at any point, at a stated distance from the centre, being proportional to the distance of the point from the bounding plane of the two hemispheres, the distribution of density may be aptly described as "hemispherical," and the state of the body may be described as one of "lateral disturbance." The concentration of density towards one radius, on which the centre of gravity lies, has the effect of diminishing the potential energy of gravitation, and this diminution may more than counterbalance the increment of potential energy due to strain. The proved existence of a critical value for $\lambda + 2\mu$ (in the case of a homogeneous body) indicates that this state of things really can occur. An illustration of the nature of a hemispherical distribution of density will be found in §§ 47, 48 below.

38. The results found by Jeans (1903) in the solution of the problem of the gravitating sphere subjected to an external field of force, which balances gravitation throughout the sphere when it is at rest, may be compared with those obtained above in the case where the gravitation is balanced by initial pressure. In Jeans' solution, just as here, the modes of vibration are specified by the spherical harmonics which enter into the expression for the dilatation; and, in any normal mode, the formula for the dilatation contains a single spherical harmonic, and the radial displacement at any stated distance from the centre is proportional to the same harmonic. If the degree of the harmonic exceeds zero, instability can occur for a sufficiently small value of the resistance to compression, whatever the degree of the harmonic may be. It is not restricted to the case where the degree is unity, as it is in our problem of initial stress; but the value of the resistance to compression required for instability diminishes rapidly as the degree of the harmonic increases. Instability enters first when the harmonic is of the first degree,* that is to say, for lateral disturbances. The critical values of $\delta^2\omega^2$ are 6.72 when $\nu = 0$ and 5.33 when $\nu = \frac{1}{4}$, the degree of the harmonic being unity. Since these values are a little less than the critical values found in the solution of the problem of initial stress, it may be concluded that the effect of initial stress, as compared with that of an external field of force, is to

* The question of radial instability was not considered by Jeans.
increase slightly the stability of the body in respect of disturbances specified by harmonics of the first degree, and to increase it enormously in respect of disturbances specified by harmonics of higher degrees.

Application to the Problem of the Gravitational Stability of the Earth.

39. For a body of the same size and mass as the Earth, the values of $\alpha$ and $\rho_0$ in C.G.S. units are $6.37 \times 10^8$ and $5.53$; the value of $\gamma$ being $6.65 \times 10^{-8}$, the value of $\frac{3}{2}\pi\gamma\rho_0^2\alpha^2$ is $3.46 \times 10^{12}$. In the following table the first column gives a value of $s^2\alpha^2$, the second column gives the corresponding value of $\lambda + 2\mu$ (the body being of the same size and mass as the Earth), the third and fourth columns give the values of the corresponding moduluses of compression in the cases where $\nu = 0$ and $\nu = \frac{1}{4}$, irrelevant entries being omitted. These moduluses are denoted by $k_0$ and $k_1$. The quantities given in the fifth, sixth, and seventh columns are the moduluses of compression of steel, glass, and mercury (denoted by $k_s$, $k_g$, $k_m$).

<table>
<thead>
<tr>
<th>$s^2\alpha^2$</th>
<th>$\lambda + 2\mu$</th>
<th>$k_0$</th>
<th>$k_1$</th>
<th>$k_s$</th>
<th>$k_g$</th>
<th>$k_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$1.15 \times 10^{12}$</td>
<td></td>
<td>$7.68 \times 10^{11}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$8.64 \times 10^{11}$</td>
<td>$8.64 \times 10^{11}$</td>
<td>$5.76 \times 10^{11}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$6.91 \times 10^{11}$</td>
<td>$6.91 \times 10^{11}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$4.54 \times 10^{11}$</td>
<td></td>
</tr>
<tr>
<td>7.22</td>
<td>$5.33 \times 10^{11}$</td>
<td>$3.57 \times 10^{11}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$4.79 \times 10^{11}$</td>
<td>$4.79 \times 10^{11}$</td>
<td>$3.19 \times 10^{11}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4.32 \times 10^{11}$</td>
<td>$4.32 \times 10^{11}$</td>
<td></td>
<td></td>
<td></td>
<td>$2.60 \times 10^{11}$</td>
</tr>
</tbody>
</table>

According to these results, a homogeneous solid body of the same size and mass as the Earth, with a modulus of compression as great as that of steel, would have complete gravitational stability. If the modulus of compression were equal to, or less than that of glass, the planet would be unstable as regards radial disturbances, and a concentration of density towards the centre would take place. If the critical value of
\( \lambda + 2 \mu \), which was found in the case of lateral disturbances, is assumed to be the critical mean value of \( \lambda + 2 \mu \) for a planet in which the mass is condensed towards the centre, then we may say that, if the mean modulus of compression were about equal to that of glass, and there were very little rigidity, the planet would be unstable as regards lateral disturbances; but, if there were considerable rigidity, it would be stable. If, on the other hand, the mean modulus of compression were decidedly less than that of glass, though not so small as that of mercury, the planet would be unstable as regards lateral disturbances, even though it possessed a considerable mean rigidity.

40. In order to settle the question of the gravitational stability or instability of the Earth, we must assign the appropriate values to the constants \( \lambda \) and \( \mu \). Lord Kelvin's theory of elastic tides in a solid sphere led to the result that the tidal effective rigidity of the Earth is not less than that of steel. This result suggests that \( \mu \) should not be taken to be less than \( 8.19 \times 10^4 \) C.G.S. units; but, since it was obtained by treating the Earth as incompressible, it affords no means of determining the value of \( \lambda \). Jeans (1903) proposed to deduce the values of \( \lambda \) and \( \mu \) from the observed velocities of propagation of earthquake shocks. In a homogeneous elastic solid body, free from gravitation and initial stress, irrotational waves of dilatation are propagated with the velocity \( \left[ \frac{(\lambda + 2 \mu)}{\rho_0} \right]^\frac{1}{3} \), where \( \rho_0 \) is the density, and equivoluminal waves of distortion are propagated with the velocity \( \left[ \frac{\mu}{\rho_0} \right]^\frac{1}{3} \), while waves of a third type are propagated over the surface with a velocity approximately equal to \( (0.9) \left[ \frac{\mu}{\rho_0} \right]^\frac{1}{3} \). When a great earthquake takes place, the disturbance received at a distance from the source consists of three sets of disturbances: two sets of "preliminary tremors," and the "main shock." The first set of preliminary tremors is received at distant places at such times as it would be if it travelled directly through the Earth with a velocity of about 10 kiloms. per second. The second set of tremors is propagated apparently in a rather less regular fashion, but the times at which it can be observed at distant stations are nearly the same as they would be if it travelled directly through the Earth with a velocity of about 5 kiloms. per second. The main shock is received at distant places at such times as it would be if it travelled over the surface of the Earth with a velocity of about 3 kiloms. per second. The identification of the three sets of disturbances with the three sets of waves which are theoretically known seems to be inevitable, and the discrepancy between the ratio of velocities of equivoluminal and superficial waves and the ratio of velocities of the second set of tremors and the main shock may be explained by the supposition that, while the velocity of transmission of these tremors depends upon the mean rigidity of the Earth as a whole, the velocity of transmission of the main shock depends upon the average

rigidity of surface rock. Assuming this explanation, we are led to attribute to surface rocks an average rigidity approximately equal to \(6 \times 10^{11}\) C.G.S. units, and to the Earth as a whole the much higher mean rigidity \(1.38 \times 10^{12}\) C.G.S. units; further, since the ratio of velocities of the first and second set of tremors is approximately 2 : 1, we are led to assume for \(\lambda + 2\mu\) the value \(5.53 \times 10^{12}\) C.G.S. units, and for \(\nu\), or \(\mu/(\lambda + 2\mu)\), the value \(\frac{1}{3}\). By analogy to the "tidal effective rigidity" we may introduce the phrases "seismic effective rigidity" and "seismic effective modulus of compression"; and the values of these quantities would be \(1.38 \times 10^{12}\) and \(3.69 \times 10^{12}\) C.G.S. units respectively. When the value of \(\lambda + 2\mu\) for the Earth is taken to be \(5.53 \times 10^{12}\), the corresponding value of \(s^2a^2\) is 0.625. The results of § 39 appear to warrant the conclusion that the moduluses of elasticity of the Earth in its present state are sufficiently great to render a spherically symmetrical configuration completely stable.

41. In obtaining the above values for \(\lambda + 2\mu\) and \(\mu\) no account is taken of gravitation or initial stress, and it is possible that the most appropriate values would be a little different from those found above if gravitation and initial stress, to say nothing of heterogeneity of density, could be taken into account. For this reason, although a complete solution of the problem of wave-propagation in a gravitating planet, even when it is regarded as homogeneous, cannot be obtained, the following argument may not be without value:—The equations of vibratory motion of a gravitating sphere in a state of initial pressure have been obtained in § 3 above. From equations (10) and (11) of § 3 we can deduce the equation

\[
\frac{\partial^2 \Delta}{\partial t^2} = \frac{\lambda + 2\mu}{\rho_0} \left\{ \nabla^2 \Delta + 6s^2 \Delta + s^2 \frac{\partial \Delta}{\partial r} \right\}, \quad \ldots \quad (103)
\]

and the three equations of the type

\[
\frac{\partial^2 \varphi}{\partial t^2} = \frac{\mu}{\rho_0} \left\{ \nabla^2 \varphi - \frac{s^2}{2\nu} \left( \frac{\partial \Delta}{\partial y} - \frac{z \partial \Delta}{\partial y} \right) \right\}, \quad \ldots \quad (104)
\]

where \(\varphi_x, \varphi_y, \varphi_z\) denote the components of rotation, so that

\[
2\varphi_z = \frac{\partial w}{\partial y} - \frac{\partial v}{\partial z}, \quad \ldots \quad (105)
\]

In a general way we can see that the terms which contain \(s^2\) in these equations are small compared with the remaining terms; for, if waves of length \(L\) are propagated, \(\nabla^2 \Delta\) is of the order \(L^{-2}\Delta\), and \(s^2 \Delta\) is small in comparison with this in the order \(s^2L^2\), which is comparable with \(L^2/\alpha^2\), since \(s^2a^2\) is comparable with unity. It would thus appear that the velocities of propagation of the waves are not much affected by gravitation and initial stress when the wave-length is small compared with the radius of the sphere; and the conclusion would be applicable to superficial waves as well as to waves of dilatation and waves of distortion, because such waves are, in any case, to be investigated by means of equations of the types (103) and (104).
42. In the case of waves of dilatation the argument can be put in a more definite shape. Let us suppose that, near a place, the waves are plane, so that $\Delta$ is a function of $x$ and $t$, and let us write

$$V_1^2 = (\lambda + 2\mu)/\rho_0,$$  \hspace{1cm} (106)

so that $V_1$ is the velocity of waves of dilatation when gravitation and initial stress are disregarded. We have the equation

$$\frac{\partial^2 \Delta}{\partial x^2} + s^2x \frac{\partial \Delta}{\partial x} + 6s^2\Delta = \frac{1}{V_1^2} \frac{\partial^2 \Delta}{\partial t^2},$$

or

$$\frac{\partial^2}{\partial x^2}(e^{ix\Delta}) + s^2\left(\frac{11}{2} - \frac{1}{4}s^2x^2\right)(e^{ix\Delta}) = \frac{1}{V_1^2} \frac{\partial^2}{\partial t^2}(e^{ix\Delta}).$$

In considering the passage of waves near a place, we may treat the term $-\frac{1}{4}s^2x^2$ in the coefficient of $e^{ix\Delta}$ as a constant; and then the equation is satisfied by putting

$$e^{ix\Delta} = B \cos \left\{2\pi L^{-1}(x-x_0-V't)\right\},$$

provided that

$$V_1^2 = V_1^2 \left\{1 - \frac{s^2L^2}{4\pi^2} \left(\frac{11}{2} - \frac{1}{4}s^2x^2\right)\right\}.$$  \hspace{1cm} (107)

Since the greatest values of $s^2x^2$ are comparable with unity, the value of $V_1$, the local velocity of transmission, is a little less than $V_1$, or the actual value of $\lambda + 2\mu$ is a little greater than the seismic effective value. The result (107) may be accepted as being not far from the truth in a region large compared with the wave-length, and small compared with the radius, and situated at a considerable distance from the source of disturbance.

43. Since the equations of type (104) contain the dilatation as well as the components of rotation, it appears that the customary law of independence of waves of dilatation and waves of distortion ceases to hold when gravitation and initial stress are taken into account. It appears also that the velocities of propagation, both of those waves which are mainly dilatational and of those which are mainly distortional, depend on the wave-lengths, and, for the same wave-length, they vary from place to place. When the theory can be developed further, these results may possibly prove to be useful in explaining the observed irregularities in the propagation of the tremors which are recorded in the case of great earthquakes. The high values which seismic observations lead us to attribute to the elastic constants of the earth as a whole are in accord with Lord Rayleigh’s view* that great initial stress increases the effective values both of resistance to compression and of rigidity.

PART II.

A Past State of Gravitational Instability as a Reason for the existing Distribution of Land and Water.

44. Although the conclusion reached by Jeans (1903), that a spherical planet of the same size, mass and elasticity as the Earth, in its present state, would be in a condition of gravitational stability, is confirmed and strengthened by the present investigation, it by no means follows that the Earth has always been in such a state as it is now. The fact that the mean density of the Earth as a whole is greater than the average density of surface rocks points to a concentration of mass towards the centre, and suggests that such a concentration may have come about through the elasticity having once been too small for a homogeneous state to be stable. We have seen that this would have been the case if the modulus of compression was once as small as, or smaller than, that of glass. But we also saw reason to think that, if the mean modulus of compression was once decidedly less than that of glass, spherically symmetrical states of aggregation would also have been unstable, and the body would have existed in some other state. Further, we saw that, if the body was at rest, the state in which it would have existed is that which we have described as a state of lateral disturbance with a hemispherical distribution of density. The excess of density in one hemisphere and defect in the antipodal hemisphere would have existed alongside of the concentration of mass towards the centre.

45. In the paper already cited Jeans (1903) struck out the idea that the distribution of land and water on the surface of the globe is associated with a past state of gravitational instability. He had found that such instability would manifest itself in what has been called above a hemispherical distribution of density. When the square of the irregularity is neglected, the figure of a planet at rest, with such a distribution of density, is a sphere, but the centre of figure does not coincide with the centre of gravity. On taking account of the square of the irregularity, Jeans found that the surface of the planet, still supposed to be at rest, would be such as can be described roughly as a nearly spherical ellipsoid of revolution, with one half slightly flattened at the middle, and the other slightly tapered in the antipodal direction. The figure was described as "pear-shaped," the "pear" having a blunt end, a sharper end, and a waist. The waters of the ocean would presumably collect in the hollow of the waist, and Jeans pointed out that there is some resemblance of the shape of the Earth to this figure, although the "stalk" end of the "pear" was difficult to discover.

In the same year a paper was published by W. J. Sollas,* in which it was concluded from a discussion of the geographical facts that the shape of the Earth

* "The Figure of the Earth," 'Quart. J. Geol. Soc.,' 59 (1903), p. 180.
resembles that of a "pear"; but Sollas' and Jeans' "pears" have little in common beyond the name. Jeans' ideal distribution would consist of a hemisphere which is nearly all land, and an antipodal hemisphere which is nearly all ocean, with a central island in the middle of this ocean. Solls' account of the actual distribution is that in one hemisphere there is a central continent (Africa) nearly surrounded by a belt of seas, while in the antipodal hemisphere there is a central ocean (the Pacific) nearly surrounded by a ring of land, the belt and ring being broken at three places, which are distributed nearly symmetrically around the centres of the two hemispheres. This description suggests very strongly a mathematical account expressed in terms of surface harmonics of the third degree.

If we neglect the rotation of the planet, and regard it as at rest under no external forces, we can reach no other result than that reached by Jeans, viz., that, if the modulus of compression was once so small that a spherically symmetrical state of aggregation would have been unstable, the state of the planet would have been one of lateral disturbance with a hemispherical distribution of density. We should not be in a position to account at all for the geographical facts as presented by Sollas.

46. The Earth is a rotating globe, and it is now generally believed to be the larger of two fragments into which a single body has been broken up; the other fragment is the Moon. In the early history of the Earth-Moon system the two fragments rotated, nearly as a single rigid body; the period of revolution of the Moon was nearly the same as the period of rotation of the Earth. We wish to trace the consequences of supposing that the average elasticity of the material was once much smaller than it is at present—that the average modulus of compression was more of the order of that of mercury, or even water, than of that of glass or steel, and the average rigidity was smaller in comparison with the modulus of compression than it is to-day. We have the problem of determining the distribution of density within the planet, and the consequent shape of its surface. The problem cannot be solved completely, but we can make some progress with it; and we can then attempt to discover the extent to which our results accord with geographical observation. In so far as the accord is good we may regard geography as supporting the hypothesis as to the past state of the Earth.

Illustration of the Nature of a Hemispherical Distribution of Density.

47. We have reason to think that, in the absence of rotation and external forces, the planet, if of sufficiently small elasticity, would have been in the state which we have described as a state of lateral disturbance with a hemispherical distribution of density. Before proceeding to take account of the rotation and external attractions, we consider further the nature of such a disturbance. For this purpose we take the problem of a spherical body, homogeneous when unstrained, and devoid of all rigidity, and suppose that in the initial state the self-atraction of the body is balanced by
hydrostatic pressure. We suppose also that the law of elasticity of the body is that the increment of pressure is proportional to the increment of density. We show that equilibrium is possible in strained states, in which the excess of density at any assigned distance from the centre is proportional to a spherical surface harmonic of the first degree.

In the initial state the pressure $p_0$ and potential $V_0$ are given by the formulae

$$p_0 = \frac{2}{3} \pi \gamma \rho_0^2 \left( \alpha^2 - \gamma^2 \right), \quad V_0 = \frac{2}{3} \pi \gamma \rho_0 (3 \alpha^2 - \gamma^2).$$

In the strained state the pressure $P$, density $\rho$, and potential $V$ are expressed by the formulae

$$P = p_0 + \lambda \xi, \quad \rho = \rho_0 (1 + \xi), \quad V = V_0 + W,$$

where $\xi$ denotes the condensation. The equations of equilibrium are

$$\rho \frac{\partial V}{\partial x} - \frac{\partial P}{\partial x} = 0, \quad \rho \frac{\partial V}{\partial y} - \frac{\partial P}{\partial y} = 0, \quad \rho \frac{\partial V}{\partial z} - \frac{\partial P}{\partial z} = 0,$$

and $W$ is connected with $\xi$ by the equation

$$\nabla^2 W = -4 \pi \gamma \rho_0 \xi.$$

When terms of the second order in the small quantity $\xi$ are neglected, the equations of equilibrium become three equations of the type

$$\rho_0 \frac{\partial W}{\partial x} - \frac{2}{3} \pi \gamma \rho_0^2 x \xi - \lambda \frac{\partial \xi}{\partial x} = 0; \quad \ldots \quad \ldots \quad (108)$$

and, on eliminating $W$, and writing $s^2$ for $\frac{2}{3} \pi \gamma \rho_0^2 / \lambda$, we have

$$\nabla^2 \xi + s^2 \gamma \frac{\partial \xi}{\partial r} + 6 s^2 \xi = 0. \quad \ldots \quad \ldots \quad (109)$$

This equation is satisfied by putting

$$\xi = A (1 - \frac{1}{3} s^2 r^2) e^{-i \omega r} \omega_1,$$

where $A$ is an arbitrary constant and $\omega_1$ is a spherical solid harmonic of the first degree, and this is the most general form of solution in which $\xi$ is finite at $r = 0$, and is proportional when $r = \text{const.}$ to a surface harmonic of the first degree. The additional potential $W$ has the form

$$W = 4 \pi \gamma \rho_0 \left\{ \frac{1}{2} A s^{-2} e^{-i \omega r} \omega_1 + F_1 \right\},$$

where $F_1$ denotes a spherical solid harmonic of the first degree.

Let the bounding surface become

$$r = a + U_\alpha.$$
Since the pressure vanishes at this surface, the expression
\[ \frac{3}{2} \pi \gamma \rho \alpha^2 \left\{ \alpha^2 - (a + U_a)^2 \right\} + \lambda \Lambda \left( 1 - \frac{1}{3} s^2 \alpha^2 \right) e^{-i \omega \alpha} a (\omega_j/r) \]
vanishes, or we have, neglecting \( U_a^2 \),
\[ U_a r^2 = - \left( \frac{1}{3} s^2 \alpha^2 - 1 \right) e^{-i \omega \alpha} A (\omega_j/r), \]
so that \( U_a \) contains the same surface harmonic as \( \omega_j \). The form of \( F_1 \) is determined by the condition that \( W \) is the potential of a distribution of density \( \rho \xi \) through the volume of the sphere \( r = \alpha \), together with a distribution of density \( \rho U_a \) on its surface. Just as in \( \S \) 14, this condition leads to the equation
\[ F_1 = \frac{2}{1} \pi \rho \alpha s^{-2} e^{-i \omega \alpha} \omega_j. \]

48. Now let the bounding surface in the strained state be
\[ r = \alpha + b \cos \theta, \]
which represents a sphere with its centre at a small distance \( b \) from the origin in the direction of the axis of the harmonic. We find
\[ \xi = \frac{s^2 \rho^2 - 5}{s^2 \alpha^2 - 5} e^{i \omega (\alpha - r)} b s^2 r \cos \theta, \]
\[ W = - \frac{4 \pi \gamma \rho}{s^2 \alpha^2 - 5} \left( \frac{3}{2} + e^{i \omega (\alpha - r)} \right) b r \cos \theta. \]

If \( s^2 \alpha^2 > 5 \), the condensation is greatest near the centre, and it is positive on the side remote from the surface which the surface is displaced, so that the centre of gravity is displaced in the opposite sense to the surface. The distance of the centre of gravity from the origin is easily proved to be \( 5b/(s^2 \alpha^2 - 5) \).
GRavitational Stability OF THE Earth.

The variation of the excess density along the axis of the harmonic is illustrated in fig. 1. The surface \( r = a (1 + \epsilon \cos \theta) \) can be an equipotential surface if

\[
\alpha \epsilon = -5b/(s^2 \alpha^2 - 5),
\]

and thus a sphere of radius \( a \) with its centre at the displaced centre of gravity is an equipotential surface. The relative situation of the bounding surface and of this equipotential is illustrated in fig. 2, in which \( O \) denotes the undisplaced centre, \( C \) the centre of the displaced surface, and \( G \) the centre of gravity of the strained sphere. The figures are drawn for the case in which \( s^2 \alpha^2 = 10 \).

The type of disturbance which has been called above a lateral disturbance with a hemispherical distribution of density would be the same in a body possessing some degree of rigidity, but the numerical details would be different.

49. If the equipotential surfaces of a nearly spherical body, with a nearly symmetrical distribution of density, are referred to the centre of gravity of the body as origin, their equations take such forms as

\[
r = a \left(1 + \epsilon_2 S_2 + \epsilon_3 S_3 + \ldots\right),
\]

in which \( \epsilon_2, \ldots \) denote small coefficients, and \( S_2, \ldots \) denote spherical surface harmonics of degrees indicated by the suffixes. There is no term of the form \( \epsilon_1 S_1 \). In the case of the Earth, the coefficients \( \epsilon_2, \ldots \) can be determined by means of pendulum experiments. If we referred to a different origin, near the centre of gravity, a term of the form \( \epsilon_1 S_1 \) would be introduced, but the coefficient \( \epsilon_1 \) could not be determined by means of pendulum experiments, for it does not affect the formula for the variation of gravity over the surface.\(^*\) If we choose an origin in accordance with geometrical considerations, e.g., as the centre of that oblate spheroid which most nearly coincides with the surface of the ocean, the results of pendulum experiments cannot tell us whether this origin coincides with the centre of gravity or not.

Effect of Rotation upon a Planet with a Hemispherical Distribution of Density.

50. In all the preceding work the rotation of the Earth has been neglected. We have now to consider the effect of rotation upon a nearly spherical planet which, in the absence of rotation, would have a hemispherical distribution of density. To simplify the analysis, we shall disregard the concentration of mass towards the centre and also the rigidity of the body. We shall take as the "initial" state of the body a state in which the density is uniform and the stress is hydrostatic pressure,

\(^*\) The result may be inferred from Stokes' investigation of the "Variation of Gravity over the Surface of the Earth," Cambridge, 'Trans. Phil. Soc.,' 8 (1849), or 'Math. and Phys. Papers,' vol. 2, Cambridge, 1883. It is easy to prove it independently.
while the body is rotating, as if rigid, about the axis of $z$ with angular velocity $\omega$; and we shall seek a strained state in which the body could exist without the application of any external forces, this state being such that, in the absence of rotation, the distribution of density would be hemispherical. In the notation of § 47 the equations of steady motion of the body are

$$-\rho \omega^2 x = \rho \frac{\partial V}{\partial x} - \frac{\partial P}{\partial x}, \quad -\rho \omega^2 y = \rho \frac{\partial V}{\partial y} - \frac{\partial P}{\partial y}, \quad 0 = \rho \frac{\partial V}{\partial z} - \frac{\partial P}{\partial z}. \quad \cdots (110)$$

The initial state is determined by the same equations with $\rho_0$, $V_0$, $p_0$ substituted for $\rho$, $V$, $P$. Now the initial figure is an oblate spheroid, and the initial form of $V$ is

$$V_0 = \text{const.} - \frac{1}{2} \left\{ A'(x^2 + y^2) + C' z^2 \right\},$$

where $A'$ and $C'$ are constants; also the initial form of $P$ is

$$P_0 = \text{const.} + \rho_0 \left\{ V_0 + \frac{1}{2} \omega^2 (x^2 + y^2) \right\},$$

$$= \text{const.} - \frac{1}{2} \rho_0 \left\{ (A' - \omega^2) (x^2 + y^2) + C' z^2 \right\}.$$

When we write, as in § 47,

$$\rho = \rho_0 (1 + \xi), \quad P = p_0 + \lambda \xi, \quad V = V_0 + W,$$

and neglect terms which cancel on account of the values of $p_0$ and $V_0$, and also neglect terms which are of the second order in the small quantity $\xi$, the equations (110) become

$$\begin{align*}
\rho_0 \omega^2 x \xi &= -\rho_0 \xi A' x + \rho_0 \frac{\partial W}{\partial x} - \lambda \frac{\partial \xi}{\partial x}, \\
-\rho_0 \omega^2 y \xi &= -\rho_0 \xi A' y + \rho_0 \frac{\partial W}{\partial y} - \lambda \frac{\partial \xi}{\partial y}, \\
0 &= -\rho_0 \xi C' z + \rho_0 \frac{\partial W}{\partial z} - \lambda \frac{\partial \xi}{\partial z}.
\end{align*} \quad \cdots \cdots \cdots (111)$$

Now we have the equations

$$2A' + C' = 4\pi \gamma \rho_0, \quad \nabla^2 W = -4\pi \gamma \rho_0 \xi,$$

and therefore we can eliminate $W$ and obtain the equation

$$\nabla^2 \xi + \left( 6 \omega^2 - 2 \omega^2 \frac{p_0}{\lambda} \right) \xi + \frac{p_0}{\lambda} \left\{ (A' - \omega^2) \left( x \frac{\partial \xi}{\partial x} + y \frac{\partial \xi}{\partial y} + C' z \frac{\partial \xi}{\partial z} \right) \right\} = 0, \quad \cdots (112)$$

where $s^2$ is written for $\frac{4}{3} \pi \gamma \rho_0^2 / \lambda$. If $\omega$ were zero, $A'$ and $C'$ would both be equal to $\frac{4}{3} \pi \gamma \rho_0$, and we therefore put

$$A' = \frac{4}{3} \pi \gamma \rho_0 + A'', \quad C' = \frac{4}{3} \pi \gamma \rho_0 + C'';$$
then equation (112) becomes
\[ \nabla^2 \xi + s^2 r \frac{\partial^2 \xi}{\partial r^2} + 6 s^2 \xi = 2 \omega^2 \frac{p_0}{\lambda} \xi + \frac{p_0}{\lambda} \left\{ \left( A'' - \omega^2 \right) \left( x \frac{\partial \xi}{\partial x} + y \frac{\partial \xi}{\partial y} \right) + C'' z \frac{\partial \xi}{\partial z} \right\}. \] (113)

The left-hand member of this equation is the same as that of equation (107) in \( \S \) 47 above; and therefore, when \( \omega^2 \) is neglected, \( \xi \) can be of the form \( \xi_1 \), where
\[ \xi_1 = A \left( 1 - \frac{1}{2} s^2 r^2 \right) e^{-is^n} \omega_1, \]
the notation being the same as in \( \S \) 48. Now we shall suppose that \( \omega^2 \) is not large, so that we may treat \( \xi_1 \) as an approximation to \( \xi \), and substitute \( \xi_1 \) for \( \xi \) in the right-hand member of equation (113), for all the terms of this member are small of the order \( \omega^2 \xi \). We are then neglecting \( \xi_2 \), but not \( \omega^2 \xi \). To obtain a second approximation, we put
\[ \xi = \xi_1 + \xi', \]
and seek a particular integral of the equation
\[ \nabla^2 \xi' + s^2 r \frac{\partial^2 \xi'}{\partial r^2} + 6 s^2 \xi' = 2 \omega^2 \frac{p_0}{\lambda} \xi_1 + \frac{p_0}{\lambda} \left\{ \left( A'' - \omega^2 \right) \left( x \frac{\partial \xi_1}{\partial x} + y \frac{\partial \xi_1}{\partial y} \right) + C'' z \frac{\partial \xi_1}{\partial z} \right\}. \] (114)

There would be no special difficulty in obtaining a solution of the equation, but it will be sufficient for our purpose to find the form of the solution. The function \( \xi_1 \) may be expressed in terms of polar co-ordinates \( r, \theta, \phi \) in the form
\[ \xi_1 = f(r) \left( \alpha, \sin \theta \cos \phi + \beta, \sin \theta \sin \phi + \gamma, \cos \theta \right), \]
where \( \alpha, \beta, \gamma \) are constants, and \( f(r) \) is a certain function of \( r \) which has been determined. Hence we have
\[ x \frac{\partial \xi_1}{\partial x} + y \frac{\partial \xi_1}{\partial y} = rf(r) \left( \alpha, \sin \theta \cos \phi + \beta, \sin \theta \sin \phi \right) + \frac{1}{2} r^2 f'(r) \sin^2 \theta \left( \alpha, \sin \theta \cos \phi + \beta, \sin \theta \sin \phi + \gamma, \cos \theta \right), \]
\[ z \frac{\partial \xi_1}{\partial z} = rf(r) \gamma, \cos \theta + \frac{1}{2} r^2 f'(r) \cos^3 \theta \left( \alpha, \sin \theta \cos \phi + \beta, \sin \theta \sin \phi + \gamma, \cos \theta \right); \]
and these can be expressed in the forms
\[ x \frac{\partial \xi_1}{\partial x} + y \frac{\partial \xi_1}{\partial y} = rf(r) + r^2 f'(r) \left\{ \sin \theta \left( \alpha, \cos \phi + \beta, \sin \phi \right) + \frac{1}{2} r^2 f'(r) \gamma, \cos \theta \right\} - r^2 f'(r) \left( \cos^2 \theta - \frac{1}{2} \right) \sin \theta \left( \alpha, \cos \phi + \beta, \sin \phi \right) - r^2 f'(r) \gamma, \left( \cos^2 \theta - \frac{1}{2} \cos \theta \right), \]
\[ z \frac{\partial \xi_1}{\partial z} = \frac{1}{2} r^2 f'(r) \sin \theta \left( \alpha, \cos \phi + \beta, \sin \phi \right) + r f(r) + \frac{1}{2} r^2 f'(r) \gamma, \cos \theta + \frac{1}{2} r^2 f'(r) \sin \theta \left( \cos^2 \theta - \frac{1}{2} \right) \left( \alpha, \cos \phi + \beta, \sin \phi \right) + r^2 f'(r) \gamma, \left( \cos^2 \theta - \frac{1}{2} \cos \theta \right) \]
Hence the right-hand member of (114) can be expressed as a sum of terms each of which is the product of a function of \( r \) and a spherical surface harmonic, and the
surface harmonics which occur are those of the first degree and the following harmonics of the third degree:

\[ \cos^3 \theta - \frac{3}{3} \cos \theta, \quad (\cos^2 \theta - \frac{1}{3}) \sin \theta \cos \phi, \quad (\cos^2 \theta - \frac{1}{3}) \sin \theta \sin \phi. \]

To each of these terms there corresponds a term of the same form in \( \xi' \), and therefore also in \( P, \) or \( p_0 + \lambda \xi \); and it follows that the displacement of the bounding surface from its initial form (which is a slightly elliptic oblate spheroid appropriate to the rotation) is expressed by a radial displacement, which consists of a part proportional to a spherical surface harmonic of the first degree, together with parts proportional to the above surface harmonics of the third degree. In like manner all the terms of the additional potential \( W \) are the products of functions of \( r \) and surface harmonics, which are either of the first degree or are the above harmonics of the third degree; but the coefficients of the various harmonics in \( W \) are different from their coefficients in \( \xi \). The equation of the equipotentials under gravity, modified by the rotation, is

\[ V_0 + W + \frac{1}{2} \omega^2 (x^2 + y^2) = \text{const.}, \quad \text{or} \quad p_0 / \rho_0 + W = \text{const.}; \]

and thus the situation of the bounding surface relative to the equipotentials is expressed by a difference of radii at corresponding points, this difference being a sum of terms of the form \( bS \), where \( b \) denotes a constant and \( S \) denotes a surface harmonic; and the surface harmonics which can occur are those of the first degree and the three of the third degree written above.

51. It appears from this investigation that, if a gravitating body, which is rotating about an axis, has so small a modulus of compression that, if the body were at rest, a spherically symmetrical distribution of density would be unstable, it would tend to take up a state in which the distribution of density would not be exactly hemispherical, but the excess density would also contain terms expressed by spherical harmonics of the third degree. The figure of the body would differ from the oblate spheroidal figure appropriate to the rotation by a radial displacement at each point; and this displacement would be expressed partly by spherical surface harmonics of the first degree, indicating that the centre of gravity does not coincide with the centre of figure, and partly by spherical harmonics of the third degree. If the body were entirely devoid of rigidity, the oblate figure appropriate to the rotation would be the same as that of an equipotential surface under gravity, modified by the rotation; and the figure of the body, as determined by difference of level above or below a certain equipotential surface, would be an harmonic spheroid of the third degree, and the situation of the body would be that of such a spheroid when displaced towards one side. If the body possessed some rigidity, the oblate figure appropriate to the rotation would differ a little from that of a nearly coincident equipotential surface, and the shape of it, determined as before, would be that derived from a certain oblate spheroid of small ellipticity by a displacement proportional to a surface harmonic of the third degree. The surface harmonic would be of a somewhat specialised type.
GRavitational Stability of the Earth.

Effect of Certain External Forces.

52. The effect of forces such as the attraction of the Moon at the time when its period of orbital revolution did not differ much from the period of rotation of the Earth would be to draw the planet out into a shape more nearly ellipsoidal, with three unequal axes, than spheroidal. If the planet could have had a symmetrical shape it would have been practically ellipsoidal, and the surfaces of equal density would have been ellipsoids. Whereas the effect of rotation is the same as that of forces derived from a potential of the second degree, symmetrical about the axis of rotation; such forces as we are now considering are derived from a potential, the most important terms of which would be of the second degree, but not symmetrical about the axis of rotation. If the elasticity was too small for an ellipsoidal figure to be stable, the planet would have been in a disturbed state, the nature of which can be inferred from the preceding investigation. We have only to replace in § 50 the initial potential, modified by the rotation, by a general expression of the second degree in the co-ordinates. The only change that would be made in the result would be that those terms in the radial displacement which are expressed by harmonics of the third degree would not be of the specialised type introduced by the rotation, but would be of general type. The figure of the planet would be derived from the ellipsoidal figure appropriate to the rotation, and to the external forces, by a radial inequality expressed by surface harmonics of the first and third degrees. The equipotential surfaces would be obtained from the ellipsoidal equipotentials appropriate to gravity, modified by the rotation and the external forces, by surface harmonics of the same degrees. The result would be that the shape of the planet, as determined by difference of level above or below a certain equipotential, would be a wrinkled ellipsoid, displaced towards one side; and the wrinkle would be expressible by means of a spherical surface harmonic of the third degree.

The Problem of the Shape of the Lithosphere.

53. The problem of determining the form of the equipotentials near the surface of the Earth includes the problem of determining the figure of the surface of the ocean (the "hydrosphere"). The equipotentials which lie outside the nucleus (or "lithosphere") on one side, and sufficiently near to it, cut the surface of the lithosphere towards the other side. Among these equipotential surfaces that one which, outside the lithosphere, coincides with the surface of the ocean is known as the "geoid." The surface of that part of the lithosphere which lies outside the geoid is occupied by land, and can be observed directly; the surface of that part which lies within the geoid can only be observed indirectly by means of soundings. We have no means of investigating the form of the surface of this part of the lithosphere except by estimating its depth at a point below the geoid. The most important deviations from sphericity both of the lithosphere and of the geoid are of such
a nature that these surfaces are nearly oblate spheroids. If the lithosphere were exactly in the form of an oblate spheroid, and its centre of gravity coincided with its centre of figure, it would either lie entirely within the geoid or would protrude from it symmetrically at the North and South Poles. Owing to the rigidity of the lithosphere the ellipticity produced in the geoid by rotation would be slightly greater than that produced in the lithosphere, and thus there is a tendency to lay bare the polar regions; but, since the land of the globe does not consist of two circular islands at the poles, there are other deviations from sphericity, both of lithosphere and geoid, and the relative amounts of these at different places can be expressed by the difference of radii drawn from the centre of gravity. According to the theory which has been here advanced this difference of radii should be, at least in its general features, expressible as a sum of spherical harmonics of the first, second and third degrees.

54. It is easy to verify the presence of some of these harmonics. The effect of a term of the first degree would be to make the lithosphere protrude from the geoid towards one side. If this term were the only one, the land of the globe would form a circular island or continent. It is the fact that most of the land is in one hemisphere. The great circle of the globe which contains most land has a pole situated between Orléans and Le Mans* (latitude 48° N., longitude 30' E.). Again, the zonal harmonic of the third degree vanishes at three circles, one being a great circle. If this term were the only one, the land of the globe would consist of a circular island surrounded by a belt of ocean in one hemisphere, and in the antipodal hemisphere there would be a circular ocean surrounded by a ring of land. This arrangement corresponds to two features of Sollas' description of the Earth's surface. The nearly symmetrical breaking at three places of the belt and three of the ring, which he also noticed, indicates the presence of the sectorial harmonic of the third degree. If we refer to the polar axis, instead of any other morphological axis, the presence of the zonal harmonic of the third degree is indicated by the existence of an Antarctic continent, and by the fact that most of the land of the globe is north of the Equator. The harmonic of the third degree and second rank, referred to the polar axis, vanishes at the Equator and at four meridians symmetrically placed. If this term were the only one, then, in two northern quadrants there would be land, and also in the two alternate southern quadrants, an arrangement which suggests Central Asia and North America as the land quadrants of the northern hemisphere, Australia and South America as those of the southern.

Spherical Harmonic Analysis of the Distribution of Land and Water.

55. By such arguments as the foregoing, and by some trials with small numerical coefficients for the various harmonics, I had convinced myself that many features of the distribution of land and water could be represented by means of harmonics of the third degree, when Professor H. H. Turner suggested to me the advisability of

* E. Brücker, 'Die feste Erdrinde und ihre Formen,' Wien, 1897.
adopting a systematic process for the discovery of appropriate coefficients. He very kindly made, and placed at my disposal, a rough preliminary calculation, and the results were sufficiently encouraging to warrant the undertaking of a considerable piece of computation. A professional computer was employed for a time, but eventually I relied upon my own calculations, taking many precautions to ensure accuracy. The systematic process consists in devising a function to represent the "value of land" at any point, and determining, by the method of approximate quadrature, the coefficients of an expansion of the function in spherical harmonics. The results of such a computation clearly depend upon the chosen "value of land," and judgment must be exercised in selecting appropriate values. Little importance can be attached to the heights of mountains, because the highest mountain ranges are, geologically speaking, modern, the ancient mountains being worn down by denudation and erosion. Too much importance is not to be attributed to the actual coast-line, because this line is subject to many causes of change. The coast-line is but one of the contour-lines of the continental block (the geoid being the level of reckoning), and the shape of the block at considerable depths differs a good deal from that at the surface. At mean-sphere-level (8400 feet below sea-level) the continents, with the exception of the Antarctic continent, form a continuous block.* The Arctic Ocean is reduced, so far as is known, to a trough running nearly along the meridian of Greenwich, from about latitude 65° N. to about latitude 80° N. It may extend to the North Pole and surround it. The polar block spreads southwards in two great masses—America and Eurasia. These are joined through the British Isles, Iceland and Greenland on the one side, and across Behring's Strait on the other; the contour-line at mean-sphere-level runs practically along the 60th parallel between America and Europe and along the 50th parallel between America and Asia. The Eurasian division of the block forks near the Persian Gulf, and tapers southwards in two branches, one containing Africa and the other the Malay Peninsula, adjacent islands, Australia and New Zealand. The Red Sea does not go down to mean-sphere-level, and the Mediterranean does so only in two small patches. The American division of the block is continuous across the Gulf of Mexico, the West Indies and the Caribbean Sea, which, at this depth, equally with Mexico, Central America, and the Isthmus of Panama, form part of the ridge joining North and South America. The ridge has some local depressions. The block tapers towards Cape Horn, in the neighbourhood of which, however, it has a great eastward extension, and this extension turns westward and nearly joins the northern continental block to the Antarctic continental block through the South Shetland Islands.† The Antarctic block also shows a

* The information here detailed in regard to the distribution of the continental blocks and oceanic regions at mean-sphere-level is taken from a map drawn by H. R. MILL in 'The Scottish Geographical Magazine' (Edinburgh), vol. 6 (1890), p. 184. Reference may be made to the rough map on p. 237 below.

† It is now known that the depth of the channel is not so great as it was for a long time supposed to be. See a paper by W. S. BRUCE in 'The Scottish Geographical Magazine' (Edinburgh), vol. 21 (1905), p. 402.
northward extension towards Australasia. The contour-line of the continental blocks at mean-sphere-level is a very important and fairly well ascertained datum of the problem. If, however, we attend exclusively to it, we are liable to emphasise unduly those parts of the block which do not rise above the level of the sea.

56. I calculated the coefficients of a spherical harmonic expansion up to harmonics of the third degree for two different assumptions as to the "value of land." In the first assumption the value $-1$ was attached to those points of the surface which are below mean-sphere-level and the value $0$ to those points which are above it. In the second assumption the value $1$ was attached to those points of the surface which are above sea-level and the value $0$ to those below it. The coefficients obtained by the two assumptions were then added. The somewhat greater importance of the mean sphere may perhaps be sufficiently represented by the result that the maxima obtained by using the first set of coefficients are larger than those obtained by using the second set. The combined distribution for the two sets of coefficients is shown in the following table, in which $\theta$ stands for co-latitude measured from the North Pole, and $\phi$ for longitude measured eastwards from the meridian of Greenwich:—
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| \( \phi \) | \( 90^\circ \) | \( 95^\circ \) | \( 100^\circ \) | \( 105^\circ \) | \( 110^\circ \) | \( 115^\circ \) | \( 120^\circ \) | \( 125^\circ \) | \( 130^\circ \) | \( 135^\circ \) | \( 140^\circ \) | \( 145^\circ \) | \( 150^\circ \) | \( 155^\circ \) | \( 160^\circ \) | \( 165^\circ \) | \( 170^\circ \) | \( 175^\circ \) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
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</table>

57. The surface harmonics of the first degree expressed in ordinary spherical polar co-ordinates \( \theta, \phi \) are 
\[
\sin \theta \cos \phi, \quad \sin \theta \sin \phi, \quad \cos \theta;
\]
and any spherical surface harmonic of the first degree can be expressed in the form
\[
(p \cos \phi + q \sin \phi) \sin \theta + r \cos \theta, \quad \ldots \ldots \quad (115)
\]
where \( p, q, r \) are numbers. The spherical surface harmonics of the second degree are
\[
\sin 2\theta \cos \phi, \quad \sin 2\theta \sin \phi, \quad \sin^2 \theta \cos 2\phi, \quad \sin^2 \theta \sin 2\phi, \quad 3 \cos 2\theta + 1;
\]
and any spherical surface harmonic of the second degree can be expressed in the form
\[
(\alpha \cos \phi + \beta \sin \phi) \sin 2\theta + (\gamma \cos 2\phi + \delta \sin 2\phi) \sin^2 \theta + \epsilon (3 \cos 2\theta + 1). \quad (116)
\]
The spherical surface harmonics of the third degree are
(i.) The zonal harmonic
\[
5 \cos^3 \theta - 3 \cos \theta;
\]
(ii.) The tesseral harmonics of the first rank
\[
(5 \cos^2 \theta - 1) \sin \theta \cos \phi, \quad (5 \cos^2 \theta - 1) \sin \theta \sin \phi;
\]
(iii.) The tesseral harmonics of the second rank
\[
\sin^2 \theta \cos \theta \cos 2\phi, \quad \sin^2 \theta \cos \theta \sin 2\phi;
\]
(iv.) The sectorial harmonics
\[
\sin^3 \theta \cos 3\phi, \quad \sin^3 \theta \sin 3\phi.
\]
Since
\[
5 \cos^3 \theta - 3 \cos \theta = \frac{5}{4} (\cos 3\theta + \frac{3}{3} \cos \theta),
\]
\[
(5 \cos^2 \theta - 1) \sin \theta = \frac{1}{4} (\sin \theta + 5 \sin 3\theta),
\]
\[
\sin^2 \theta \cos \theta = \frac{1}{4} (\cos \theta - \cos 3\theta),
\]
\[
\sin^3 \theta = \frac{1}{4} (3 \sin \theta - \sin 3\theta),
\]
any spherical surface harmonic of the third degree can be expressed in the form
\[
\alpha W + X (b \cos \phi + c \sin \phi) + Y (d \cos 2\phi + e \sin 2\phi) + Z (f \cos 3\phi + g \sin 3\phi), \quad (117)
\]
where \( \alpha, b, c, d, e, f, g \) are numbers, and
\[
W = \cos 3\theta + (0.6) \cos \theta,
\]
\[
X = \sin \theta + 5 \sin 3\theta,
\]
\[
Y = \cos \theta - \cos 3\theta,
\]
\[
Z = 3 \sin \theta - \sin 3\theta.
\]
\[\begin{aligned}
W &= \cos 3\theta + 0.6 \cos \theta, \\
X &= \sin \theta + 5 \sin 3\theta, \\
Y &= \cos \theta - \cos 3\theta, \\
Z &= 3 \sin \theta - \sin 3\theta.
\end{aligned} \quad (118)
\]
* The form \( 3 \cos 2\theta + 1 \) for the zonal harmonic is \( 4 (\frac{3}{5} \cos^2 \theta - \frac{1}{3}) \), and is taken as being more convenient for calculation.

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58. Let \( F(\theta, \phi) \) denote the function to be expanded. The coefficients are expressed by equations of the type

\[
p \int_0^{2\pi} d\phi \int_0^{\pi} d\theta (\cos \phi \sin \theta)^2 \sin \theta = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta F(\theta, \phi)(\cos \phi \sin \theta) \sin \theta. \quad (119)
\]

The factors multiplying the coefficients \( p, \&c. \) in the left-hand members are the integrals of the squares of the several harmonics over the surface of a unit sphere. The integrals in the right-hand members are the integrals, over the surface of the same sphere, of the product of the function to be expanded and the corresponding harmonics. The values of the integrated squares multiplying \( p, \&c. \), are recorded in the following table:

<table>
<thead>
<tr>
<th>Coefficient.</th>
<th>Value of integrated square.</th>
<th>Reciprocals.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p, q, r )</td>
<td>( \frac{4}{3} \pi )</td>
<td>( (1,9,2) \times \frac{59}{236} \pi^{-1} )</td>
</tr>
<tr>
<td>( a, \beta, \gamma, \delta )</td>
<td>( \frac{1}{12} \pi )</td>
<td>( (4) \times \frac{59}{236} \pi^{-1} )</td>
</tr>
<tr>
<td>( e )</td>
<td>( \frac{4}{5} \pi )</td>
<td>( \frac{4}{5} \pi \times \frac{59}{236} \pi^{-1} )</td>
</tr>
<tr>
<td>( a )</td>
<td>( \frac{5}{13} \pi )</td>
<td>( (5) \times \frac{59}{236} \pi^{-1} )</td>
</tr>
<tr>
<td>( b, c )</td>
<td>( \frac{5}{15} \pi )</td>
<td>( (0,3) \times \frac{59}{236} \pi^{-1} )</td>
</tr>
<tr>
<td>( d, e )</td>
<td>( \frac{5}{10} \pi )</td>
<td>( (3) \times \frac{59}{236} \pi^{-1} )</td>
</tr>
<tr>
<td>( f, g )</td>
<td>( \frac{5}{3} \pi )</td>
<td>( (0,5) \times \frac{59}{236} \pi^{-1} )</td>
</tr>
</tbody>
</table>

Since the ratios only are relevant, the integrals in the right-hand members of such equations as (119) are to be multiplied by the numbers in brackets in the third column.

59. To evaluate integrals of the type in the right-hand member of (119), when the value of \( F(\theta, \phi) \) is given by the table of § 56, or any similar table, we treat the integral as a double sum, e.g.,

\[
\sum_{m=0}^{35} \sum_{n=1}^{35} \left( \frac{\pi}{36} \right) F \left( \frac{n\pi}{36}, \frac{m\pi}{36} \right) \left( \cos \frac{m\pi}{36} \sin \frac{n\pi}{36} \right) \sin \frac{n\pi}{36} ;
\]

then we have to evaluate such a double sum as

\[
\sum_{m=0}^{71} \sum_{n=1}^{35} F \left( \frac{n\pi}{36}, \frac{m\pi}{36} \right) \cos \frac{m\pi}{36} \sin \frac{n\pi}{36} ;
\]
We sum first with respect to $m$; but in forming the sum we take account of the fact that $\sin^2(n\pi/36)$ does not change when $n$ is replaced by $36-n$. For example, let $F'$ be equal to 1 at the points indicated in the table, and zero at other points. Then the contribution to the terms containing any $m$ of the two parallels given by $n$ and $36-n$ is either 0, 1, or 2, according as a 1 occurs on neither parallel (for the particular $m$ in question), on one, or on both. This number 0, 1, or 2 is to be multiplied by the value of $\cos(m\pi/36)$ for the chosen $m$; but the same value for the cosine occurs at the meridian given by $72-m$, and the same numerical value with the opposite sign occurs at the meridians given by $36-m$ and $36+m$. We condense into one term the contributions of the eight points given by $n$, $36-n$, $m$, $72-m$, $36\pm m$, and take the ranges of $m$ and $n$ to be respectively 0 to 17 and 1 to 18. Thus, as the multiplier of $\cos(m\pi/36)\sin^2(n\pi/36)$, we have an integral number which necessarily lies between $-4$ and 4, and may be zero, and we have transformed the sum into a double sum of the form

$$\sum_{n=0}^{17} \sum_{m=1}^{18} F'(n, m) \cos \frac{m\pi}{36} \sin^2 \frac{n\pi}{36},$$

where $F'$ is the number in question. The most troublesome part of the process is the determination of $F'$. When $F'$ has been found it is very easy to form the sum of such a series as that written immediately above by summing first with respect to $m$ and then with respect to $n$. When we are dealing with tesseral harmonics of the second rank, we can thus condense into one term the contributions of 16 points of the table, and, when the tesseral harmonic is of the third rank, those of 24 points. Much labour is saved by going through this process, troublesome though it is, and much greater accuracy can be secured, because in the multiplication of $\cos(m\pi/36)$ by $F'$, when $F'$ is, say, 5 or 6, and the value of the cosine to any chosen number of decimal places is used, it is easier to correct the figure in the last place than it is when the same cosine occurs five or six times in a long column of figures which have to be added together.

60. By the use of this method I computed the values of the coefficients $p$, &c., for the function $F(\theta, \phi)$ which is given by the $-1$'s in the table of § 56, the 1's being replaced by zeros. Up to the stage of summation with respect to $m$, inclusive, I kept four decimal figures. Of the terms of the type

$$\sum_{n=0}^{17} \left(F'(n, m) \cos \frac{m\pi}{36}\right) \sin^2 \frac{n\pi}{36},$$

I then kept two decimal figures, formed the sums with respect to $n$, and multiplied them by the corresponding numbers placed in brackets in the third column of the table in § 58. This process gave the coefficients in the second column of the annexed table. The integral parts only were retained. I computed the values of the coefficients $p$, &c., in the same way for the function given by the 1's in the table of § 56, the $-1$'s being replaced by zero. This process gave the coefficients in the third
column of the annexed table. It is to be understood that in both cases the common factors \( \frac{35}{256} \pi^{-1} \) and \( (\pi/36)^2 \) have been omitted.

<table>
<thead>
<tr>
<th></th>
<th>F(θ, φ) = 0 or -1.</th>
<th>F(θ, φ) = 1 or 0.</th>
<th>Sum.</th>
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</thead>
<tbody>
<tr>
<td>p</td>
<td>604</td>
<td>557</td>
<td>1161</td>
</tr>
<tr>
<td>q</td>
<td>495</td>
<td>329</td>
<td>824</td>
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<tr>
<td>r</td>
<td>777</td>
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<td>a</td>
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<td>243</td>
<td>593</td>
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<tr>
<td>β</td>
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<td>366</td>
<td>661</td>
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<tr>
<td>γ</td>
<td>-443</td>
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<td>δ</td>
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<td>98</td>
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</tr>
<tr>
<td>a</td>
<td>-213</td>
<td>-134</td>
<td>-347</td>
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<tr>
<td>b</td>
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<td>d</td>
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<td>-256</td>
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<tr>
<td>e</td>
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<tr>
<td>f</td>
<td>56</td>
<td>26</td>
<td>82</td>
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<td>122</td>
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The Continental Blocks and Oceanic Regions as expressed by Spherical Harmonics of the First, Second and Third Degrees.

61. I then computed the values of the harmonics expressed by (115), (116), (117), for values of θ and φ, which are multiples of 15° (or \( \frac{1}{12} \pi \)), using first the coefficients
given in the second column of the table in § 60, and then the coefficients which are
given in the third column of the same table. Finally I added the values belonging
to the same $\theta$ and $\phi$. The results are shown in the diagram (fig. 3), where the fine

![Fig. 3.](image)

continuous line is the contour-line along which the calculated harmonic inequality
vanishes, the heavy continuous line is the contour-line along which this inequality is
10 per cent. of its maximum below zero, and the dotted line is the contour-line along

![Fig. 4.](image)
which this inequality is 10 per cent. of its maximum above zero. It is to be observed that an inequality expressed by harmonics of uneven degrees has numerically equal values with opposite signs at antipodal points, and therefore the area on the sphere within which such an inequality is positive is equal to the area within which it is negative. But this equality of positive and negative areas does not hold when the harmonics of the second degree are present. A rough calculation showed that the zero line of the inequality illustrated in fig. 3 divides the surface of the sphere into two unequal areas, and the inequality is negative in the larger area. The excess of the negative area above the positive is nearly 10 per cent. of the whole surface. The heavy line in fig. 3 corresponds more nearly than the other lines to the principle by which geographers construct the contour-line at mean-sphere-level. The diagram in fig. 3 suggests many features of the outline of the continental block, and there can be no doubt that the coefficients could be adjusted so as to secure a better agreement.* It seems best, however, to record the results as they are. For the sake of comparison a rough map of the world is added (fig. 4). The heavy continuous line is the outline of the continental block at mean-sphere-level, and the fine continuous line is the coast-line. I have not attempted to draw the map with minute accuracy, and have omitted many small islands and some small enclosed patches of deep sea, because the object aimed at is a comparison of the general features of the map of the world with those of the diagram in fig. 3. The map is drawn by taking the longitude east of Greenwich and the latitude of any point as the Cartesian co-ordinates of the corresponding point of the map. Fig. 3 is drawn in the same way.

The defects of the arrangement in fig. 3, considered as representing the shape of the continental block, are sufficiently obvious, the chief being the absence of any indication of an Arctic ocean, and the almost complete submersion of South America. On the other hand, the fact that even tolerable agreement in so many respects is obtained from a spherical harmonic analysis of the extremely simple distribution detailed in the table of § 56 may be regarded as a confirmation of the theory which led us to assume that harmonics of the first, second, and third degrees should be predominant.

* The coefficients r, ε, a, b, c are especially sensitive to changes in the assumed distribution in the Arctic and Antarctic regions where the actual distribution is least known.
the geoid, is expressible, at least roughly and approximately, by means of harmonics of the first, second, and third degrees. Now, if the shape of the lithosphere is at all close to that in which it may be presumed to have consolidated, the inference would seem to be that, in respect of general features, as distinguished from local irregularities, the positions of the continental blocks and oceanic regions have not changed much since the date of consolidation. This view has in recent times met with considerable support among geologists.

The theory also enables us to make some attempt to indicate the general nature of those changes which could be expected to take place. In estimating the value of such an attempt some allowance must be made for the fact that the theory of an elastic body in a state of initial stress is very far from complete. We try to follow out certain clues drawn from the scanty knowledge we possess of bodies in states of initial stress. Among these the behaviour of cast iron under tensile tests is perhaps important. It is well known that cast iron which has not previously been tested exhibits a stress-strain curve which is essentially different from that of mild steel, but that, after several tests, its behaviour approaches to that of steel. It has been conjectured that the tests have the effect of gradually removing a state of initial stress, and thus reducing the substance to a "state of ease." That state of a rotating gravitating planet which would correspond to a state of ease in solid bodies at its surface would seem to be a state in which the material would be arranged in concentric spheroidal layers of equal density, and the external surface would be an oblate spheroid, the ellipticity being determined by the speed of rotation and the distribution of density; the state of stress in the planet, when in this state of ease, would be one of hydrostatic pressure, and the surface would be an equipotential surface under gravity modified by the rotation. The partial reduction of the body to the state of ease would be effected by gradual stages, probably of the nature of local fractures. Now the wrinkling of the surface, expressed by harmonics of the third degree, arose as a consequence of the displacement of the centre of gravity and of the ellipsoidal configuration. It would at first be small in comparison with the deviations from spherical symmetry which are expressed by harmonics of the first and second degrees. We should therefore expect that the tendency of secular change in the shape of the lithosphere would be to diminish the coefficients of the harmonics of the first and second degrees. An exception must be made in the case of the coefficient \( \epsilon \) of the zonal harmonic of the second degree; for this coefficient represents a difference of ellipticity of the meridians of lithosphere and geoid, and these ellipticities depend upon the speed of rotation. When this coefficient is left out of account, the harmonic inequality of the second degree represents ellipticity of the equator\(^*\) and obliquity of the principal planes; the harmonic inequality of the first degree represents displacement of the centre of gravity from the centre of figure. If the coefficients of

\(^*\) G. H. Darwin concluded from his theory of the tidal deformation of a viscou s spheroid that an initial ellipticity of the equator would tend to be obliterated. 'Phil. Trans. Roy. Soc.,' vol. 170 (1879), p. 30.
the harmonics of the first degree have ratios anywhere near to those given in the table of § 60, the great circle along which the harmonic inequality of the first degree vanishes has a pole somewhere in south-eastern Europe and the opposite pole in the Pacific Ocean. The inequality is positive in Europe, most of Asia, Africa, North America, the northern and central parts of the Atlantic Ocean, and the Arctic regions. The effect of a gradual diminution of the coefficients of the harmonies of the first degree would be a gradual emptying of the Pacific Ocean, accompanied by a rise of sea-level around the shores of the Atlantic Ocean (except towards the southern parts of Africa and South America) and around the northern and western parts of the Indian Ocean. It has been held that such an effect has taken place and constitutes the reason for the difference between a "Pacific coast" and an "Atlantic coast."* The ratios of the coefficients of the various harmonics of the second degree for the two distributions considered in §§ 56–60 are widely divergent, but they agree in leading to negative values for the harmonic inequality of the second degree in the regions contained within oval curves which lie within the basin of the Pacific, and also in the antipodal regions. In a large part of the Pacific region the harmonics of the first and second degrees reinforce each other; in the antipodal region they are antagonistic. Diminution of the coefficients of the harmonics of the second degree would be manifested by a fall of sea-level in the Pacific, and also in a region antipodal to some part of the Pacific. It may not, perhaps, be altogether fanciful to see in the gradual reduction of area of the "Central Mediterranean Sea" of Mesozoic and Tertiary times† the effect of a continual reduction of those coefficients of harmonic inequalities of the second degree which represent ellipticity of the equator and obliquity of the principal planes. Whether these conjectures as to the particular regions which may have been affected are acceptable or not, it can safely be said that the effects of changes in the harmonic inequality of the first degree, and in those of the second degree which we are now considering, would be progressive in the same sense at the same place. They would be manifested in a tendency of the sea to fall in certain regions and to rise in certain complementary regions and gradually to flood wide areas. The gradual character of the positive movements of the strand-line, by which wide areas have been submerged, has been emphasized by Suess.‡

The surface of the lithosphere is nearly an oblate spheroid which does not coincide precisely with an equipotential under gravity modified by the rotation; it is less oblate than the geoid. The surface of a shallow ocean covering an oblate spheroidal planet, whose outer surface is not exactly an equipotential surface, is an oblate spheroid, and its ellipticity is a certain multiple of the ellipticity of the surface of the planet. The ratio of the two ellipticities depends partly on the rigidity of the planet,

† Ibid., pp. 258, 299.
‡ Ibid., p. 543.
partly on the ratio of the density of the ocean to the mean density of the planet, and partly on the angular velocity. Owing to tidal friction, the angular velocity of the Earth's rotation is being gradually diminished. The effect of this is that both the ellipticity of the lithosphere and that of the geoid are being diminished, and the difference of these ellipticities is also being diminished. If, therefore, the shape of the lithosphere were continually adjusted to the instantaneous angular velocity, the value of the coefficient $\epsilon$ of § 57 would diminish continually, and the adjustment would involve a continually increasing deformation. Eventually the deformation would be so great that the strength of the material would be too small to withstand it, and local fractures would take place.* There is, therefore, a constant tendency for the sea-level to rise in the polar regions and to fall in the equatorial regions, the separation between the regions of rising and falling sea-level being marked by the zero-lines of the zonal harmonic of the second degree, that is, by the parallels of latitude, about $35^\circ$ N. and $35^\circ$ S. This rise and fall would be checked at intervals by subsidences, accompanied by series of earthquakes, in equatorial regions.

The effects produced by diminution of the displacement of the centre of gravity, and by changes in the ellipticity of the equator and in the obliquity of the principal planes, appear to be of a different character from the effect of diminishing angular velocity. The former would seem to be spasmodic and occasional, but always in the same sense at the same place; the latter would appear to consist of continuous movements in the same sense, extending over long periods, which are followed by comparatively short periods of spasmodic change in the opposite sense.

These remarks are frankly speculative, and I am well aware that many causes which have contributed to geological changes have been left out of sight. They are put forward as tentative suggestions which, it is hoped, may prove to be of some assistance in the solution of some of the still unsolved problems of geology.

My best thanks are due to Professor W. J. Sollas and Dr. H. N. Dickson for much kind help in regard to geological and geographical questions.

* According to a "Note" in 'Nature,' vol. 39 (1889), p. 613, this effect of diminishing speed of rotation was noted by M. A. Blytt. I have not seen the paper referred to in the "Note."
VI. Investigation of the Law of Burning of Modified Cordite.

By Major J. H. Mansell, Royal Artillery.

Communicated by Sir A. Noble, F.R.S.

Received November 9, 1906,—Read February 14, 1907.

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Some years ago the eminent French chemist Vieille first propounded the law of combustion by parallel surfaces for smokeless propellants. By a propellant we distinguish an explosive which explodes from one that detonates; and it is this combustion by parallel surfaces which is the distinguishing characteristic of the difference of the two phenomena.

Since Vieille first propounded his theory it has been generally accepted as correct. Investigators, however, have not, so far as I am aware, definitely determined what the law is. The general assumption has been that the law is of the form \( S = \alpha P^n \), where \( S \) is the skin burnt in a given time under the average pressure \( P \), \( \alpha \) and \( n \) being constants for the given explosive.

Now, the investigators who have dealt with this subject have all done so with the primary object of finding out what goes on inside a gun when the charge is fired. That has also been my primary object. In fact, it is the practical as distinguished from the purely scientific result of the law which has appealed to all investigators.

Now, the gun is a most complex gas-engine, and in the past has upset the most carefully conceived and elaborated theories. Previous investigators have therefore...
gone straight to the gun and endeavoured to solve the constants $\alpha$ and $n$ in the
general form of the above equation by a system of trial and error.* Some have
concluded that $n$ is unity, others that $n$ is $\frac{1}{2}$ (Ingalis, America), $\frac{3}{4}$ (Gossot and
Liouville, France), 0.9 (Centervall, Sweden), &c. These are wide variations, and,
as I shall show, are due in part to the form of the explosive that different investigators
have experimented with and in part to the following causes.

The principle of calculation in the gun is that the space behind the projectile is
treated as a closed vessel. Now, as the projectile moves down the bore the size of
the vessel increases. The size of the vessel therefore directly depends on the distance
the projectile will move in a given time under a given pressure. Here at once is the
difficulty, and it entirely depends upon what friction or resistance to forward movement
is assumed as to what values of $\alpha$ and $n$ may be determined. This friction is made
up of (1) the resistance to engraving of the driving band, (2) the resolved part of the
rotational thrust due to the lands of the rifling, and (3) perhaps forcement of the
projectile through the gun, which is possibly conical in form at any point where the
projectile may be during its passage down the bore.

Now it is obvious that, however elaborate the theory, many large assumptions have
to be made in determining the combined effect of (1), (2), and (3), and on these
assumptions the whole resulting edifice must stand or fall.

In my investigations I tried to avoid the pit-fall of the practical application to the
gun until I was entirely satisfied that I had determined the law of burning by parallel
surfaces in a closed vessel of constant capacity. This paper, then, is a description of
the methods I have used and the results I have arrived at in my investigations. A
considerable amount of laborious arithmetical calculation has been involved, and I
desire here to express my indebtedness to Captains A. R. Izat and C. H. Newcombe,
Royal Artillery, who have rendered me valuable assistance in preparing the diagrams
and in working out some of the calculations.

* Description of the Apparatus used.

Fig. 1 shows a section of the type of closed vessel used. The pressure is registered
by the compression of the copper A by the piston B. This piston carries a pen C
which traces its movement on blackened paper carried on a revolving drum D (shown
in fig. 2). E is a valve for releasing the gases from the vessel after firing. F shows
the arrangements for electrically firing the charge. The internal capacity of the
vessel I used was 28.18 cubic inches, and its internal length and diameter were nearly
equal. The type of vessel shown in fig. 1 is unsatisfactory, because its great length
as compared with its diameter is liable to set up wave actions.

* Gossot and Liouville (tome XIII, 'Mémorial des Poudres et Salpêtres') have recently compared
closed-vessel time rises with those calculated when using their factors. The results are not very satisfactory,
I think.
The drum D is driven by a motor and carries blackened paper on its periphery. G is an electrically sustained tuning-fork of the ordinary Sébert type. The one used
in these experiments made 500 vibrations a second. The electro-magnet H and cam K are for the purpose of momentarily allowing the stylus on the end of the tuning-fork to trace a record on the drum and so give its speed—the spring N pulling the arm O (which carries the cam) away from the electro-magnet.

The use of the apparatus is as follows:—The charge having been placed in the vessel, the copper is placed in position and M is screwed home. The stylus on C is then adjusted on the drum, as is also the stylus on G in the position of release. The circuit of the electro-magnet H is carried by an adjustable joint to C in such a manner that the circuit is broken by the first movement of C as the copper compresses. The circuit being complete, the electro-magnet holds the arm O and lifts the stylus off the drum. When the circuit is broken the arm O is revolved by the spring N, and the cam K thus lowers the stylus G on to the drum and then lifts it off again. We thus obtain a record of the speed of the drum at the actual moment of firing. All being ready, the drum D is set in motion by the motor, whose speed can be regulated by a rheostat. The tuning-fork is started in the usual way, and the charge is then fired.

An example of an actual record is subjoined. These records are measured under a micrometer with a telescopic eye-piece carrying cross wires, the telescope being carried on a compound lathe rest. It measures centimetres to four places of decimals in both directions of movement.

![Record Example](image)

**Characteristics of the Explosive.**

1. *Relation of Pressure and Density.*—The first step in the investigation of the burning of an explosive is to find the relation between the maximum pressure and the density at which the explosive is fired. The explosive I have experimented with is the latest British one, known as modified cordite. The Service abbreviation for this is M.D. cordite, and it will be so called throughout this paper, the original type of cordite being referred to as Mark I. In a closed vessel the maximum pressure is independent of the temperature of the cordite, but temperature has an influence on the time taken by the cordite to develop that pressure. The higher the temperature
the quicker the time rise of pressure. In the gun, therefore, the temperature of the cordite has an influence on ballistics, since at a higher temperature, the pressure being raised more quickly, the projectile has less time in which to move forward; consequently there is a smaller space behind the projectile at times of equal developments of gas, and higher pressures are therefore realised. Temperature, therefore, is of no importance in determining the pressure-density relation, but is all-important in the investigation of time rises. I am not clear that other investigators have borne this in mind—their publications take no note of the fact.

The pressure-density relation of M.D. cordite is shown graphically on fig. 3, and is tabulated in Table A.

![Graph of pressures and densities, M.D. cordite.](image)

The equation connecting the two variables is

\[ P = 360\Delta^3 - 54\Delta^2 + 69.8\Delta, \]

where \( P \) is the pressure in tons on the square inch, and \( \Delta \) is the gravimetric density of loading. Since artillerists work with the lb. as the unit of weight and the cubic inch as the unit of volume, and since 1 lb. of water occupies 27.73 cubic inches at 60° F., density is given by the formula 27.73 \( \times \) weight of charge in lbs. \( \div \) capacity in cubic inches, and is then known as the gravimetric density.
The cubical form of this equation is of interest when one compares it with Van der Waals' general equation

\[(p + \frac{a}{v^2})(v - b) = RT,\]

which may be written

\[p(1-b\Delta) = ab\Delta^2 - a\Delta^2 + RT\Delta.\]

It would appear, then, that in any general deduction of a pressure-density relation from Van der Waals' equation omission of the term \(a/v^2\) is not justified. Petavel neglected this term in his investigation of Mark I cordite.*

---

Cordite in manufacture is made in lots, and the above pressure-density relation is true of the general run of the cordite. In the earlier stages of the manufacture of some experimental forms of M.D. cordite the pressure-density relation was different. This may have been due to slightly different chemical constitution, to the presence of an excess quantity of volatile matter, or to minor variations in manufacture. The point is unimportant, because with experience in manufacture this variation disappears; but I mention it, as in one of the experiments I shall refer to later such an

exceptional lot was used, and it will have to be referred to a special pressure-density curve.

2. Investigation of the Time Rise of Pressure (Cord Form).—M.D. cordite has been made in various forms, some of which are only experimental. As with Mark I cordite, the first form was cords; since that time tubes, strips, and double tubular forms have been made and experimented with.

The first time rises I investigated were, then, of M.D. cordite in the cord form. A time rise of such a cord, measuring 0.1265 inch in diameter, fired at 80° F. at a density of 0.2448, is shown on fig. 4. The close agreement of this beautiful curve with the points actually measured by the apparatus used in the experiment is an indication of the accuracy of the arrangements. Having obtained this time rise, the next step was the investigation of the law of combustion by parallel surfaces.

The method employed was the following:—Intervals of 0.001 second were worked to. From the curve the pressure at 0.001–0.002, &c. second was obtained. This pressure corresponds to a certain density of gas obtained from Table A. Now this gas is produced by a small reduction $dr$ in the radius $r$ of the cord, in other words, a skin or lamina is burnt off and converted into gas. The available capacity of the vessel for this quantity of gas is the total capacity less the volume occupied by the unburnt cordite. One has therefore only to solve for $dr$ under these known conditions. This reduction $dr$ then takes place in 0.001 second under an average pressure which is obtained from the time rise. The average pressures I have taken are those at half time in the interval. For instance, the average pressure during the first 0.001 second is the actual pressure shown on the curve at 0.0005 second. In actual practice, instead of working on the reduction of radius I have worked on the reduction of diameter.

Fig. 5 shows the results of this calculation for fig. 4 plotted in terms of reduction in diameter and pressure. This figure also shows the lines I have selected to represent the relation at temperatures of 60° F. and 80° F.

It appears quite clear that the relation is expressed by a straight line, and that therefore the power $n$ is unity. The equation to the lines is of the form $S = aP + C$, $a$ varying with the temperature of the cordite.

It is the existence of this constant $C$ which has not been suspected before, and which, I think, shows the danger of assuming an equation of a theoretically perfect form and then trying to deduce constants by trial and error.

The meaning of the constant $C$ can only be that below about 0.1 ton pressure the law of reduction in diameter does not hold. Obviously, when $P = 0$, $S$ cannot equal $C$.

The cause of this change of law is, I suggest, that until some definite pressure is attained in the vessel true explosion does not commence. I advance the following explanation:—When the charge is first ignited, only the cordite in immediate contact with the igniter commences to burn. Cordite being a bad conductor of heat, this
burning does not run along the cordite rapidly. This can easily be seen by burning cordite in the air, when it burns slowly along its length in the manner of slow-match and the flash is not rapidly transmitted as with gunpowder. Consequently, in the vessel the lighted ends of the cords burn non-explosively until such time as the vessel is completely filled with flame at a high temperature. At that moment there

![Graph](image.png)

**Fig. 5.** M.D. cordite—reduction in diameter in 0.001 second when burning under a given average pressure.

is a definite pressure in the vessel which tends to separate the cords one from another. The cords now are lighted over their whole length and the true time of combustion by parallel surfaces commences. The constant C is thus due to the amount of gas produced by combustion of the ends of the sticks, when regarded as if produced by combustion over the whole length of the stick. The error introduced into the length of the sticks by this assumption is insignificant and can be neglected.

If this explanation is correct, one would expect the amount of cordite burnt previous to complete ignition of the charge to be independent of the temperature. That this is so was experimentally determined before the theoretical explanation of the constant suggested itself to me. Undoubtedly the time to complete ignition is different with change of temperature of the cordite, but this does not affect the ultimate time rise. Its sole effect is a small variation in the hang-fire of the charge. Theoretically the constant C must vary with the density of loading. It has been determined at a density of 0.25, and the small variation at lower densities does not affect the general accuracy of the calculation.
3. Reconciliation of the Law of Reduction.—Now the equation for reduction in diameter in 0.001 second at 80° F. has been determined as

\[ \text{Redn.} = 0.0013361 \times P + 0.00028, \]

where \( P \) is the pressure in tons on the square inch.

At 60° F. the equation is

\[ \text{Redn.} = 0.001223 \times P + 0.00028. \]

Both these results are tabulated in Tables B and C. In order to justify the selection of the lines shown on fig. 5 as representing the above relations, I have calculated the time rise of pressure of the charge of Cord M.D. shown in fig. 4, using Tables A and B. The calculated points are shown on fig. 4, and below I tabulate the results for comparison:

<table>
<thead>
<tr>
<th>Time, second.</th>
<th>Pressure in tons/inch².</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As measured from the record.</td>
</tr>
<tr>
<td>0.001</td>
<td>Not definitely measurable</td>
</tr>
<tr>
<td>0.002</td>
<td>0.4</td>
</tr>
<tr>
<td>0.003</td>
<td>0.7</td>
</tr>
<tr>
<td>0.004</td>
<td>1.1</td>
</tr>
<tr>
<td>0.005</td>
<td>1.65</td>
</tr>
<tr>
<td>0.006</td>
<td>2.37</td>
</tr>
<tr>
<td>0.007</td>
<td>3.4</td>
</tr>
<tr>
<td>0.008</td>
<td>5.05</td>
</tr>
<tr>
<td>0.009</td>
<td>6.95</td>
</tr>
<tr>
<td>0.01</td>
<td>9.35</td>
</tr>
<tr>
<td>0.011</td>
<td>12.1</td>
</tr>
<tr>
<td>0.012</td>
<td>14.95</td>
</tr>
<tr>
<td>0.013</td>
<td>17.5</td>
</tr>
<tr>
<td>0.014</td>
<td>18.95</td>
</tr>
<tr>
<td>0.014345</td>
<td>—</td>
</tr>
<tr>
<td>0.0144</td>
<td>19.15</td>
</tr>
</tbody>
</table>

The variations in pressure are within the limits of experimental error, and the difference in total time of combustion is only 0.000055 of a second.

4. Investigation of the Time Rise of Pressure (Tube Form).—Fig. 6 shows the time rise of pressure of a certain sample of Tube M.D. Cordite (Batch 88). This class of cordite is known as M.D.T., and one of the governing factors of its rate of burning is the thickness of its annulus. On the same figure I show the calculated time rise of pressure of this sample, using the law I have established.

It is evident by inspection that the M.D.T. time rise does not directly follow the cord law of reduction in diameter. The rise of pressure at the beginning is much more rapid than when calculated as for cords. This difference presented a problem
full of great difficulties and which I sought to solve for a long time at the expense of most laborious arithmetical calculations before I arrived at the solution which I now put forward.

Certain phenomena in connection with the burning of M.D.T. have always been apparent and indicated the lines on which I must work. If a stick of M.D.T. be ignited in the open air the burning does not proceed regularly, but is accompanied by a succession of reports, the tube at the same time being projected about. The action, in fact, is very similar to that of the "cracker" firework.

Now these explosions and jumps are due to the formation of gas inside the tube at
a quicker rate than it can get away at atmospheric pressure. The pressure inside the tube therefore rises to some point at which it bursts out explosively, the tube at the same time being projected in an opposite direction. This action goes on to such an extent that holes are often blown through the walls of the tube.

On firing M.D.T. in a gun, when any unconsumed is blown out I have often found tubes with these holes or splits in their walls. The distance between these holes is generally exceedingly regular. It is therefore clear that under certain conditions an excess pressure exists inside the tube, even when burning under pressure, i.e., explosively.

Now, from the nature of my law of reduction, it follows that if an excess pressure exists inside the tube more cordite will be burnt in a given time. There is thus a reaction of cause and effect, and the internal excess pressure of itself tends to raise the inside pressure more rapidly. When the gas so formed escapes into the vessel it in turn raises the pressure existing in the vessel, and an increased rate of combustion is the consequence.

The time rise on fig. 6 very clearly shows this acceleration of the rate of burning. Since I saw no reason why there should be a departure from my fundamental law, my efforts were directed to determining what the excess internal pressure was and on what it depended. The principle adopted was as follows:

The time rise gives the average and end pressure of any interval. The outsides of the tubes are burning under the cord law and produce a certain quantity of gas in the interval which can be calculated. The total amount of gas produced is known from the end pressure. The difference between these two amounts of gas has come from the inside of the tube, and hence the amount of cordite burnt from the inside can be calculated. Referring to Table B, we determine what pressure the inside of the tube must have been burning under to consume that amount of cordite in the time. From this the excess internal pressure is calculated.

The results of the calculation for Batch 88 are subjoined:

<table>
<thead>
<tr>
<th>Time, second.</th>
<th>During the 0·0005 second interval.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average pressure in the vessel, tons/inch².</td>
</tr>
<tr>
<td>0·0005</td>
<td>0·16</td>
</tr>
<tr>
<td>0·0010</td>
<td>0·83</td>
</tr>
<tr>
<td>0·0015</td>
<td>1·45</td>
</tr>
<tr>
<td>0·0020</td>
<td>2·09</td>
</tr>
<tr>
<td>0·0025</td>
<td>2·90</td>
</tr>
<tr>
<td>0·0030</td>
<td>3·87</td>
</tr>
<tr>
<td>0·0035</td>
<td>5·04</td>
</tr>
<tr>
<td>0·0040</td>
<td>6·41</td>
</tr>
</tbody>
</table>
Now the first results of this calculation are not at all obvious. But by adjusting the zero of the curve calculated on the cord law and comparing it with the actual record it seemed possible that at some point, to be determined, excess internal pressure disappeared and the tubes then burnt in strict accordance with the law in Table B. In adjusting the calculated curve so that its general lie was in closest agreement with the measured one, I found they crossed at about 5.7 tons. It then seemed that if internal excess pressure disappears at any point it must start at some maximum. A simple way of considering the decrease of excess internal pressure from a maximum to zero is to consider that the internal pressure in the tube is a constant until the pressure in the vessel reaches that given pressure. From that moment internal and external pressures will be equal.

Referring to the tabulated results of total internal pressure, it will be seen that the average of the pressures given is 4.56 tons. This was the first pressure tried, but a better result was given assuming 4.85 tons.

The calculation, then, was made on the assumption that the internal pressure was 4.85 tons up to the moment at which the pressure in the vessel reached that figure. The external and internal diameters of the tubes at that moment are given by the calculation which then proceeds on the assumption that the internal and external pressures are equal.
The points obtained by this calculation are shown on fig. 6. Their general agreement with the measured curve is not so close as one would wish; but for a first attempt they appeared to support the idea that there are two phases in the combustion of a tubular propellant: (1) when excess pressure exists inside the tube, and (2) when this excess pressure disappears. Another batch, No. 97, was then tried. Its time rise is shown on fig. 7. The calculation gave:

<table>
<thead>
<tr>
<th>Time, second.</th>
<th>Average pressure in the vessel, tons/inch^2.</th>
<th>Excess pressure in the tube, tons/inch^2.</th>
<th>Total internal pressure in the tube, tons/inch^2.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0005</td>
<td>0.05</td>
<td>3.6</td>
<td>3.65</td>
</tr>
<tr>
<td>0.001</td>
<td>0.15</td>
<td>3.15</td>
<td>3.3</td>
</tr>
<tr>
<td>0.002</td>
<td>0.28</td>
<td>1.3</td>
<td>1.58</td>
</tr>
<tr>
<td>0.0025</td>
<td>0.38</td>
<td>0.56</td>
<td>0.94</td>
</tr>
<tr>
<td>0.003</td>
<td>0.43</td>
<td>-0.26 (deficit)</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Average internal P = 1.93 tons.

We now have two cases of calculated internal pressure, and the next point for consideration was: on what does this internal pressure depend? Looking at it from a theoretical point of view, it would seem to depend on the area of the hole and the length of the tube. The larger the hole the more readily can the gas get away. The longer the tube, for a given hole, the more difficult will be the escape of the gas.

In my closed-vessel experiments the cordite is cut to the internal length of the vessel to avoid the wave pressures which occur if the cordite is banked up at one end. The length variable does not therefore come in.

The internal radius and pressure of the two samples were:

<table>
<thead>
<tr>
<th>Batch.</th>
<th>Radius of hole.</th>
<th>Internal pressure.</th>
</tr>
</thead>
<tbody>
<tr>
<td>88</td>
<td>0.04575</td>
<td>4.85</td>
</tr>
<tr>
<td>97</td>
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Now, if internal pressure varies inversely as the area of the hole, the pressure of Batch 97 from Batch 88 would be given by \[ \frac{P}{4.85} = \left(\frac{0.04575}{0.09003}\right)^2 \]; and, from this, P would be 1.25 tons against 1.93 tons found by the calculation. Having regard to the great variations which may be caused in my calculations by small experimental errors, this result was not as discouraging as it appears on the face of it.
On fig. 4 (lower curve) is shown the time rise and particulars of another batch of M.D.T., No. 89. This batch was one of the exceptional batches I have previously referred to, and did not show the same pressure density relation as the average run of M.D. cordite. The pressure density curve for this batch is shown on fig. 3 (lower curve).

Having obtained the time rise, I tested my theories by calculating a time rise under the two-phase condition I have explained.

The internal pressure, if proportional to the inverse ratio of the area of the holes, is 1.896 tons, using Batch 88 as the standard. The points of this calculated time rise are shown on fig. 4 (lower curve), and, except at the end of the rise, show a very close agreement with the actual condition of affairs.

The end of the rise shows disagreement. But if the actual rise of Batch 89 be compared with the others, it will be seen that the falling away of Batch 89 is a most exceptional condition of affairs for M.D.T. Whether the falling away was due to experimental errors or to some chance peculiarity of an exceptional sample I was not able to determine, as there was no more of the batch left.

The determination of the length influence on internal pressure requires a closed vessel of different dimensions, and I have not dealt with this aspect.

From the visible behaviour of M.D.T. when burning in air it is obvious that special actions are taking place. I venture to think that the calculations and experiments I here set forth support the theory that in the combustion of tubular propellants there are two distinct phases: the first when excess pressure exists inside the tube, and the second when internal excess pressure has ceased. With such a complicated problem it is clear that those investigators who have only had tubular forms of propellants to deal with would be faced with a most intractable problem in endeavouring to discover the true law of combustion by parallel surfaces. It is this difficulty which in part accounts for the various formulas which have been advanced.

Another somewhat important consideration is that, if you assume an equation of the form $S = aP^n$ for a tubular propellant, all tubes that have the same annulus should give the same ballistics. It seems clear from experimental firings in guns that the size of hole for a given annulus has an influence on ballistics. There is no explanation of this fact in the simple equation formula, but it is at once explained by the system of calculation which I have here set forth. The system also explains the splits in the tubes and all the various phenomena connected with the combustion of tubular propellants.

At the same time it is possible to obtain also for tubes a reduction equation of the form $\text{Redn.} = aP + C$. I originally obtained an equation of this form, which is set out in Table D. By this table I am able to calculate time rises very approximately with various tubes. But it is liable to break down, gives no explanation of the various phenomena, and is scientifically unsatisfactory in that there is no reason why the fundamental law of reduction should differ for tubes from cords.
WHilst admitting that Table D is merely an expedient, it offers the advantage of being quicker to work with, and the results are fairly consistent with the tubes as supplied.

5. Investigation of the Time Rise of Double Tubular M.D. Cordite.—It will be clear from a slight consideration that with the propellant in the cord form a decreasing surface is exposed as combustion proceeds. With the tube form an approximately constant surface is exposed. If it were not for excess internal pressure the surface would actually be constant. For if $dr$ is the skin burnt at any time, and $R$ and $r$ the external and internal radii, the original surface is proportional to $2\pi (R + r)$; so when a skin $dr$ is burnt the surface is proportional to $2\pi \{(R - dr) + (r + dr)\} = 2\pi (R + r)$.

Without going deeply into the science of internal ballistics it will be apparent that the longer maximum pressure can be sustained in the gun the greater will be the efficiency of that gun for a given length as regards muzzle velocity. Of course, there are limiting conditions as regards the capability of the gun to withstand this sustained maximum pressure, but such considerations are outside the scope of this paper. Speaking generally, however, there may be advantages in sustaining the maximum pressure in a gun. Now a double tubular form will present an increasing surface as combustion proceeds, and this will tend to sustain the maximum pressure in the gun.

The time rise of pressure of a sample of a double tube is shown on fig. 7 (left-hand curve). The dimensions of this double tube are given on the figure, the firm lines showing the actual shape which in manufacture had not come out as true arcs of circles. A mean circle was therefore determined for the purpose of calculation, and the adjusted double tube is shown by the dotted lines.

With the view of showing the results given by Table D, I have calculated the time rise of the double tube, using that table. The calculated points are shown on the figure. It will be seen that there is a very close agreement in the curves, except at the beginning. The error at the beginning is, of course, due to the excess internal pressure effect being greater with the double than with the single tube.

The American powder is a multitubular one, that is, short cylinders pierced with a number of holes. Excess internal pressure would have a very magnified effect on such a powder, and this, I think, accounts for the wide difference in value of the exponent of $P$ as used by Ingalls.

Conclusion.

In the foregoing I have, after giving the reconciliation of my law for the cord form, confined myself to the cases where it apparently fails. I have endeavoured to show the cause of the failure and at the same time present the solution. I have not given examples of time rises of the strip form, for with them there is no disturbing cause so long as manufacture is not varied.
Undoubtedly it would be a great convenience in working if the integration of these curves were possible. Much thought has been given by different investigators in the past to this problem and much mathematical ingenuity has been displayed. But in these problems one does not obtain expressions which are directly integrable, and assumptions and approximations have necessarily to be made. Such approximations give exceedingly good results within limits, but when one comes to their application to the gun, and its many variables, the limits are so widened that a break-down under certain conditions is an ever-present danger.

I have, therefore, preferred to follow the system adopted by Mr. Bashforth in his calculations of extended trajectories, that is to say, I break up my time-rise curves into small arcs, and, assuming a mean pressure for the interval, find from the calculated end pressure if my assumption has been correct. If not, I have now a guide to the mean pressure to assume, and so on. In this manner each arc can generally be calculated in three trials, and with practice many arcs are obtained at the first attempt.

The application of this law to the practical case of the gun is outside the scope of this paper, and it is obviously undesirable to publish such investigations in connection with English ordnance.

For reasons which I have alluded to, the application to the gun presented more complications than the experiments which I have here outlined.

Having adopted certain frictional laws for the gun, based on the law of burning which I now put forward, I have found that the application holds over a very wide range of varying conditions of loading and calibre, when using cords which is the form with which we have most experience. There can be no higher test than this of the fundamental truth of the law,
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Table B.—M.D. Cordite. Reduction in Diameter at 80° F. in 0.001 second.

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VII. On the Dispersion in Artificial Double Refraction.


Communicated by Professor F. T. Trouton, F.R.S.

Received January 25.—Read February 28, 1907.

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VOL. CCVII.—A 419. 26.7.07
§ 1. Introduction.

It is well known that glass and other transparent isotropic substances, when compressed unequally in different directions, behave like doubly-refracting substances and exhibit the colours of polarized light. Attention was first called to this by Fresnel (‘Annales de Chimie et de Physique,’ vol. XX.), and by Sir David Brewster (‘Phil. Trans.’, 1816). For further investigations in this field, reference may be made to F. E. Neumann (‘Abhandlungen der k. Acad. v. Wissenschaften zu Berlin,’ 1841, II.; see also ‘Pogg. Ann.,’ vol. LIV.); to Clerk Maxwell (‘Trans. Roy. Soc. Edin.,’ vol. XX., Part I.; or ‘Collected Papers,’ vol. I.); to G. Wertheim (‘Annales de Chimie et de Physique,’ ser. 3, vol. XL., p. 156); to J. Kerr (‘Phil. Mag.,’ October, 1888); and to F. Pockels (“Über die Änderung des optischen Verhaltens verschiedener Gläser durch elastische Deformation,” ‘Ann. d. Physik,’ 1902, ser. IV., vol. VII., p. 745). Of these only Wertheim and Pockels have considered how the effect varies with the nature of the light employed.

If homogeneous parallel light is passed perpendicularly through a plate of thickness $\tau$ which is subjected to principal stresses $P$, $Q$ in its plane, these stresses being uniform throughout, then it is found that the light on traversing the plate is broken up into two rays polarized in the directions of principal stress. The relative retardation in centimetres of these rays on emergence is given by

$$R = (\mu_1 - \mu_2) \tau,$$

where $\mu_1$, $\mu_2$ are the indices of refraction of the two rays.

Now experiments have shown that $\mu_1 - \mu_2$ is very approximately proportional to the principal stress difference in the wave-front, $P - Q$. Whether this is true for high values of $P - Q$ is not certain, and some experiments to be described in the following pages (see § 19) will show that the proportionality of $\mu_1 - \mu_2$ to $P - Q$ in all cases must still be regarded as doubtful. Assuming, however, this law, which is certainly very nearly true in most cases, at all events when $P$, $Q$ are stresses of the same type (tensions, or pressures), we have

$$R = C (P - Q) \tau,$$

where $C$ is a coefficient depending only on the nature of the material and on the wave-length of the light used. This coefficient $C$ will be spoken of in what follows as the “stress-optical coefficient.”

Wertheim, from observations of a uniformly compressed block of glass through which he passed successively (i.) sodium light, (ii.) white light, (iii.) white light filtered through a red glass, stated the following law:—

The relative retardation in air is constant for all colours. In other words, the stress-optical coefficient $C$ is independent of the wave-length; the difference of the refractive indices is therefore likewise independent of the wave-length, that is, the double refraction due to elastic strain exhibits no dispersion.
Pockels, in his more recent investigation, observed the artificial double refraction in a number of Jena glasses. His observations, though not primarily intended to test the effect of colour, nevertheless gave exceedingly valuable results in this connection, insomuch as Pockels experimented with three different kinds of nearly homogeneous light, namely, those of sodium, lithium, and thallium. The results would therefore be far more precise than those obtained with very mixed colours by Wertheim. They show that, in certain glasses, the stress-optical coefficient does vary with the wavelength, being numerically greater in the green than in the red; and in very heavy lead glasses this variation is more rapid as we approach the blue end of the spectrum.

Some years ago the present author, being at the time unaware of Pockels' experiments, devised a method of observing the variation of the coefficient $C$ continuously throughout the spectrum, the object being to test the exactness of Wertheim's law.

An account of this method, which was modified and improved from time to time, and of the experiments undertaken to carry it out, will be found in the 'Camb. Phil. Soc. Proc.,' vol. XI., Part VI.; vol. XII., Part I.; vol. XII., Part V. These experiments amply confirmed the results of Pockels. They also showed that the chief desideratum for obtaining accurate results was that the stress in the glass slab through which the light was passed should be sufficiently uniform. Now the compression apparatus which was used by the author, and by previous experimenters, suffered from the defect that it was practically impossible to adjust it so as to obtain a uniform pressure in the slab of glass under observation. Moreover, what adjustment could be made was long and difficult, and could be attained only by trial; it appeared further that this adjustment was disturbed, in a way that could not be calculated and allowed for, when the load was altered. This greatly reduced the accuracy expected.

An apparatus was then devised, with a view to obtaining a system in which the stresses should be known exactly and in which the optical effects should be the same as those due to uniform pressure in a slab of constant thickness. For the purposes of this research a Government Grant was kindly placed at the disposal of the author by the Royal Society, whereby the necessary apparatus could be constructed and the expensive glasses required for the research purchased. The present paper is an account of the experiments carried out with the new apparatus and of the results reached.

PART I.

Theory of the Experiment and Discussion of the Various Errors.

§ 2. Simple Theory of the Experiment.

Let $N$, $F$ (fig. 1) be two rectangular slabs of glass, whose cross-sections are shown in the figure. The slabs are bent in a vertical plane by couples without shear, whose axes are horizontal and parallel to the plane of the cross-section. How such couples are obtained will be explained subsequently.
The horizontal and vertical sides of the cross-sections of $N$ and $F$ are $(2a_1, 2b_1)$, $(2a_2, 2b_2)$ respectively, and the centres of the two cross-sections are $O_1$ and $O_2$. Let $S$ be a point-source of light; $S'$ its image after passing through $N$; $P_1$, $P_2$, the points in which any ray through $S$ meets the vertical midplanes of $N$, $F$ respectively.

![Fig. 1.](image)

Let $P'_1$ be the image of $P_1$, after a single refraction at the inner face of $N$ (the one towards $F$), and $P'_2$ the image of $P_2$ after a single refraction at the inner face of $F$ (the one towards $N$).

Then it is evident that $S'$, $P'_1$, $P'_2$ must be in one straight line.

Let

- $h$ = height of $S$ above a fixed horizontal plane,
- $z_1 = \ldots O_1 \ldots$ the same plane,
- $z_2 = \ldots O_2 \ldots$,
- $y_1 = \ldots P_1 \ldots O_1$,
- $y_2 = \ldots P_2 \ldots O_2$,
- $d$ = distance of $S$ from the nearer face of $N$,
- $l$ = between midplanes of $N$, $F$,
- $\mu_1, \mu_2$ = refractive indices of $N$, $F$ respectively.

We have

$$SS' = 2a_1(\mu_1-1)/\mu_1, \quad P_1P'_1 = a_1(\mu_1-1)/\mu_1, \quad P_2P'_2 = a_2(\mu_2-1)/\mu_2,$$

and since $S'$, $P'_1$, $P'_2$ are collinear

$$\frac{z_2+y_2-(z_1+y_1)}{l-a_1-a_2+\alpha_1/\mu_1+\alpha_2/\mu_2} = \frac{z_1+y_1-h}{d+a_1/\mu_1} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1),$$

or, writing

$$l-a_1-a_2+\alpha_1/\mu_1+\alpha_2/\mu_2 = \sigma (d+a_1/\mu_1). \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2),$$

(1) becomes

$$z_2+y_2 = (z_1+y_1)(1+\sigma) - \sigma h \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3),$$

Suppose now monochromatic light proceeds from $S$.

Let $C_1$, $C_2$ be the stress-optical coefficients of the two slabs for this kind of light, $M_1$, $M_2$ their bending moments reckoned positive when the slabs are bent concave downwards.
DISPERSION IN ARTIFICIAL DOUBLE REFRACTION.

The relative retardation after traversing the first slab for any ray which passes through P, at a small angle to the horizontal = \(2a_1 \cdot C_1 \left(3M_1y_1/4a_1b_1^3\right)\).

For, although the stress is not uniform along the path of the ray, the mean stress along the ray = stress at the middle point, since the stress varies linearly as the distance from the neutral axis. Also the length of the ray differs from the breadth of the slab only by quantities of the second order. Hence the result above.

Accordingly the total relative retardation, after passing through the two slabs, is given by

\[ R = (3M_1/2b_1^3) C_1 y_1 + (3M_2/2b_2^3) C_2 y_2. \] (4)

Substituting for \(y_2\) from (3) into (4),

\[ R = (3M_1/2b_1^3) C_1 y_1 - (3M_2/2b_2^3) C_2 x_2 + (3M_3/2b_3^3) C_3 \left[(z_1 + y_1) (1 + \sigma) - \sigma h\right] \] (5).

Now, if \(R\) is to be independent of \(y_1\), we must have

\[ 3M_1C_1/2b_1^3 + 3M_2C_2 (1 + \sigma)/2b_2^3 = 0. \] (6)

This condition will not of course be accurately fulfilled for all colours at the same time; in the first place, because \(C_1\) and \(C_2\) do not in general follow the same law of variation for the two slabs; in the second place, because \(\sigma\) contains \(\mu\), and therefore involves the wave-length.

It is easy to see that the latter cause of error is quite negligible. For if \(d\) be large compared with \(a_1\) or \(a_2\), which was the case in all the experiments, the error introduced in \(\sigma\) by a variation \(\delta\mu\) in the refractive index (taking \(\mu_1 = \mu_2\), which is practically true) is approximately

\( (a_1 + a_2) \delta\mu/\mu^3d. \)

Now, \(a_1 + a_2 = 3\) centims. in the experiments to be described; \(d = 250\) centims. about (or larger), \(\delta\mu = 0.01\) between the C and F lines of the spectrum which represent fairly well the extreme range of the observations.

Hence, \(\mu\) being about 1.5,

\( (a_1 + a_2) \delta\mu/\mu^3d = 0.01/187.5 < 0.00006. \)

Accordingly the error introduced by this cause would correspond to an error in \(C_3\) of less than 6 in a hundred thousand, an error which is absolutely negligible, since the errors of ordinary observations in the method to be described amount to \(\frac{1}{400}\) or \(\frac{1}{300}\) of \(C\). (See 'Camb. Phil. Soc. Proc.' vol. XII., p. 58.)

The different variation of \(C_1\) and \(C_2\) with the wave-length would be far more important. This, however, need not be considered, for the two slabs N and F are taken from the same cast, so far as possible, so that \(C_1\) and \(C_2\) should be identical. In some cases it was found that \(C_1\) and \(C_2\) differed; but, at the same time, the
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experiments showed conclusively that for slabs of the same material $C_1$ and $C_2$ remained very approximately proportional one to the other for all the values of $\lambda$ examined. In this way condition (6) is satisfied independently of the wave-length.

It follows from (5), using (6), that the relative retardation is given by

$$R = (3M_2C_2/2b_2^2) [z_1 - z_2 + \sigma (z_1 - h)] \cdots \cdots \cdots (7).$$

Accordingly the relative retardation, after the light from such a point-source has traversed the two slabs, is the same for all the rays from S. Two such slabs are therefore optically equivalent to a single slab which would be under an accurately uniform tension.

By properly adjusting the differences of height, $z_1 - z_2$, $z_1 - h$, the amount of relative retardation may be adjusted within certain limits.

In general, $l$ will be chosen small with respect to $d$. Thus $\sigma$ is a proper fraction, say of order $\frac{1}{10}$. Equation (6) thus shows that $M_1$ and $M_2$ are to be chosen of opposite signs, and approximately equal in magnitude.

This gives at once the physical explanation of the result (6). The rays pass through approximately horizontally. If we compare two rays passing through at different levels, the ray which passes through the regions of greater tension in N passes through the regions of lesser tension (or greater pressure) in F, and the two variations balance one another.

Further, since the amount of relative retardation as given by (7) involves only the relative heights of the axes of the slabs and the source of light, the latter may be moved parallel to the axes of the slabs without affecting the relative retardation. Hence a horizontal line-source, parallel to the axes of the slabs, may be used instead of a point-source. This was, in fact, indispensable in order to obtain the required intensity.

§ 3. Description of the Apparatus.

Light from an arc lamp L was passed through a condensing lens C and through a thin horizontal slit T (fig. 2), which was placed from $2\frac{1}{2}$ to 3 metres away from the

![Fig. 2.](image)

glasses and straining apparatus. It was polarized by a Nicol P, whose polarizing plane was roughly at $45^\circ$ to the horizontal, and then passed through the two slabs N and F. These were adjusted so that their levels differed very nearly by $\frac{1}{2}$ centim.
The two slabs were cut from the same piece of glass, and every precaution was taken to ensure that they should be as nearly identical as possible. The dimensions of the cross-sections were practically the same, namely, in the notation of the last section, \(2a_1 = 2a_2 = 3\) centims. and \(2b_1 = 2b_2 = 1\) centim. 

The length of each slab was about 13 centims. 

Bending moments of opposite sign, in a vertical plane, were applied to these, so that the light passed through parts of the glass either altogether under tension, or altogether under pressure, according to the manner in which the bending moment was applied. Of the method of applying such bending moment a fuller account will be given below.

After emerging from the two beams the pencil of light traversed a Nicol A, which was crossed with the Nicol P. It was then focussed by a cylindrical lens Y (which consisted in practice of a glass beaker filled with water) upon the vertical slit of a spectroscopic Q and the spectrum observed in the usual way. 

The condensing lens C was focussed approximately upon the Nicol P; both C and Y were introduced in order to improve the illumination. It was found otherwise that so much light was lost that only a very faint spectrum could be obtained, and this was useless for the purpose of the observations. 

The latter consisted in measuring accurately the position in the spectrum of the black bands corresponding to light completely quenched between the Nics P and A. Light of any colour will, of course, be quenched between crossed Nicols when the relative retardation of the two rays (polarized in horizontal and vertical planes respectively) in which it is split up by the strained glass amounts to an integral multiple of the wave-length. 

Referring to formula (7) this occurs when 

\[ n\lambda = (3M_0C_2/2b_2^2)[z_1 - z_2 + \sigma(z_1 - h)] \ldots \ldots \ldots \ldots \ldots (8), \]

\(n\) being an integer. If \(C_2\) were independent of the wave-length, as Wertheim's law would require, then, for a band of a given order, \(n\) is fixed and the wave-length \(\lambda\) of extinction is proportional to \(M_2\). 

If, however, \(C_2\) varies with \(\lambda\), then \(\lambda/C_2\) is proportional to \(M_2\). 

By observing the values of \(\lambda\) corresponding to a given \(M_2\), and varying \(M_2\), we obtain the relative magnitude of the coefficient \(C_2\) for these varying values of \(\lambda\). 

The probable error of setting on the centre of a black band was calculated by the author in the 'Camb. Phil. Soc. Proc.,' vol. XII., Pt. V., pp. 314–315, and was found to be about 1', so that the wave-length of extinction is determined with a proportional error smaller than 0·002. The average error due to inaccuracy in setting the cross-wires in the eye-piece upon the centre of the black band is then about 8 to 10 tenth-metres, so that the wave-lengths may be considered known accurately to three figures.

The bending moments were applied to the slabs by means of the apparatus shown.
in fig. 3. The slab G rested on two knife-edges R and S. On it rested two other knife-edges U and V, supporting a graduated steel bar I. Fixed to the top of I was a triangular knife-edge K, from the projecting extremities of which hung two symmetrical hangers A. These passed through holes cut in the bed-plate P, which supported the whole apparatus, and by means of a cross-piece C and another hanger H a load W was applied which acted on I vertically downwards at its middle point.

In order to ensure that the reactions between G and the knife-edges R, V should be vertical, the knife-edge R rested on steel bicycle balls B, so that it would readily move under horizontal friction; V was made a double knife-edge, the plane containing the two edges being carefully adjusted to be vertical. The knife-edge U could slide along I and be clamped in any desired position. When U was clamped and the load applied, the apparatus was perfectly stable, the knife-edge S being kept in its place by the friction of the bed-plate. In order to prevent the knife-edges from cutting into the glass and breaking it under the large loads applied, four small slips of steel Q were inserted between the knife-edges and the glass. These distributed the actual stress without altering the actual statical resultants, and at points near the centre of
the slab the effect of such local perturbations must be negligible. (See 'Phil. Trans.,' A, vol. 201, pp. 114, 145.)

When the apparatus is in perfect adjustment \(K\) is exactly midway (measured horizontally) between \(U\) and \(V\), and the horizontal distances between the edges of \(V\) and \(R\) and of \(U\) and \(S\) are equal. If these be each \(c\), then the bending moment applied to the part of the slab between \(R\) and \(S\) is constant and equal to \(\frac{3}{2}cW\).

For, since the reaction at the upper edge of \(V\) is vertical and the load at \(K\) is vertical, then the reaction at the lower edge of \(U\) is shown to be vertical by considering \(U\), \(I\), \(K\) as one system. Thus the reactions at the lower edge of \(U\) and \(V\) are each equal to \(\frac{1}{2}W\). Again, the reaction at the upper edge of \(R\) is vertical and therefore the reaction at the upper edge of \(S\) is also vertical. Hence these reactions also are equal to \(\frac{1}{2}W\).

Also it is to be noted that, if the adjustment be perfect, the bending moment applied to the beam or slab is a pure bending moment. There is no total shear across any cross-section between \(R\) and \(S\).

In such a case it is well known that the distribution of stress obeys accurately the Euler-Bernouilli laws and consists only of a tension \(M\frac{y}{\Delta k^2}\) parallel to the axis of the beam, where \(M = \) applied bending moment, \(y = \) height above neutral axis (horizontal line drawn through the centroid of the cross-section in the plane of the cross-section), \(\Delta = \) area of cross-section, \(k = \) its radius of gyration about neutral axis. The formulae (4) and (7) are therefore verified.

In fig. 3 the knife-edges \(U\) and \(V\) are outside \(R\) and \(S\). The bending moment is therefore positive, with the convention of p. 266. For the second beam the arrangement is the same, except that now \(U\) and \(V\) are inside \(R\) and \(S\), so that the bending moment is negative.

The difference of height between the slabs was obtained by placing the knife-edges \(R, S\) for one of the beams upon two steel blocks of height 0·5 centim. instead of directly upon the bed-plate. The bed-plate itself was a solid plate of steel, very strong and resting upon two heavy tables \(T\) of the same height.

In the above description no account has been taken of a large number of small errors which must theoretically affect the method.

The principal are the following:—(1) In the theory explained in § 2 modifications will be introduced owing to the fact that a polarizing Nicol is introduced in the path of the rays of light between the source and the slabs. (2) The source of light is not a line-source, but a slit of finite breadth. (3) When the load is applied, the middle part of one beam rises and the other sinks: thus the heights \(z_1, z_2\) and the relative height \(z_1 - z_2\) in formula (7) are not fixed. (4) The bed-plate \(P\) and the tables \(T\) are not absolutely rigid. This will alter \(z_1\) and \(z_2\), but not \(z_1 - z_2\). (5) The rays do not go through the glass horizontally and at right angles to the axes of the slabs, and the assumption that the mean retardation = retardation at mid-point of path is only an approximation. (6) The slit used as a source of light is not accurately horizontal.
(7) The knife-edges are never quite accurately adjusted. (8) The weight of the beams themselves will affect the stresses. (9) The beams are not always perfectly annealed and the permanent stresses in the glass modify the appearances.

In the following sections the corrections due to these errors will be investigated.

§ 4. Effect of Introducing the Polarizing Nicol.

We shall now consider the effect of introducing the polarizing Nicol upon the inclination of the rays of light. In order to estimate the magnitude of this effect, it will be sufficient to treat the Nicol as a singly-refracting substance. If the larger index of refraction be adopted this should, in general, give us an upper limit to the error introduced. If no sensible disturbance is found to be thus introduced, we may assume that this will be the case in the actual experiment.

Let S (fig. 4) be the source of light, P the image of a point of the mid-plane of the nearer slab, viewed by refraction through the face nearest S. If the Nicol were not present the light would travel along the line SP. In consequence of the introduction of the Nicol it travels along the broken path SCDP.

Let \( \phi, \psi \) be the angles of incidence and refraction, \( \chi \) the angle which SP makes with the normal to the faces of the Nicol.

Let the perpendicular distances of S and P from the nearer faces of the Nicol be \( m \) and \( n \), and the thickness of the Nicol be \( t \).

Then

\[
(m+n) \tan \phi + t \tan \psi = (m+n+t) \tan \chi,
\]

or, writing \( t/(m+n+t) = \gamma \),

\[
\tan \chi - \tan \phi = \gamma (\tan \psi - \tan \phi) \ldots \ldots \ldots \ldots \ldots (9).
\]

Using \( \mu \sin \psi = \sin \phi \),

\[
\tan \psi = \tan \phi [\mu^2 + (\mu^2-1) \tan^2 \phi]^{-1/2}.
\]

Hence (9) becomes, retaining only first powers of \( \gamma \),

\[
\tan \chi - \tan \phi = \gamma \tan \chi ([\mu^2 + (\mu^2-1) \tan^2 \chi]^{-1/2} - 1) \ldots \ldots (10).
\]
Now in the experiments \( \gamma < \frac{1}{30} \) and the maximum variation in \( \chi \) for rays passing through the slabs amounts only to \( \frac{1}{30} \).

But from (10)

\[
\frac{d}{d\chi} (\tan \chi - \tan \phi) = \gamma \sec^2 \chi \{ \mu^2 (\mu^2 + [\mu^2 - 1] \tan^2 \chi)^{-32} - 1 \} \ldots \quad (11).
\]

Accordingly the greatest variation in \( \tan \chi - \tan \phi \) for the rays passing through the slabs is less than

\[
(\frac{1}{30}) \sec^2 \chi \{ \mu^2 (\mu^2 + [\mu^2 - 1] \tan^2 \chi)^{-32} - 1 \} \ldots \quad (12).
\]

To compute the order of this expression take \( \mu = 1.5 \) and \( \chi = 30^\circ \), which last is an extreme estimate. (12) gives

\[
\delta (\tan \chi - \tan \phi) = -0.000033,
\]

that is,

\[
\delta (\chi - \phi) = -0.000033 \cos^2 \chi = -0.000025 \text{ about.}
\]

The change in relative level of the points \( P_1, P_2 \) of fig. 1 due to the above amounts to \( 0.000025 \) \( l \), and in the experiments \( l = 18 \) centims. roughly. Thus the change in relative level = \( 0.00045 \) centim. The proportional change in the total effective stress = change of relative level \( \div \) semi-height of slab = \( 0.0009 \), and this will produce a negligible error in the stress-optical coefficient. Accordingly for monochromatic light the effect is to increase the obliquity of all rays by a small constant amount, or to change the effective height \( h \) of the slit. As the absolute value of \( h \) is not known, and will be found not to enter into the calculations, the presence of the Nicol will not affect the observations for monochromatic light.

For white light, however, it may do so if the quantity \( \tan \phi - \tan \chi \) vary sensibly with the colour of the light used, other things remaining the same.

From (10)

\[
\delta (\tan \chi - \tan \phi) = -\mu \gamma \delta \mu \sin \chi (\mu^2 - \sin^2 \chi)^{-32}.
\]

Now for calcite

\[
\lambda = 6708, \quad \mu_\varepsilon = 1.484, \quad \mu_0 = 1.653,
\]

\[
\lambda = 5350, \quad \mu_\varepsilon = 1.488, \quad \mu_0 = 1.658,
\]

\[
\delta \mu_\varepsilon = 0.004, \quad \delta \mu_0 = 0.005.
\]

Taking the ordinary index as the basis of computation and \( \chi = 30^\circ \) as before,

\[
\delta (\tan \chi - \tan \phi) = -0.000026 \text{ nearly.}
\]

The proportional error in \( C \) deduced from this is obtained by multiplying by \( l \cos^2 \chi / b \), i.e., by 27. It is therefore 0.00070. This error corresponds only to the
dispersion between the lithium and thallium lines. The error will be greater when we reach the violet end of the spectrum, but it will still be too small to affect the observations.

In experiments demanding great accuracy it might be desirable to polarize the light before it passes through the slit. The accuracy possible under the present circumstances did not seem to justify this additional complication in the apparatus.

§ 5. *Effect of Finite Breadth of the Source.*

It may be shown that if the slit have a finite breadth $2e$, the intensity of the light that gets through is proportional to

$$1 - \frac{\sin \theta \theta}{g \theta} \cos \theta,$$

where

$$\theta = 2\pi R_0/\lambda, \quad g = \sigma e/[z_1 - z_2 + \sigma (z_1 - h)],$$

$R_0$ being the relative retardation corresponding to the middle of the slit.

In the actual case $g = 1^{1/5}$ approximately.

The minima are given approximately by

$$\theta = 2n\pi (1 - \frac{1}{3}g^2).$$

The proportional error in the wave-length of extinction is therefore $\approx 1^{1/5}0$, which is negligible.

Also the minimum no longer corresponds theoretically to perfect darkness, but with a slit between $1/2$ millim. and 1 millim. wide the bands were very dark and quite definite.


Owing to the elasticity of the glass, the middle parts of the beams will undergo a vertical shift owing to flexure, and the bed-plate and apparatus as a whole will sink.

In consequence we have variations $\delta z_1$, $\delta z_2$, $\delta h$ depending on the applied load.

Thus the right-hand side of equation (8) is multiplied by a factor

$$1 + [\delta z_1 - \delta z_2 + \sigma (\delta z_1 - \delta h)]/[z_1 - z_2 + \sigma (z_1 - h)].$$

This may be allowed for by supposing $M_2$ (or $W$) multiplied by the same factor, equation (8) remaining otherwise unaltered.

The effect is then to add to the applied weight a correction

$$W [\delta z_1 - \delta z_2 + \sigma (\delta z_1 - \delta h)]/[z_1 - z_2 + \sigma (z_1 - h)].$$

Now the relative rise and fall of the beams themselves is an elastic effect and may be taken, in such a small correction, strictly proportional to the load.
The sinking of the bed-plate was measured experimentally and found to be elastic in its nature, the recovery being complete.

Generally the experiments showed no trace of permanent set, the readings being the same when unloading as when loading.

We may safely assume therefore that 
\[
\delta_2 = \delta_2 + \sigma (\delta_z - \delta h)
\]

is proportional to \( W \), so that the correction to be applied to \( W \) on account of these errors is of the form

\[
KW^2.
\]

The value of \( K \) is uncertain and depends very largely on the circumstances of each experiment.

Using Everett's and Amagat's values of Young's modulus for glass (i.e., between 600,000 and 700,000 kilogs.-weight per square centimetre), the part of \( K \) due to relative rise and fall of the two beams was calculated to be about 0.0004. Thus for \( W = 50 \) kilogs. the proportional correction is as high as 2 per cent.

The part of \( K \) due to the sinking of the bed-plate was found experimentally to be of order 0.00026. Also the experiments could be arranged in such a manner that the two corrections operated in different senses; and this precaution was always taken. Their combined effect will give \( K \) of order 0.0001, and even for the highest loads used the correction will be small.

In practice this correction \( KW^2 \) was determined from the observations themselves, in a manner explained in § 17. For most sets of observations it was found to be insensible.

### § 7. Influence of Obliquity on Relative Retardation.

We may consider the glass as optically made up of a series of horizontal homogeneous layers. In passing from one of these layers to another, the refraction takes place approximately in a plane perpendicular to the optic axis.

It will be sufficient for our purpose to consider a ray passing through in a cross-section, that is, in a plane throughout perpendicular to the optic axis. If the curvature of such a ray be negligible, we may take it that we can neglect the curvature of all oblique rays.

Now if \( \mu \) be the index of refraction at a point in the glass distant \( y \) from the neutral plane,

\[
\mu = \mu_0 + \mu_y y,
\]

\( \mu_0 \) being the index of refraction for the unstrained glass. It may then be proved that the curvature of a ray passing through nearly horizontally is approximately \( \mu / \mu_0 \).

Now it has been shown by Kerr ('Phil. Mag.,' October, 1888), and by Pockels ('Ann. d. Physik,' 1902, p. 745), that the absolute variation due to stress in the index of refraction for either ray is of the same order as the difference in the two indices due to the same cause. In general, for the highest stress employed, the
\( (\mu_{\text{ex}} - \mu_{\text{ow}}) \text{-gradient} \text{ is of the order } 10^{-4}. \) Taking \( \mu_0 = \frac{3}{2} \), the curvature is of order \( \frac{3}{2} 10^{-4} \). Hence the greatest deviation from the straight line = \( \frac{1}{2} \) (curvature) (thickness of slab)^2 = \( 3 \times 10^{-4} \) — a divergence which cannot possibly affect the results.

Thus we are justified in treating the paths of the rays as linear. Moreover, the divergence of the ordinary and extraordinary rays after refraction at entrance \( = \mu^{-2}(\mu_{\text{ex}} - \mu_{\text{ow}}) \) (angle of incidence) very nearly, and it is easily verified that the effect of this is also entirely negligible. Therefore we may treat the two rays as geometrically coincident.

The paths of the rays being linear, the planes of polarization are fixed throughout. For these can be proved to be the plane through the ray, and the line of strain and the plane through the ray perpendicular to the first plane. And the line of strain is always parallel to the axis of the slab.

Also if \( \beta \) = angle between ray and line of strain, the relative retardation introduced by an element \( ds \) of path is

\[
dR = CT \sin^2 \beta \, ds.
\]

Hence the total relative retardation is

\[
R = 2\alpha CT_0 \sin^2 \beta \sec \gamma,
\]

where
- \( T_0 \) = tension at mid-point of path,
- \( 2\alpha \) = thickness of slab,
- \( \gamma \) = inclination of ray to the horizontal perpendicular to the axis.

In practice the limits for \( \cos \beta \) are \( \pm 0.01 \), and for \( \gamma \) are \( \pm 0.02 \). It follows that the factor \( \sin^2 \beta \sec \gamma \) introduces a proportional error less than \( 10^{-4} \) in the relative retardation. It may therefore be altogether neglected.

§ 8. **Combined Effect of Flexure and Obliquity.**

The relative vertical displacement of the two slabs due to flexure varies with the cross-section taken. Now the pencil of rays used passes through a comparatively large region of the beams, extending to about 1 centim. on either side of the central cross-section. It is readily shown that the changes in \( z_1, z_2 \), due to flexure as we pass from the central cross-section to sections distant \( x \) from the central one are given by

\[
\begin{align*}
\delta z_1 &= -3c_2x^2W/(16E_2a_1b_1^3) = -3W/E, \\
\delta z_2 &= +3c_2x^2W/(16E_2a_2b_2^3) = +3W/E
\end{align*}
\]

if \( x = 1 \),

the slab \( N \) being bent concave downwards and \( F \) concave upwards.

The greatest possible change in \( \delta z_1 - \delta z_2 \), due to this cause, is numerically equal to \( 6W/E \) or (taking \( E = 600,000 \) kilogs.-weight per square centimetre) = \( W \times 10^{-5} \).

The proportional correction in the stress amounts to \( 10^{-5} \, W/(z_1 - z_2) \) nearly, i.e., to
10^{-8} \text{ kilogs.} \) Thus for the extreme load of 50 kilogs, it is only 10^{-8}, and may be disregarded.


If the slit be not horizontal its different parts will act as different sources of light at different heights \( h \).

It is clear that if the inclination be too great the different parts of the slit will give different dark bands in the spectrum, all overlapping. The integral band will be diffuse in consequence and not readily measureable. It is quite easy, however, to make this adjustment to a nicety, as follows:

Let \( AB \) (fig. 5) be the slit, \( A'B' \) the image of \( AB \) in the cylindrical lens (\( Y \) of fig. 2) for rays proceeding in a horizontal plane. Then each element \( P \) of the slit gives a vertical line of light through \( P' \). Let \( S_1S_2 \) be the opening of the slit of the spectroscope. The latter is a good deal smaller than the image \( A'B' \), so that in practice only a moderate length of the luminous slit is used. If now the cylindrical lens be moved to one side or the other, so that \( S_1S_2 \) travels from one end of \( A'B' \) to the other, then, if the luminous slit be not horizontal, the band will shift in the spectrum in consequence. When no such shift occurs, we know that the adjustment is very exact. There is very little difficulty in making this adjustment, and accordingly there is no reason for anticipating any sensible error from this cause.

§ 10. Imperfect Horizontal Adjustment of the Knife-edges.

In practice it is impossible to ensure that the two pairs of knife-edges shall be exactly symmetrical with regard to the vertical through the load. Failure to satisfy this condition introduces shearing stresses in the beams, so that the axes of polarization are no longer horizontal and vertical and further the bending moment varies from cross-section to cross-section.

The complete analytical investigation of the correction in this case is long and difficult, but the results may be summed up as follows, for the simplest case, when only one of the slabs is supposed imperfectly adjusted.

In general there is no longer perfect extinction, so that the band is not quite black. Assuming that the "overlap" of the two slabs is half their height, the position of the band for rays passing through the edge of either slab is unaltered.

The position of the band for a ray passing exactly at mid-level is shifted towards the red end of the spectrum by an amount not exceeding 0.6 of a tenth-metre.

Thus, remembering that rays which have passed through the glass at different
levels correspond to parts of the spectrum also at different levels, we see that the band is no longer straight and vertical, but curved, the convexity being towards the red. This convexity is, however, so small that it would not in any case be observable. If the condition (6) of § 2 is not exactly satisfied the band will still be straight, to a first approximation, but no longer vertical. Thus when the bending moment varies from cross-section to cross-section for light passing to the right of the mid-section the band is tilted one way, for light passing to the left it is tilted the reverse way. The integral effect will be that the thickness of the band will no longer be uniform, but the band is still symmetrical with regard to a vertical line, corresponding to light going through the mid-section. The settings which are made on the middle of the band are therefore unaffected.

§ 11. Imperfect Vertical Adjustment of the Knife-edges.

It will also happen that the knife-edges will not all be at exactly the same height, so that the axes of the two slabs are not exactly horizontal and parallel. The effect will be that for rays passing through in a plane distant \( x \) from the central section

\[
z_1-z_2 + \sigma (z_1-h) = A + Bx
\]

instead of being exactly constant, \( B \) being a small coefficient.

This will broaden the band and render it more diffuse, but will not shift its centre. Observation shows that this effect must be very small, as, in general, the band is very well defined.

§ 12. Error due to Weight of Beams themselves.

In computing the stresses no heed has, so far, been paid to the fact that the weights of the glasses themselves will introduce certain stresses in the slabs. The weight of each slab is on the average 120 grammes. This, although very small compared with the total load in most cases, may introduce a small error in the case of the band of the first order, which corresponds to a smaller load.

For the beam \( N \) the weight of the glass was found to introduce practically no bending moment in the centre, as the supports were very nearly at the quarter and three-quarter span points.

For the beam \( F \) the moment introduced is the same as if the weight on this slab were increased by exactly its own weight.

It is quite easy in practice to eliminate this by adding a small counterpoise to the weight on \( N \).

§ 13. Error due to Imperfect Annealing.

We now come to the only error—with the exception of that due to rise and fall—which is sufficiently important to be allowed for in the reduction of the observations.
The annealing of the glasses used, which were supplied by Messrs. Zeiss of Jena, was found to be by no means perfect. In some cases this was revealed even by a cursory inspection between crossed Nicols. In other cases, the glasses being unloaded, a one-wave plate of selenite was introduced between the Nicols, its axes being horizontal and vertical. This showed a black band, on the same principle that the strained glass shows such a band.

Now if the glasses had no residual stress the relative retardations should be the same when the azimuth of the axes of polarization of the selenite plate is altered by 90°.

If there be residual stress, however, it will affect the light differently in these two cases and the band will be shifted. In most cases the existence of such a residual stress was exhibited very plainly by this method. As a rule the band due to the selenite plate was straight and vertical, showing that the residual stress was fairly constant.

If $\Delta T$, $\Delta U$, $\Delta S$ be the three components of residual stress in a vertical plane parallel to the axis of the beam, then the axes of polarization make an angle $\phi$ with the horizontal, where

$$\tan 2\phi = \frac{2\Delta S}{(T + \Delta T - \Delta U)}$$

and the principal stress difference

$$P - Q = \sqrt{(T + \Delta T - \Delta U)^2 + 4(\Delta S)^2}.$$  

If we neglect squares of $\Delta T/T$, $\Delta U/T$, $\Delta S/T$ it is easy to calculate that the retardation

$$2C_1T_1a_1 + 2C_2T_2a_2$$

has to be increased by

$$2C_1(\Delta T_1a_1 - \Delta U_1a_1) + 2C_2(\Delta T_2a_2 - \Delta U_2a_2),$$

or, taking

$$C_1 = C_2 = C$$

in these corrective terms, the retardation must be increased by

$$2C[\Delta T_1a_1 - \Delta U_1a_1 + \Delta T_2a_2 - \Delta U_2a_2],$$

and this is equivalent to putting in a constant correction $W_0$ to $W$.

PART II.

EXPERIMENTAL RESULTS.


The glasses used in this research were made for me by the firm of Zeiss in Jena. The makers being unable to communicate to me the chemical composition
of the glasses, the latter were analysed for me by Mr. W. J. Rees, on the staff of Messrs. Chance Bros. To Mr. Rees' skill I am indebted for the following results:

<table>
<thead>
<tr>
<th>Number of glass</th>
<th>1809.</th>
<th>3453.</th>
<th>2783.</th>
<th>3296.</th>
<th>935.</th>
<th>3413.</th>
<th>3749.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ per cent.</td>
<td>35·4</td>
<td></td>
<td>52·7</td>
<td>67·5</td>
<td></td>
<td>31·6</td>
<td>70·2</td>
</tr>
<tr>
<td>PbO</td>
<td></td>
<td>31·6</td>
<td></td>
<td></td>
<td>28·2</td>
<td>23·6</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3·7</td>
<td></td>
<td>0·6</td>
<td></td>
<td>8·5</td>
<td>8·0</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>1·2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0·5</td>
<td>5·4</td>
<td>0·4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₂O₃</td>
<td>34·3</td>
<td>5·7</td>
<td>1·4</td>
<td>15·4</td>
<td>27·7</td>
<td>33·0</td>
<td>5·9</td>
</tr>
<tr>
<td>K₂O</td>
<td>7·4</td>
<td>20·8</td>
<td>12·5</td>
<td>16·7</td>
<td>3·1</td>
<td>3·8</td>
<td>23·9</td>
</tr>
</tbody>
</table>

The majority of these glasses belong to the borosilicate variety, excepting 2783. 2783 is a flint glass, and was stated by the makers to be identical in composition with another glass, O 154, the composition of which (see 'Camb. Phil. Soc. Proc.' vol. XII., Part V., p. 314) was stated by Messrs. Zeiss to include Na₂O and BaO. It seems probable that the composition of the later glass is a little different to that of O 154.

§ 15. Linear Law connecting λ and the Stress.

Since it was known beforehand that corrections to W of the type W₀+KW² would have to be applied, W₀ being due to the imperfect annealing, and KW² to relative and absolute rise and fall (see §§ 6, 13), instead of calculating the stress-optical coefficient C directly, as was done in previous experiments, the relation between W and λ was first studied, with a view to disengaging the corrections.

In practice, readings for W and λ were taken for both first and second orders of the band, and even, where possible, for third orders—for both tension and pressure. The tension and pressure observations were obtained by altering the relative heights of the two slabs by interchanging two steel slips which raised the supports of one of the slabs. The bending moments were not altered.

A typical set of results is embodied in Table I. below.
Table I.—Observations of Glass 1809.

<table>
<thead>
<tr>
<th>A.</th>
<th>B.</th>
<th>C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_1$</td>
<td>$\lambda_{\text{obs.}}$</td>
<td>$\Delta \lambda_{\text{obs.}}$</td>
</tr>
<tr>
<td>14.25</td>
<td>4506</td>
<td></td>
</tr>
<tr>
<td>15.25</td>
<td>4891</td>
<td>385</td>
</tr>
<tr>
<td>16.25</td>
<td>5206</td>
<td>315</td>
</tr>
<tr>
<td>17.25</td>
<td>5570</td>
<td>364</td>
</tr>
<tr>
<td>18.25</td>
<td>5895</td>
<td>325</td>
</tr>
<tr>
<td>19.25</td>
<td>6265</td>
<td>370</td>
</tr>
<tr>
<td>20.25</td>
<td>6600</td>
<td>335</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A'.</th>
<th>B'.</th>
<th>C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_1$</td>
<td>$\lambda_{\text{obs.}}$</td>
<td>$\Delta \lambda_{\text{obs.}}$</td>
</tr>
<tr>
<td>11.25</td>
<td>4430</td>
<td></td>
</tr>
<tr>
<td>12.25</td>
<td>4750</td>
<td>320</td>
</tr>
<tr>
<td>13.25</td>
<td>5000</td>
<td>250</td>
</tr>
<tr>
<td>14.25</td>
<td>5310</td>
<td>310</td>
</tr>
<tr>
<td>15.25</td>
<td>5600</td>
<td>290</td>
</tr>
<tr>
<td>16.25</td>
<td>5890</td>
<td>290</td>
</tr>
<tr>
<td>17.25</td>
<td>6160</td>
<td>270</td>
</tr>
<tr>
<td>18.25</td>
<td>6460</td>
<td>300</td>
</tr>
</tbody>
</table>
The parts A, B, C refer to observations for tension: A', B', C' to observations for pressure. In the columns headed $W_n$ ($n = \pm 1, 2, 3$) are placed the observed weights, the suffix $n$ indicating the order of the band observed, bands in pressure observations being taken of a negative order. The same notation will be kept throughout. The columns headed $\lambda_{obs}$ contain the observed value of the wave-length of the light quenched, in tenth-metres. They are deduced from circle readings of the spectroscope, the law connecting these circle readings with the wave-lengths being obtained from observations of a known comparison spectrum. The spectrum of the arc between carbons soaked in calcium salt was used for this purpose.

Now, if we look at Table I., A., under the heading $\Delta \lambda_{obs}$, we see that the differences of the observed $\lambda$ for unit differences of $W$ have a fairly constant average value, as is well shown on taking differences corresponding to differences of $W$ of three units. This is done in the column headed $3\Delta \lambda_{obs}$ of Table I., A.

It would seem, therefore, that the relation between $\lambda$ and $W$ is approximately linear. This impression is found to be confirmed when differences are taken in Table I., B, C, A', B', C'. In each case the differences are sensibly constant, especially if we bear in mind that an experimental error of 10 tenth-metres is to be expected.

There are some local inequalities, some of which will be shown later to be probably significant, but as a first approximation it seems we may assume a linear relation between $\lambda$ and $W$.

Fig. 6 shows the observed $\lambda$ plotted to $W$ for the set of observations of Table I., B'. The observations obviously lie very close to the straight line given by the equation

$$\lambda = 949 + 145W.$$ 

This equation was obtained by assuming a formula

$$\lambda = \lambda_0 + kW \ldots \ldots \ldots \ldots \ldots (13).$$

$k = \frac{d\lambda}{dW}$ was obtained by taking the mean value of the differences in the columns headed $3\Delta \lambda_{obs}$ of Table I., B', and $\lambda_0$ was then determined from the condition that the best straight line must pass through the centre of gravity of the observations.

The equation (13) clearly leads to the relation

$$\lambda (1 - \lambda_0/\lambda) = kW,$$

or, $R$ being the relative retardation for a band of $n^{th}$ order,

$$R = n kW/(1 - \lambda_0/\lambda) = C_0 T \tau/(1 - \lambda_0/\lambda),$$

where $T =$ effective tension, $\tau =$ thickness, $C_0 =$ a constant independent of the wave-length.
Thus, the stress-optical coefficient \( C = \mu_1 - \mu_2 \text{ for unit stress} \) is given by the approximate formula

\[
C = C_0/(1-\lambda_0/\lambda) \quad \cdots \cdots \quad (14),
\]
or

\[
(C-C_0)(\lambda-\lambda_0) = C_0\lambda_0 \quad \cdots \cdots \quad (15).
\]

The curve connecting \( C \) and \( \lambda \) is therefore a rectangular hyperbola. When \( \lambda = \lambda_0 \), \( C = \infty \), and as \( \lambda \) increases without limit, \( C \) decreases to its limiting value \( C_0 \).

Thus, if the law continued to hold accurately for small wave-lengths, then for light of the critical wave-length \( \lambda_0 \) the stress-optical effect would become actually infinite.

No doubt this law is purely empirical so far, and will very probably not hold for very small wave-lengths. It is, however, sufficient to indicate that, as we approach
critical values in the ultra-violet, the stress-optical effect will very likely be largely increased.

In order to show the accuracy with which the observations above determine the value of \( \lambda _0 \), the straight line passing through the origin and through the centre of gravity of the observations has also been plotted on fig. 6.

Its equation is

\[
\lambda = 175.35 \times W,
\]

and on looking at the diagram it is obvious that no such straight line can fit the observations.

Further, it will be shown that all the observations, not merely of the glass 1809, but of the six other glasses examined, conform to a first approximation to the linear law.

§ 16. Significance of this Linear Law.

We have now to enquire how far this linear law has a physical meaning otherwise than as the expression of the trivial result that within a certain range of values all continuous variation is approximately represented by a straight line.

In previous papers, when \( C \) and \( \lambda \) were the quantities plotted, the relation was not well expressed by a straight line, the observations lying, in some cases, on a very decided curve (see 'Camb. Phil. Soc. Proc.' vol. XII., Part V.). The observations which led to such curves were therefore re-reduced. The glasses selected which showed the effect most strongly were the Jena lead glasses O 152 and S 57.

Both of these were very closely fitted by a linear relation between \( \lambda \) and \( W \). How close the fit was may be inferred from Table II. below, which shows the observed and calculated values of \( \lambda \) for one set of experiments with S 57, which is a very heavy flint glass, containing 80 per cent. of PbO.

In the table, \( W \) denotes pressure in kilogrammes applied by means of a compressing apparatus described in the paper referred to, and the entries in the column headed \( \lambda _{\text{cal.}} \) are computed from the formula

\[
\lambda = 3124.9 + 4.5136W.
\]

The other sets of observations of S 57 and O 152, which have been re-reduced, show equally good agreement between the observed values of \( \lambda \) and those calculated from a formula of type (13).

Now the mean residual in Table II. is less than 5 tenth-metres, whereas the probable error of determination of the centre of a band is about 10 tenth-metres. Thus the law appears to fit the observations as closely as is possible within the limits of experimental error. It is worth noting that with these glasses, which contain a high percentage of lead, no deviations from the law, such as will be shown later to take place in some borosilicates, appear to exist.

Nevertheless one important experimental fact throws doubt on the universal validity of the linear law, even for lead glasses. Pockels has shown ('Ann. d.
Table II.—Observations of S 57 (re-reduced).

<table>
<thead>
<tr>
<th>W.</th>
<th>$\lambda_{\text{obs}}$</th>
<th>$\lambda_{\text{cal.}}$</th>
<th>$\lambda_{\text{obs.}} - \lambda_{\text{cal.}}$</th>
<th>$\lambda_{\text{obs.}} - \lambda_{\text{hyp.}}$</th>
<th>W.</th>
<th>$\lambda_{\text{obs}}$</th>
<th>$\lambda_{\text{cal.}}$</th>
<th>$\lambda_{\text{obs.}} - \lambda_{\text{cal.}}$</th>
<th>$\lambda_{\text{obs.}} - \lambda_{\text{hyp.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>318.4</td>
<td>4550</td>
<td>4562</td>
<td>-12</td>
<td>-49</td>
<td>547.8</td>
<td>5592</td>
<td>5597</td>
<td>-5</td>
<td>+9</td>
</tr>
<tr>
<td>343.4</td>
<td>4677</td>
<td>4675</td>
<td>+2</td>
<td>-23</td>
<td>572.9</td>
<td>5701</td>
<td>5711</td>
<td>-10</td>
<td>+6</td>
</tr>
<tr>
<td>364.0</td>
<td>4771</td>
<td>4768</td>
<td>+3</td>
<td>-13</td>
<td>595.0</td>
<td>5819</td>
<td>5810</td>
<td>+9</td>
<td>+23</td>
</tr>
<tr>
<td>389.2</td>
<td>4878</td>
<td>4882</td>
<td>-4</td>
<td>-12</td>
<td>620.2</td>
<td>5923</td>
<td>5924</td>
<td>-1</td>
<td>+9</td>
</tr>
<tr>
<td>409.8</td>
<td>4985</td>
<td>4975</td>
<td>+10</td>
<td>+10</td>
<td>639.5</td>
<td>6016</td>
<td>6011</td>
<td>+5</td>
<td>+12</td>
</tr>
<tr>
<td>435.0</td>
<td>5090</td>
<td>5088</td>
<td>+2</td>
<td>+7</td>
<td>664.7</td>
<td>6124</td>
<td>6125</td>
<td>-1</td>
<td>+2</td>
</tr>
<tr>
<td>455.7</td>
<td>5178</td>
<td>5182</td>
<td>-4</td>
<td>+6</td>
<td>685.7</td>
<td>6216</td>
<td>6220</td>
<td>-4</td>
<td>-8</td>
</tr>
<tr>
<td>480.8</td>
<td>5300</td>
<td>5295</td>
<td>+5</td>
<td>+20</td>
<td>710.8</td>
<td>6341</td>
<td>6333</td>
<td>+8</td>
<td>-3</td>
</tr>
<tr>
<td>501.5</td>
<td>5387</td>
<td>5388</td>
<td>-1</td>
<td>+13</td>
<td>735.6</td>
<td>6447</td>
<td>6445</td>
<td>+2</td>
<td>-19</td>
</tr>
<tr>
<td>526.6</td>
<td>5500</td>
<td>5502</td>
<td>-2</td>
<td>+15</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Physik,' 1902, p. 745) that for a glass containing between 60 and 70 per cent. of PbO the stress-optical coefficient changes sign, and an experiment made by him with such a glass pointed to the fact that the stress-optical coefficient did not vanish simultaneously for all colours, a result which has been independently confirmed by the present author from considerations of curves showing C and $\Delta C/\Delta \lambda$ plotted to percentage of lead (see 'Camb. Phil. Soc. Proc.,' vol. XXI., p. 335). Now if the law $C = C_0/(1 - \lambda_0/\lambda)$ held universally, the vanishing of $C_0$ would imply the vanishing of C for every wave-length.

Moreover, it seems impossible to find theoretical justification for such a formula. It is well known (see DRUDE'S 'Theory of Optics,' cap. V., pp. 388, 389)* that the index of refraction $\mu$ is given by the formula $\mu^2 = 1 + \Sigma \lambda_0/(1 - (\lambda_0/\lambda)^2)$, where $\lambda_0 = $ wave-length *in vacuo* of light belonging to one of the natural periods of the glass.

[*Note added July 3rd, 1907.—Throughout the paper I have followed DRUDE. But if we adopt LORENTZ's formula, viz.:

\[
\frac{(\mu^2 - 1)}{\mu^2 + 2} = \Sigma \lambda_0/(1 - (\lambda_0/\lambda)^2),
\]

or similar formulæ, the most essential part of the reasoning remains in most cases practically unaltered.]
It seems, at first sight, highly probable that the effect of stress will be, not to introduce different free periods of the atoms for differently polarized rays—that is, not to alter $\lambda_p$—but to change the coefficient $A_p$, which depends on the number and arrangement of the molecules.

This will lead to the result

\[2\mu \delta\mu = \Sigma \delta A_p / \{1 - (\lambda_p/\lambda)^2\}\]

or

\[
\mu C = \Sigma C_p / \{1 - (\lambda_p/\lambda)^2\} . . . . . . . . . (16).
\]

Now $\mu$ itself, when expanded in powers of $1/\lambda$, will involve terms in $\lambda^{-2}$, $\lambda^{-4}$, etc. Therefore $C$ will involve only such even terms. Hence no formula involving $\lambda$ to odd powers can be theoretically acceptable.

If we suppose that one term, corresponding to wave-length $\lambda_p$, is active in producing the dispersion, both in ordinary refraction and artificial double-refraction, we have

\[
\mu C = C_p / \{1 - (\lambda_p/\lambda)^2\} . . . . . . . . . (17),
\]

\[
\mu^2 = \mu_0^2 + A_p \lambda_p^2 / (\lambda^2 - \lambda_p^2) . . . . . . . . . (18).
\]

The formula (17) is open to the same objection as $C = C_0/(1 - \lambda_0/\lambda)$, namely, that it does not satisfy the case of a glass where the double-refraction vanishes for one wave-length without the dispersion vanishing at the same time. It is clear that in this case other free periods, whose effect is usually negligible, become important.

For other glasses, however, the formula (17) and (18) might be good approximations. To get $\mu$ from (18) remember that for wave-lengths greater than 4300 the dispersion terms are $< 1/100$ of the whole. Then, using the Binomial Theorem, we find that, to an accuracy of $1/10000$ nearly,

\[
\mu = \mu_0 + A_p \lambda_p^2 / 2\mu_0 (\lambda^2 - \lambda_p^2)
\]

\[
= \mu'_0 + A'_p / \{1 - (\lambda_p/\lambda)^2\}.
\]

Hence

\[C = C_p / \{1 - (\lambda_p/\lambda)^2\} . . . . . . . . . (19),\]

where

\[C'_0 = C_p / (\mu'_0 + A'_p)\]

\[\lambda'_p = \lambda_p \sqrt{(\mu'_0 + A'_p)}\]

A formula of the type (19) for $C$ would lead to a curve connecting the wave-length of extinction and the load of the type

\[(\lambda - kW) \lambda = (\lambda'_p)^2.\]

In general, when $\lambda'_p$ and $\lambda_0$ are small, it will be found that either formula,

\[C = C_0 / \{1 - (\lambda_0/\lambda)\}, \quad C = C'_0 / \{1 - (\lambda'_p/\lambda)^2\},\]

represents the observations almost equally well.
But in the case of the results of Table II. a hyperbola was fitted to the observations, its equation being
\[ \lambda - (3460)^2/\lambda = (6.2489) W. \]

The differences between \( \lambda \) as calculated from the above formula and \( \lambda \) observed are given in Table II. under the heading \( \lambda_{\text{obs.}} - \lambda_{\text{hyp.}} \). The mean value of the residuals taken without regard to sign is between 13 and 14, or nearly three times the value of the mean residual from the straight line.

Even this mean residual hardly exceeds the probable error of observation, so that this would not be conclusive against the hyperbola. But an examination of the individual numbers in the last column of Table II. shows strong systematic positive residuals in the middle and negative residuals at the ends, and these systematic divergences certainly suggest that the hyperbola is not the most suitable curve.

The index of refraction of this particular glass is tolerably represented for the visible spectrum by the formula
\[ \mu = 1.5107 + 0.39125 / \{1 - (2159.6/\lambda)^2\}. \]

Thus
\[ \lambda_p = 2159.6, \quad \mu_0 = 1.5107, \quad \lambda_p' = 0.39125. \]

From this \( \lambda_p' \) of formula (20) comes out to be 1924.7. This differs entirely from the value obtained from the experiments, namely 3460. We are thus led to the interesting conclusion that in this glass at least the free periods which produce the ordinary dispersion are probably not active in producing the dispersion of artificial double refraction.

This removes theoretical justification in this case for the formula
\[ C = C'_0 / \{1 - (\lambda'_p/\lambda)^2\}, \]
even if it had not been shown inferior as a purely empirical fit.

We may then provisionally accept the law
\[ C = C_0/(1 - \lambda_0/\lambda), \]
and the results in what follows will be reduced with reference to it.

At the same time it must be remembered that the physically significant formula is probably of type (16). It will be shown in § 21 that even in the visible spectrum there are local divergences from the linear law.

§ 17. Methods of Reduction.

In fitting a linear law
\[ \lambda = \lambda_0 + k' W \]
to a set of observations, the corrections due to the sinking and permanent stress had to be taken into account.
The correct value for the load is given by

\[ W_0 + W + \gamma W^2. \]

It is therefore a formula

\[ \lambda = \lambda_0 + k'(W_0 + W + \gamma W^2) \]

which has to be fitted.

Assuming for the present that for monochromatic light the relative retardation is strictly proportional to the load, we have, for the band of the \( r \)th order, \( k' = k/r \), where \( k \) is the same constant for observations of all orders. Thus

\[ r\lambda = r\lambda_0 + kW_0 + kW + k\gamma W^2. \]

Suppose we have \( p \) observations, the first step is to take a number of differences \( \Delta \lambda \) corresponding to differences \( \Delta W \) sufficiently large to minimise the effects of accidental irregularities and to form the fraction

\[ \Sigma (\Delta \lambda)/\Sigma (\Delta W) = \left\{ (\Delta \lambda)/(\Delta W) \right\}_r, \]

the suffix \( r \) denoting that the band observed is of the \( r \)th order.

If our \( p \) observations correspond to values of \( W \) differing by a constant increment \( \Delta W \), and if we take differences of \( \lambda \) corresponding to differences \( q\Delta W \), we obtain \( p-q \) equations

\[
\begin{align*}

r(\lambda_{q+1} - \lambda_1) &= kq \Delta W + k\gamma q \Delta W (2W + q \Delta W), \\

r(\lambda_{q+2} - \lambda_2) &= kq \Delta W + k\gamma q \Delta W (2W + q + 2 \Delta W), \\

\cdots & \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \\

r(\lambda_p - \lambda_{p-q}) &= kq \Delta W + k\gamma q \Delta W (2W + 2q - p - 2 \Delta W).
\end{align*}
\]

If these be added up, we have

\[
\begin{align*}

r \sum_{i=1}^{\frac{p-q}{2}} (\lambda_{q+i} - \lambda_i) &= kq (p-q) \Delta W + k\gamma q \Delta W (p-q) (2W + p-1 \Delta W), \\

\left[ \frac{1}{q(p-q)} \sum_{i=1}^{\frac{p-q}{2}} (\lambda_{q+i} - \lambda_i) \right] \Delta W &= k + 2k\gamma W,
\end{align*}
\]

where \( W \) = mean value of \( W \).

We have then

\[ r(\Delta \lambda/\Delta W)_r = k + 2k\gamma W \quad \cdots \cdots \cdots \cdots \cdots \quad (21). \]

A comparison of the values of \( r(\Delta \lambda/\Delta W)_r \) then enables us at once to discover whether a correction \( \gamma W^2 \) is needed for the observations or not.

For most of the glasses examined the values of \( r(\Delta \lambda/\Delta W)_r \) do not indicate a correction of this type of sensible amount. In doing the reductions for such glasses \( \gamma \) has been taken equal to zero.

For one glass \( \gamma \) has a sensible value. In this case a suitable value of \( \gamma \) having been
formed, corrections were applied to the observed load and the observations re-reduced
with $\gamma = 0$.

From this point onward, therefore, $\gamma$ may be taken zero in the reductions. $k$ is
then equal to $r (\Delta \lambda / \Delta W)$.

In practice the values of $r (\Delta \lambda / \Delta W)$ vary slightly with different $r$'s. In most
cases, however, a sufficiently good fit is obtained by taking for $k$ the mean value of
$r (\Delta \lambda / \Delta W)$, and reducing the observations of different orders by means of this single
value. In one glass Hooke's law did not seem to hold quite exactly, and the
observations of different orders were reduced independently.

$k$ having been determined, $\lambda_0 + \frac{k}{r} W_0$ is found from the condition that the best fitting
straight line

$$\lambda = \lambda_0 + \frac{k}{r} W_0 + \frac{k}{r} W.$$ (22)

must be satisfied by the mean values $\lambda = \bar{\lambda}$, $W = \bar{W}$.

We thus obtain equations

$$\Lambda_1 = \lambda_0 + k W_0 = \bar{\lambda}_1 - k \bar{W}_1,$$

$$2\Lambda_2 = 2\lambda_0 + k W_0 = 2\bar{\lambda}_2 - k \bar{W}_2,$$

$$3\Lambda_3 = 3\lambda_0 + k W_0 = 3\bar{\lambda}_3 - k \bar{W}_3,$$

etc.

Two of these equations are theoretically sufficient to determine $\lambda_0$ and $W_0$. In
practice three are often obtained. The three equations are then solved by least
squares. The solution is given by

$$\lambda_0 = (3\Lambda_3 - \Lambda_1)/2,$$

$$k W_0 = (\Lambda_1 + 2\Lambda_2 + 3\Lambda_3)/3 - 2\lambda_0.$$

From the values of $k$, $\lambda_0$, $W_0$ so determined $\lambda$ has been computed from the
formula (22) and compared with the observed value.

§ 18. Tables of Results.

The following gives a table of the constants $\lambda_0$, $k W_0$, $k$ for the various sets of
observations. Observations corresponding to tension and pressure are distinguished
by the letters T, P respectively.

When $\lambda_0$, $k$, $k W_0$ are known, the wave-length of the band of $r^{th}$ order is computed
from the load by the formula (22). The average discrepancy in tenth-metres between
$\lambda$ thus calculated and $\lambda$ observed, for each set of observations, is entered in the column
headed $(O-C)$. 

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For the glass 935 a correction $\gamma W^2$ was applied to $W$, $\gamma$ being taken +0·001 for pressure and -0·001 for tension. In (22) we have then to substitute $W + \gamma W^2$ for $W$. This glass is badly annealed and does not seem well fitted by the formula.

The glass 2783 had to be reduced differently. This is a lead glass, a specimen of which had been examined under simple pressure and whose behaviour had appeared peculiar (see 'Camb. Phil. Soc. Proc.', vol. XII., Part V., p. 323, where the glass in question is described as O 154).

There are two sets of tension observations, denoted by A, B in Table IV., and two sets of pressure observations denoted by C, D. The values of $\Lambda$, $\tau \Delta \lambda/\Delta W$, (see § 17) are given in Table IV.

<table>
<thead>
<tr>
<th>Glass.</th>
<th>$\lambda_0$</th>
<th>$kW_0$</th>
<th>$k$</th>
<th>O - C.</th>
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<td>1809 T</td>
<td>352</td>
<td>-670</td>
<td>340.25</td>
<td>15</td>
</tr>
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<td>389.07</td>
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<td>83</td>
<td>323.89</td>
<td>14</td>
</tr>
<tr>
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<td>-76</td>
<td>316.58</td>
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</tr>
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<td>439</td>
<td>113</td>
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<td>-69</td>
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\textbf{Table IV.}

<table>
<thead>
<tr>
<th>Set</th>
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<th>$r\Delta\lambda/\Delta W_r$</th>
<th>$O - C.$</th>
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In this case there seems to be a progressive increase of $r\Delta\lambda/\Delta W_r$ with the order, for both tension and pressure. This excludes a correction for sinking, since the latter must act opposite ways for tension and pressure. It is here probably due to a failure of Hooke's law, which the observations have shown otherwise, and which will be discussed in a later section.

Under the circumstances no real advantage could be derived here by attempting to reduce the various sets by means of a single formula. The sets have, therefore, been independently reduced, using the formula

$$\lambda = \Lambda_r + W (\Delta\lambda/\Delta W_r).$$

The actual observations of all glasses are given in Table V. for purposes of reference. Each column corresponds to a single set of observations. As a rule the order of the band observed will be clear from the place of the observation in the series. Wherever this is not so, or where observations of different orders correspond to the same load, Roman numerals have been added to indicate the order of the band.
**Table V.**

<table>
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§ 19. Discussion of the Values of \( \lambda_0, kW_0 \).

The first thing which strikes the eye on looking through the results of the last section is, that although tension observations of different orders and pressure observations of different orders are fairly well fitted by the same \( \lambda_0, W_0 \), and \( k \), the same does not hold of tension and pressure observations taken together.

The differences in \( k \) are only what should have been expected, since \( k \) depends on the adjustments.

With regard to \( kW_0 \) the values for pressure and tension should theoretically be equal and opposite. For if light traverse a thickness \( \tau \) of glass in which a residual tension \( T_0 \) exists, a term \( CT_0\tau \) is added to the relative retardation when external tension is applied and subtracted from it when external pressure is applied.

Again \( \lambda_0 \) should be a constant for the glass, and therefore the same for tension and pressure, if the stress-optical coefficient be independent of the nature and magnitude of the load applied.

Now Table III. shows clearly that, although the values of \( kW_0 \) differ in sign, they are only very roughly of the same order of magnitude.

Possibly this might be accounted for by the fact that in different experiments the light did not pass through the same parts of the glass, so that the value of the residual stress might have been different.

The divergences in \( \lambda_0 \) are considerable; \( \lambda_0 \) appears systematically larger for pressure than for tension.\(^*\)

§ 20. Systematic Residuals.

The residuals \( \lambda_{obs.} - \lambda_{calc.} \) have in all cases been plotted on a large scale against \( \lambda_{calc.} \). Three of these diagrams are shown in figs. 7 to 9. The pressure and tension observations have been plotted to a different base in each case, to avoid the diagrams overlapping, so that two zero-marks appear on each scale of residuals. Of these the upper zero mark refers to tension observations.

Most of them (\( e.g. \), fig. 9) are fairly irregular, which is not surprising when we bear in mind that an error of 1 division in the ordinate (10 tenth-metres) is the probable error of the observations.

Two glasses, however, 3296 and 3453, figs. 7 and 8, appear to show very strongly systematic residuals between 4200 and 5500. If we look at fig. 7 we notice that the curves rise from 4200 to a peak about 4700, after which there is a sharp fall with a trough about 5050.

After this the curves run fairly horizontal, with indications of another peak at 6300.

\( ^* \) Note added April 3rd, 1907.—Later experiments do not confirm the systematic difference between the values of \( \lambda_0 \) for tension and pressure. Very probably the divergence previously noted was due to a change in the adjustments which had to be made when passing from tension to pressure, and which rendered the observations of the two kinds not strictly comparable.

The true value of \( \lambda_0 \) appears to be the mean of the values obtained for tension and pressure.]
The course of the diagrams in fig. 8 is very similar. There is a well marked peak about 4700, followed by a depression in the neighbourhood of 5000. There are also slight indications of a depression at 6000, with a subsequent rise.

These systematic residuals, which are in most cases quite large, and which are shown in the same place by all the tension and pressure observations of these glasses, cannot be chance effects. Neither can they be affected, denoting, as they do, comparatively rapid changes in \( \lambda \), by any of the slowly varying corrections which have been discussed. They can be accounted for only in the following ways:

1. Possible erroneous identification of a spectrum reference line in the neighbourhood and consequent wrong determination of \( \lambda \) observed;
2. Bad division errors of the spectroscope circle;
3. Bad error in some of the weights employed at these points;
4. Systematic change of personality of observer in this neighbourhood, due to change of colour;
5. Actual variation of the law of stress-optical effect in this neighbourhood.

(1) is ruled out by the fact that in the glass 3453, where the effect was first
noticed, it was discovered, not from any such curve, but from the actual circle readings of the spectroscope, which usually increased by steadily increasing differences; in this glass, just after the readings corresponding to \( \lambda 5000 \), the difference decreased instead of increasing. Readings were taken several times with great care, and the effect was confirmed in each case. This demonstrated that the cause was not accidental.

![Diagram of residuals](image)

**Fig. 8. Glasses 3453. Diagram of residuals.**

Clearly a wrong determination of a reference line is out of the question; this could not cause an irregularity in the differences of circle reading.

With regard to (2) and (3), the weights and the divisions of the circle were tested with great care and found correct.

As to personality, the jump of 40 tenth-metres between \( \lambda 5000 \) and \( \lambda 4800 \) would require an error of 6' in locating the centre of the band, and a change of personality of this amount, in a fairly bright region of the spectrum, is unthinkable. Besides, if the effect is due to such a change, it should appear in all the glasses, which is not the case.

Under these conditions it seems safe to assert that between wave-lengths 4500 and
5500 there exists a definite deviation from the straight line law, which deviation takes the shape of an undulation, with a crest at about 4700 and a trough between 5000 and 5100.

To trace this effect more exactly, a new set of readings were taken with the glasses 3453. The readings were taken with special care at intervals of load of half a kilogramme. The residuals from the best straight line were computed as before, and they are shown on fig. 10. Here, the observations being much more numerous, the residuals indicate a distinct curve. The dotted curve in the figure has been drawn freehand through the points to give some idea of the general shape of this curve.

It is seen that this curve amply confirms the previous set of results, although the observations were taken at several months' interval, with different adjustments, and probably different personal equations.

On examination, only 3296 shows anything like so marked an effect. 1809 and 2783 show the effect in much the same place, but weakly, and some sets of observations do not confirm it. 935 and 3749 are hopelessly irregular. Nothing definite can be asserted about them. As to 3413, the pressure observations do not show this effect at all, and the tension observations show it only very doubtfully.
There are indications, however, in this glass, of a systematic dip at 5500, and a subsequent rise. Various glasses also show signs of a peak in the red, between 6200 and 6500. None of these, however, are more than mere indications, and it is only the curves for 3453, and in particular fig. 10, on which any safe deductions and measurements can be based.

If we refer to the table of § 14 we see that 3453 and 3296 are very much alike in chemical composition. Apart from this, no relation between this effect and chemical composition can be predicated. It seems almost certain that boric acid has nothing to do with it. The glasses richest in B₂O₃ do not show the effect. K₂O can hardly be the explanation, or 3749 should show the effect more strongly. It seems not at all unlikely that a small impurity, such as magnesium or zinc oxide, may be the cause of the result. It is noteworthy that the only glasses which seem to show the effect at all definitely, are precisely those which contain MgO and ZnO, and that the one which really shows the effect in a measurable manner contains quite a respectable percentage of MgO.

§ 21. Possible Explanation by Absorption Bands.

The shape of the curve of residuals resembles the curve of index of refraction plotted to either period or wave-length when we pass through an absorption band. This suggests that the effect may be due to some faint or latent absorption band of the glass in the visible spectrum, which band corresponds to a period active in producing the artificial double-refraction.

Following, as before, DRUDE (‘Theory of Optics,’ cap. V.), we have, μ being the index of refraction, and κ the co-efficient of absorption,

$$
\mu^2 (1-i\kappa)^2 = \text{terms not depending upon the absorption band} + Q/\{1 + i\alpha/\lambda - (\lambda_\nu/\lambda)^3\}.
$$

where λ_ν is the wave-length of the absorption band, α is a coefficient which increases with the absorption, and Q is a coefficient depending on the arrangement and number of the electrons.

This leads to

$$
\mu^2 (1-\kappa^2) = \mu_0^2 + Q \{1 - (\lambda_\nu/\lambda)^3\}/\{1 - (\lambda_\nu/\lambda)^3 + \alpha^2/\lambda^2\}
$$

$$
2\mu^2\kappa = (Q\alpha/\lambda)/\{1 - (\lambda_\nu/\lambda)^3\} + \alpha^2/\lambda^2\].
$$

Now suppose the stress T to leave λ_ν and α unaltered, and to alter Q.

$$
2\mu (1-\kappa^3) d\mu/dT - 2\mu^2\kappa d\kappa/dT = 2\mu_0 d\mu_0/dT + \{1 - (\lambda_\nu/\lambda)^3\} (dQ/dT)/\{1 - (\lambda_\nu/\lambda)^3 + \alpha^2/\lambda^2\},
$$

$$
4\mu\kappa d\mu/dT + 2\mu^2 d\kappa/dT = (\alpha/\lambda) (dQ/dT)/\{1 - (\lambda_\nu/\lambda)^3 + \alpha^2/\lambda^2\},
$$

whence, eliminating dκ/dT,

$$
2\mu (1+\kappa^3) d\mu/dT = 2\mu_0 d\mu_0/dT + \{1 - (\lambda_\nu/\lambda)^3 + \kappa\alpha/\lambda\} (dQ/dT)/\{1 - (\lambda_\nu/\lambda)^3 + \alpha^2/\lambda^2\}.
$$

\[2 Q\]
To simplify the calculation, we may suppose that in the initial state of things \( Q = 0 \), so that \( \kappa = 0, \mu = \mu_0 \). As a matter of fact \( Q \) cannot be 0, but the assumption that \( \kappa = 0, \mu = \mu_0 \) is good enough to give the characteristics of the phenomenon sufficiently well for our purpose.

We have then

\[
d\mu/dT = d\mu_0/dT + (dQ/dT)\{(1-(\lambda_p/\lambda)^2)\}/2\mu_0[1-(\lambda_p/\lambda)^2 + \alpha^2/\lambda^2].
\]

In all the above \( d/dT \) denotes rate of divergence with regard to \( T \) of a quantity for the two oppositely polarized rays. Thus

\[
d\mu/dT = C,
\]
\[
d\mu_0/dT = \text{value of } C \text{ if there were no absorption band.}
\]

Accordingly,

\[
\frac{1}{2} (dQ/dT) \{(1-(\lambda_p/\lambda)^2)\} \mu_0^{-1}[1-(\lambda_p/\lambda)^2 + \alpha^2/\lambda^2]^{-1}
\]

gives the deviation produced in the stress-optical coefficient by the absorption band. Calling this \( \delta C \), we have

\[
\lambda_{\text{obs.}} : \lambda_{\text{cal.}} = C + \delta C : C.
\]

Thus the deviation \( \lambda_{\text{obs.}} - \lambda_{\text{cal.}} \), which is given by fig. 10, is \( \lambda\delta C/C \).

\( \lambda, \mu, C \) are all comparatively slowly varying: the factor which causes the oscillation is

\[
\{1-(\lambda_p/\lambda)^2\} \{(1-(\lambda_p/\lambda)^2) + \alpha^2/\lambda^2\}^{-1}.
\]

This factor starts with the value 0 when \( \lambda = 0 \), decreases to a negative minimum \(-\lambda_p^2/\alpha(2\lambda_p + \alpha)\) when \( \lambda^2 = \lambda_p^2/(\lambda_p + \alpha) \), and then increases to a positive maximum \(\lambda_p^2/\alpha(2\lambda_p - \alpha)\) when \( \lambda^2 = \lambda_p^2/(\lambda_p - \alpha) \). It then decreases down to 1 when \( \lambda = \infty \).
\( \alpha \) being here small with regard to \( \lambda_p \), the wave-lengths of minimum and maximum are approximately \( \lambda_p - \frac{1}{2} \alpha \), \( \lambda_p + \frac{1}{2} \alpha \). Neglecting the variations of the other factors, this result gives us an easy means of obtaining \( \alpha \) from fig. 10. \( \alpha \) is the horizontal distance between the maximum and the following minimum. \( \alpha \) is therefore between 300 and 400 tenth-metres—say 350; \( \lambda_p \) from the same diagram is about 4900.

This phenomenon also gives us experimental evidence in favour of a non-alteration of the period. If we refer to the physical meaning of \( Q \), we find it to be

\[
Q = Ne^2\tau^2/m\pi,
\]

where

- \( \tau \) = period of the light corresponding to the absorption band,
- \( N \) = number of electrons in unit volume which vibrate in this particular mode,
- \( e \) = charge on such an electron,
- \( m \) = its mass.

It follows that when we suppose \( \tau \), that is \( \lambda_p \), to vary (\( \kappa \) being initially zero, as before), what we have called \( \delta C \) is given by

\[
\frac{1}{2} \mu_0^{-1} (d/dT) \left\{ Q \left[ 1 - (\lambda_p/\lambda)^2 \right] / \left( [1 - (\lambda_p/\lambda)^2]^2 + \alpha^2/\lambda^2 \right) \right\}
\]

\[
= (Ne^2/2\mu_0 m\pi) (d\lambda_p^2/dT) d/d\lambda_p \left[ \frac{\lambda_p^2 \lambda^2 (\lambda^2 - \lambda_p^2)}{(\lambda^2 - \lambda_p^2)^2 + \alpha^2/\lambda^2} \right]
\]

\[
= (Ne^2/2\mu_0 m\pi) (d\lambda_p^2/dT) \left[ \frac{\lambda^4 [(\lambda^2 - \lambda_p^2)^2 - \alpha^2(2\lambda_p^2 - \lambda^2)]}{[(\lambda^2 - \lambda_p^2)^2 + \alpha^2/\lambda^2]^2} \right]. \quad (26)
\]

Now, in the neighbourhood of \( \lambda = \lambda_p \), \( \alpha \) being small, the rapidly varying terms which determine the shape of the curve are those involving \( \lambda^2 - \lambda_p^2 \). If we call this quantity \( \chi \), and put \( \lambda = \lambda_p \) in the other terms, we obtain some conception of the shape of the curve. Taking

\[
y = (x^2 - \alpha^2\lambda_p^2) (x^2 + \alpha^2\lambda_p^2)^{-2}. \quad \ldots \ldots \ldots \quad (27),
\]

\( y \) has one minimum value \( -(\alpha^2\lambda_p^2)^{-1} \) when \( x = 0 \). It has two maximum values \( (\alpha^2\lambda_p^2)^{-1}/8 \) when \( x = \pm \sqrt{3} \alpha \lambda_p \) or \( \lambda = \lambda_p \pm \sqrt{3}\alpha/2 \). The general shape of the curve is shown in fig. 11. It is at once obvious that it does not show the alternate large maximum and minimum required to fit the curve of fig. 10. So far, then, the experiments bear out the hypothesis that the free periods are not altered.

Before we can proceed further we have to settle finally the convention about the sign of \( C \). It has been usual to call \( C \) positive for ordinary glass, such as that investigated by Brewster and Kerr, and \( C \) negative for heavy flint like S 57. This convention has been adopted by the author in previous papers.

We will now rigidly define the stress-optical coefficient as

\[
C = \left| (\mu_x - \mu_\tau)/(T_2 - T_1) \right|. \quad \ldots \ldots \ldots \ldots \quad (28),
\]
where $\mu_t$ denotes the index of refraction of the ray vibrating along the direction in which the principal stress (tension being considered positive, as usual) is $T$.

Since the direction of vibration—if we take the electric force to be the light-vector—is perpendicular to the direction of polarization, and the index of refraction is inversely proportional to the velocity, this means that a positive $C$ implies a higher velocity in the ray polarized in the direction of greatest stress. Now this ray corresponds to the ordinary ray if the glass be compared with a uniaxial crystal whose optic axis is parallel to the direction of greatest stress.

The glass, therefore, produces the same effect as a positive uniaxial crystal so placed.

This is, in fact, what does occur. This definition, therefore, agrees with the earlier one.

Now, since (for this glass) $\lambda$, $C$, $\mu_o$ are all positive, it follows that if we are to have a maximum followed by a minimum, as in fig. 10, $dQ/dT < 0$.

Now, in $Q = N e^2r^2/m\pi$, since $r$ does not change, the only quantity which can change with the polarization is $N$, the number of electrons per unit volume.

$dQ/dT$ is then $e^2r^2(N_2-N_1)/\pi m (T_2-T_1)$, where $N_2, N_1$ are the number of electrons of period $r$ which respond to vibrations in the directions of $T_2$ and $T_1$.

Our result will, therefore, signify that a tensional stress decreases the number of electrons which respond to vibrations in the direction of the stress, relatively to the number responding to vibrations in a perpendicular direction. In other words, tension appears to tend to set the electrons vibrating in a plane at right angles to the line of stress, pressure having the reverse effect.

It seems probable that if this effect were due to an absorption band, a glass
showing in its unstressed condition strong absorption bands in the visible spectrum would exhibit this effect in a most marked manner. A small slab of didymium glass was obtained and examined under direct pressure with the apparatus described in the previous paper in 'Camb. Phil. Soc. Proc.,' already referred to several times. The observations were not very precise, and it is hoped to repeat them with the flexure apparatus, when larger slabs can be obtained.* Such as they were, however, they gave a negative result. The band due to stress passed through the double absorption band in the orange without showing any marked irregularity.

It seems, therefore, that the didymium electrons which produce the absorption band are not affected by the stress in the way described. It appears possible that the didymium particles really float about, as it were, in the glass, in a free state, like particles in suspension in a fluid, and that they cannot be influenced to any great extent by stress applied to the glass. Further research in this direction is in progress.

§ 22. Determination of Absolute Values of C.

Although the experiments were primarily undertaken to show the dispersion effects, it is desirable to know also the absolute values of the stress-optical coefficients. These are not given by the experiments as described in § 2, because the differences of level $z_1 - z_2$ and $z_1 - h$ cannot be measured with sufficient accuracy.

To determine absolute values a second slit is used, of which the height is $h + \Delta h$. The two slits were cut in the same diaphragm, so that $\Delta h$ is easily measured once for all.

Referring to formula (7), the relative retardation due to the second slit,

$$R' = (3M_sC'/2b_3^2) [z_1 - z_2 + \sigma (z_1 - h - \Delta h)].$$

where $C'_z = \text{stress-optical coefficient of beam F}$ for the wave-length for which the retardation is $R'$.

Also

$$R = (3M_sC_2/2b_3^2) [z_1 - z_2 + \sigma (z_1 - h)].$$

Hence

$$\frac{R'}{C'_z} - \frac{R}{C_2} = -3M_s\sigma \Delta h/2b_3^2.$$

If therefore we know the ratio $C'_2 : C_2$ we can find the absolute values of either. If $R'$, $R$ correspond to bands of $n^{th}$ order,

$$R = n\lambda, \quad R' = n\lambda'.$$

Therefore

$$n (\lambda'/C'_2 - \lambda/C_2) = -3M_s\sigma \Delta h/2b_3^2.$$
Assuming the law connecting \( C \) and \( \lambda \) to be given by (14), we have
\[
C_2 = C_0^{(2)}/(1 - \lambda_0^{(2)}/\lambda), \quad C_2' = C_0^{(2)}/(1 - \lambda_0^{(2)}/\lambda')
\]
where \( C_0^{(2)}, \lambda_0^{(2)} \) refer to the slab \( F \).

Hence
\[
n (\lambda' - \lambda)/C_0^{(2)} = -3M_2\sigma \Delta h/2b_2^3.
\]
Therefore
\[
C_0^{(2)} = -2n (\lambda' - \lambda) b_2^2/3M_2\sigma \Delta h \ldots \ldots (32),
\]
and from equation (5),
\[
C_0^{(1)} = 2n (\lambda' - \lambda) b_1^2\left(1/\sigma + 1\right)/3M_1\Delta h \ldots \ldots (33),
\]
which give the absolute values of \( C_0 \) for both slabs.

A great many errors enter into the determination of these absolute values. It is very difficult to measure the spans with sufficient exactness, and the differences \( \lambda' - \lambda \) are not large enough to allow of very accurate determination.

§ 23. Effect of Chemical Composition on Stress-optical Properties.

The mean values for \( C_0 \) obtained in this way for each beam are shown below in Table VI. \( A, B \) denote the two individual slabs of each pair, and \( C_0 \) is expressed in a unit equal to \( 10^{-7} \) (cm.)\(^2\) per kilogramme weight.

**Table VI.**—Dependence of \( C_0, \lambda_0 \) on Chemical Composition.

<table>
<thead>
<tr>
<th>Glass.</th>
<th>( C_0 ) for A.</th>
<th>( C_0 ) for B.</th>
<th>Mean ( C_0 )</th>
<th>( \lambda_0 )</th>
<th>( B_2O_3 )</th>
<th>( K_2O )</th>
<th>( B_2O_3 - \frac{1}{2}K_2O )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3413</td>
<td>2.99</td>
<td>3.11</td>
<td>3.05</td>
<td>553</td>
<td>33.0</td>
<td>3.8</td>
<td>31.1</td>
</tr>
<tr>
<td>1809</td>
<td>2.95</td>
<td>2.94</td>
<td>2.94</td>
<td>561</td>
<td>34.3</td>
<td>7.4</td>
<td>30.6</td>
</tr>
<tr>
<td>935</td>
<td>2.82</td>
<td>2.94</td>
<td>2.88</td>
<td>451</td>
<td>27.7</td>
<td>3.1</td>
<td>26.1</td>
</tr>
<tr>
<td>3296</td>
<td>2.71</td>
<td>2.83</td>
<td>2.77</td>
<td>537</td>
<td>15.4</td>
<td>16.7</td>
<td>7.0</td>
</tr>
<tr>
<td>3749</td>
<td>2.15</td>
<td>2.19</td>
<td>2.17</td>
<td>564</td>
<td>5.9</td>
<td>23.9</td>
<td>-6.1</td>
</tr>
<tr>
<td>3453</td>
<td>2.13</td>
<td>2.10</td>
<td>2.11</td>
<td>524</td>
<td>5.7</td>
<td>20.8</td>
<td>-4.7</td>
</tr>
<tr>
<td>2783</td>
<td>1.93</td>
<td>2.21</td>
<td>1.93*</td>
<td>500†</td>
<td>1.4</td>
<td>12.5</td>
<td>-4.9</td>
</tr>
</tbody>
</table>

* 1.93 has been taken, and not the mean of the two values, because here \( C_0 \) certainly differs for slabs \( A \) and \( B \), and \( A \) was the slab analysed.
† Estimated from the values of \( A \), on p. 291.
If we refer to the diagram published in a paper previously referred to ('Camb. Phil. Soc. Proc.' vol. XII., p. 335) showing dependence of C upon percentage of PbO, we see that until this percentage reaches about 40, PbO has little influence on the stress-optical effect.

We are therefore to look at the two remaining principal constituents, B₂O₃ and K₂O, for the cause of variations in C₀.

Looking at Table VI., in which the glasses are arranged according to descending order of magnitude of C₀, we see that the four glasses with the high C₀ all contain a percentage of B₂O₃ which is considerable. On the other hand, the three glasses with a low C₀ all contain a comparatively high percentage of K₂O. We conclude that either B₂O₃ raises C₀, or K₂O lowers it, or both. Also, looking at 2783, which is the lowest of the seven, we notice that it contains the least percentage of B₂O₃, but not the highest percentage of K₂O. This suggests that B₂O₃ is more efficient in raising C₀ than K₂O in lowering it. That the effect of B₂O₃ must be predominant is otherwise evident from the fact that the order of the percentages of B₂O₃ is the same as the order of magnitude of C₀, with one exception (1809).

The last column of Table VI. shows the values of (percentage of B₂O₃) - \frac{1}{2} (percentage of K₂O). This places 1809 in the sequence, but throws out 3749. Also the marked difference between the four first and the three last is shown very clearly.

The glasses do not form a sufficiently regular series to enable us to go further and to determine exactly the law of dependence of C₀ upon the percentages of B₂O₃ and of K₂O in the glass. But the increase of B₂O₃ certainly increases C₀, and the increase of K₂O probably decreases it; and B₂O₃ seems to be at least twice as efficient as K₂O.

With regard to the mean values of λ₀, they all appear to be of the same order of magnitude. At all events no definite dependence of λ₀ upon the composition can be traced. For percentages of B₂O₃ not exceeding 35 and of K₂O not exceeding 25 it would seem that λ₀ is independent of the composition of the glass or that the dispersion is, in every case, proportional to the double refraction.


Before concluding, the peculiar phenomena shown by glass 2783 require explanation.

This glass showed a progressive increase with increase of load in \( r \Delta \lambda/\Delta W \), for both tension and pressure.

Also when the load was increased the band, which was straight and vertical for moderate loads, became curved, being convex towards the red as shown in fig. 12. The load was eventually increased to about 59 kilogrammes when one of the glasses broke. The band was observed when the glass was on the point of rupture and it exhibited a decided V shape as drawn.
This showed that the relative retardation was greater for light passing through at mid-level than for light passing through the edges of the beams.

Such an effect can be explained only in two ways. Firstly, by supposing that the law of stress across the section does indeed remain linear, but that the relative retardation is not proportional to the stress, increasing less rapidly for large stresses than for small, since here (the overlapping being assumed for simplicity to be \( \frac{1}{2} \) height of beams) \( \frac{1}{2}T + \frac{1}{2}T \) produces more effect than \( T \).

Such an effect, however, would imply an increasing falling off of the values of \( \lambda \) from the values which would be obtained if the linear law held. The result would be a progressive decrease, instead of a progressive increase, in \( r\Delta \lambda/\Delta W_r \).

Secondly, we may suppose that Hooke's law fails or stress is not proportional to strain. Consider a beam bent under constant bending moment. The axis will take the form of a circular arc. If we imagine the circle completed, then the symmetry shows that the cross-sections must remain plane and all pass through the centre of the circle.

It follows easily that, whatever be the law of stress, if we can neglect end effects, the extension follows a strictly linear law.

Thus if \( AB \) (fig. 13) represent the vertical axis of such a section, and the stress at any point \( R \) in \( AB \) be set off as \( RP \) perpendicular to \( AB \), the locus \( BPC \) of \( P \) is a
genuine stress-strain diagram. It will therefore, as is well-known, take the shape shown in fig. 13, the stress falling off rapidly as the strain approaches and passes what is known as the yield-point.

The corresponding curve for the overlapping part of the other beam is shown by AQD, and the stress effective in producing the optical effect is the sum of the two ordinates RP, RQ. It is obvious from the figure that PQ is a maximum in the middle. Thus the peculiar shape of the band is likewise accounted for on this hypothesis.

Now let the straight line BI give the stress-diagram which would be obtained for the same bending moment if Hooke's law held. This straight line and the curve must then be so related that the first moment about BX of the areas APCB and AIB are equal.

Let L be the extremity of the ordinate through the mid-point of AB. Draw BL cutting AC at J and the tangent at L cutting AC at T, BX at U. The stress-strain curve is always convex inwards, therefore CPLB always lies on one side of TU as shown.

Now the triangles BLU, TLJ are clearly equal. Hence area CPLJ > area BSL. And the mean distance from BX of the area CPLJ > mean distance from BX of the area BSL. Therefore first moment of CPLJ > first moment of BSL, or first moment of ABJ > first moment of ABLC. Therefore, if ABI and ABLC have the same first moment, ABI < ABJ, or BI must lie to the left of BJ.

If BI cut ML in K, then ML > MK. That is, the actual measured stress is greater than the computed stress. Therefore the observed values of $\lambda$ exceed those that would be obtained if Hooke's law held by a difference rapidly increasing with the stress.

The result is a progressive increase in the value of $r\Delta \lambda/\Delta W$, such as is actually observed. The discrepancies which have appeared are therefore explained.

Incidentally this confirms the conclusion (which indeed seems highly probable on theoretical grounds) that the stress-optical effect is dependent upon the stress—that is, the molecular strain—and not upon the molar strain. The latter, which is the sum of both plastic and elastic effects, is the quantity measured in most extension experiments, and is usually denoted by "strain" simply.

§ 25. Conclusion.

This completes the account of the results reached so far. The next step would be to obtain glasses of suitable chemical composition to show the effects discovered in a much stronger degree and thus allow of more precise determinations. Research in this direction is being undertaken, and it is hoped that the results will form the subject of a future communication.
In conclusion the author wishes to express his most grateful thanks for the assistance which has been rendered him by the Royal Society, without which this work could not have been undertaken. He desires also to place on record his indebtedness to Professor F. T. Trouton, F.R.S., who has most generously placed the resources of the Physical Laboratory of University College, London, at his disposal; and also to Mr. A. W. Porter, B.Sc., whose interest in the work and kindly criticisms and suggestions have been invaluable.
VIII. The Distribution of Blue-Violet Light in the Solar Corona on August 30, 1905, as derived from Photographs taken at Kalaa-es-Senam, Tunisia.

By L. Becker, Ph.D., Regius Professor of Astronomy in the University of Glasgow.

Communicated by the Joint Permanent Eclipse Committee.

Received November 27, 1906,—Read June 6,—Revised August, 1907.

PLATE 1.

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Table I., § 4 (c), and §§ 7 and 8 contain the results derived from the measurements made on the photographs, viz., equal-intensity curves of the corona and a formula (D) expressing the intensity of the corona as a function of the mean distance from the solar limb of an equal-intensity curve.

§ 1. The Apparatus.

The object of my expedition to Kalaa-es-Senam, Tunisia, was to obtain a series of photographs from which might be determined the distribution of light in the corona.

In designing my apparatus, I was led by two considerations: (1) the photographs had to be taken automatically, as I had to work without assistance, (2) standardising of the photographs was to be avoided. All the photographs were therefore taken on the two halves of a whole plate placed end to end and developed in the same tray during the same time. The automatic apparatus gives 10 exposures, and it is governed electrically by a pendulum clock. I employed two cameras, one with a...
Cooke triple achromatic lens of 3\(\frac{1}{2}\) inches aperture and 58.5 inches focal length, which belongs to the Glasgow spectrograph, the other with a Ross portrait lens of 2 inches aperture and 12 inches focal length. The pictures obtained with the larger camera are so much superior to the small size ones of the portrait lens that I have not made use of the latter in this paper. The cameras were fed by a coelostat of 8 inches aperture, which had been kindly lent to me by the Royal Dublin Society. In front of the two object-glasses, and about an inch from them, a rotating shutter was mounted which served both cameras. The rotating shutter has four oblong apertures, 90 degrees apart (its back view is shown at \(D_2\), fig. 1); it is rotated by clockwork driven by a spring, and its motion is governed by the armature of an electro-magnet (\(f\)). When the armature is attracted, the shutter rotates through about 45 degrees until it presses against one of the four stops \(d\) and brings an opening opposite the object-
glasses, and when the armature is released the shutter turns again 45 degrees, as far as one of the stops c, and shuts off the light. The contacts are made by a pendulum clock, and they are so devised that make or break can occur only when the pendulum is at or near its position of rest.

I arranged for five exposures each of 1 second duration, and five exposures lasting respectively 3, 9, 20, 46 and 89 seconds. Their actual durations are 0.84, 0.80, 0.78, 0.80, 0.85, 2.82, 9.02, 20.84, 45.91 and 89.04 seconds, as determined automatically on the chronograph at the Observatory after my return from the eclipse expedition. I have deducted 0.02 second from the figures recorded on the chronograph to allow for the peculiar motion of the shutter. At the first four exposures of 1 second, different screens, each with 13 holes, are in front of the object-glass. The diameters of the openings are respectively 0.210, 0.296, 0.410, 0.595 inch. At the first exposure the screen leaves 1/21.4 of the object-glass free, at the second 1/10.8, at the third 1/3.6, and at the fourth 1/2.7. These screens are geared to the clockwork which rotates the shutter and fall out of gear after the fourth exposure. The illustration shows them out of gear.

The plate-holder (C) of the Cooke camera is 17 x 3 inches; it slides lengthways inside a metal box 32 x 4 inches. It is moved by rack and pinion, the rack being attached to the plate-holder, and the bearings of the axle of the pinion to the cover (C3) of the box. Spring-driven clockwork (B) communicates its motion by means of a shaft (a) to the pinion. The clockwork is governed (at b) by the armature of an electro-magnet (the armature and the revolving stop with its axle appear white in fig. 1). When the armature is attracted, the plate-holder moves 1 inch onwards, and when it is released it moves another inch. The necessary contacts are made by the pendulum clock. I arranged the contacts in such a way that for the first four exposures the plate moves one step onwards, for all the others two steps, and when the plate has been pushed along, 2 seconds are allowed for the camera to settle before the next exposure is made. Of the 206 seconds for which I made provision, 173 seconds are occupied by the exposures, 15 seconds are taken up by changing of plates, and 18 seconds are lost.

The pendulum clock is shown at A. It is provided with four circular steel-sheet discs, into which notches are cut. The axle which carries the discs has a period of 240 seconds, i.e., about half a minute more than totality lasted. Two of the discs (A, B) are represented in the diagram, fig. 2, which also shows the contact levers. The diagram gives the position immediately before making of contact. At the next second a will fall on b, making contact at c, and after another second b will fall away from a, thus breaking the contact. The duration of contacts depends slightly on the position of the notches, as will be seen from the figures given above for a second's contact, which show a range of 0.07 second.
It can be shown from the observed durations that the clock was off-beat at the Observatory, and probably it was so, too, at the eclipse, and possibly in the opposite way. This would not affect the relative duration of the first five contacts, as they all lie between an uneven and even second, but their errors would appear relative to the long exposures.

The sequence of events governed by the clock takes place at the moments of time shown in the following table, where the numerals denote the seconds elapsed from second 0, when the pendulum is started:

<table>
<thead>
<tr>
<th>Contacts for exposure.</th>
<th>Contacts for change of plate.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2</td>
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<td>5</td>
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<td>42</td>
<td>131</td>
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<tr>
<td>135</td>
<td>156</td>
</tr>
<tr>
<td>161</td>
<td>207</td>
</tr>
</tbody>
</table>

1. Exposure of 0.84 second, first screen, \( r = 77 \). Plate moves 1 inch.
2. Exposure of 0.80 second, second screen, \( r = 55 \). Plate moves 1 inch.
3. Exposure of 0.78 second, third screen, \( r = 39 \). Plate moves 1 inch.
4. Exposure of 0.80 second, fourth screen, \( r = 27 \). Plate moves 1 inch.
5. Exposure of 0.85 second, full aperture, \( r = 16.7 \). Plate moves 2 inches.
7. Exposure of 2.82 seconds, full aperture. Plate moves 2 inches.
8. Exposure of 89.04 seconds, full aperture. Plate moves 2 inches.
9. Exposure of 20.84 seconds, full aperture. Plate moves 2 inches.
10. Exposure of 45.91 seconds, full aperture.

\( r \) designates the ratio of the focal-length and the diameter of a lens, which has the same area as the lens reduced by the screen.

There are several points in the design of the apparatus which have proved unsatisfactory. The shutter must have a smaller moment of inertia, and its motion should be recorded on a chronograph; the plate-holder ought to run on wheels instead of sliding on a rod. The mutual distances of the pictures ought to be, say, four solar diameters, and, especially, the side of the square opening in front of the plate must be twice as great as the distance between the pictures [see § 5 (f), (g), (h)]. One of the pictures (not the last) must be 8 diameters from its neighbours [see § 4 (c)]. The screen for cutting down the aperture of the lens ought not to contain a series of small openings, but have a central opening and an annular opening, whose diameter is about two-thirds of that of the lens (see Appendix I, p. 332).
§ 2. The Photographs (Plate I).

The pendulum was started about a second after Mr. H. Mavor, who watched the contact, gave the signal that totality had begun. Before the last exposure was finished sunlight appeared, but I shut it off by stepping in front of the object-glass, and it was about 3 seconds before the shutter automatically closed. That is to say, totality lasted about \(1 + 207 - 3 = 205\) seconds, as compared with the calculated time of 210 seconds. Accordingly, the tenth exposure lasted about 43 seconds.

The plates (two halves of a whole plate) were developed together in the same tray by a strong developer (Imperial standard) for 7 minutes. I developed at the open window at star-light, keeping the plates covered most of the time. The photographs show a great deal of contrast, and this has proved an advantage in measuring them. The background of the long-exposed negatives is dense, due to the brightness of the sky. This diffused light, whose intensity I had underrated in the design of the apparatus, produced an impression even for the shortest exposures, darkening a square on the plate equal in size to the opening in the plate-holder. I find, from measurements, that the intensity of the diffused light equals that of the corona at a distance of 1.1 solar diameter from the sun's limb, \(i.e.\) 0.6 in unit of the intensity of the corona at a point 1 solar diameter distant from the limb as found from the formula § 7.

In the preliminary report I have said that the plate-holder failed to move in the designed manner, due to some parts of the apparatus having been damaged in transit. Owing to this accident, there is a multiplication of images in the sixth and seventh pictures, and not only the first five photographs are an inch (2 solar diameters) apart, but also the next two, which were meant to be at twice that distance. In consequence, the successive exposures to the diffused light overlap on the plate, with the effect that on one half of each of Photographs I. to VII. there is the same duration of exposure to the diffused light as on the adjoining half of the neighbouring photograph. This has enabled me to separate the intensity of the corona from that of the sky. There is no overlapping on Photographs VIII. and IX., and though they did not, on that account, furnish data for the intensity formula, they supplied a series of equal-intensity curves of the corona, which are required for the reduction of the other pictures. Fig. 3 explains the conditions.

![Diagram](image-url)

The photographs are numbered I., II., &c., and the exposures (see § 1), 1, 2, &c. The lines at the top give the extent of the area illuminated at each exposure by the
diffused light. The left and right halves of a photograph will be designated by $a$ and $b$. Photographs I. to VII. occupy the first half-plate, and VIII. and IX. half of the second half-plate.

Photographs VI. and VII. are, from an ideal point of view, marred by defects—No. VI. by some instantaneous pictures of the protuberances which appear on the lunar disc, and No. VII. by two short exposure pictures which are eccentrically superposed on it. These defects are of no consequence (see §6). Owing to the failure of the automatic apparatus, the exposures of Nos. VI. and VII. are uncertain to about a second, but the sum of the two exposures, which equals the sum of the sixth, seventh and eighth exposures, is accurately known.

To get the negatives, from which the Plate was prepared, I first made enlarged positives, copying those pictures together whose background have the same density on the original. I have attempted to make the coronas of VI$a$. and VI$b$. extend equally far, and in the attempt the coronas of pictures Va. and VIII. have come out too small. I should say that on the original negative the corona of VIII. covers the whole breadth of the plate, which towards the top is three-quarters of a solar diameter broader than shown in the reproduction. The enlargement is 1:7.

§ 3. The Measurements.

The observations made on the photographs, and utilised in this paper, consist in the selection of points on the several corona pictures at which the photographic film shows the same degree of blackness, and in the measurement of their distance from the lunar disc. The measurements were actually made on positives, and not one but twenty-four points of an equal-blackness curve, 15 degrees apart, were measured. The positives are contact prints on slow plates obtained at a distance of 10 feet from a gas jet. The twelve sets which I prepared belong to different exposures, and were developed for contrast. I copied the negatives I. to Va., Vb. and VI$a$. , VI$b$. and VII. separately on account of the differences in density of the background. Sixteen sets of measurements of equal-density curves were made on these twelve sets of positives. The measurements were easy to make, and proved to be consistent. The positives show a perfectly transparent ring round the lunar disc, the diameter of which depends on the exposure and development. Seen against black paper, this ring furnishes a well-defined outline to set upon. Some of the curves at great distance from the sun, where the intensity changes little with the distance, were measured on enlargements (10 diameters) on bromide paper, in which the contrasts are much increased.

I further made twenty copies of each of Photographs VIII. and IX. at all kinds of exposures. These negatives are very dense, and, apparently, evenly dense up to about half a diameter from the sun's limb, and show no detail to the eye when inspected against a strong light. On the other hand, the positives contain detail as near as 0·12 diameter, and as distinctly as if they were replicas of the first six
negatives. The measurements furnished 79 curves of equal density, which belong to mean distances between 0·12 and 1 solar diameter. As each of the two photographs has a background of equal density all round, these curves will be employed in reducing measured distances on other photographs as described in § 4 (c) and § 4 (d).

The apparatus which I employed in measuring the photographs consists of a low-power microscope mounted on a slide whose position can be read by vernier to 0·001 of an inch. The slide is mounted on a circular plate which turns in a ring, so that measurements can be made at any position-angle.

The measurements were made at position-angles 0 degree, 15 degrees, &c. The position-angles refer to the north pole of the sun. I obtained the zero of the position-angles from the calculated position-angles referred to the north pole of the sun and the positions of the second and third contacts on the first and last photographs. The position-angles of the contacts referred to the celestial pole were found from the data given in the 'Nautical Almanac' (124 degrees and 287 degrees), and the position-angle of the north pole of the sun is 20·7 degrees.

On the photographs published with this paper the line joining the centres of the lunar discs has a position-angle of 239 degrees, 59 degrees being to the left and 149 degrees at the top.

I observed the following rule in measuring:—After clamping the microscope at a certain position-angle, I set the wire successively on the moon's limb, then on a point of the corona where the blackness had a certain density and, without turning the microscope, made similar measurements 180 degrees from the first position. Keeping the degree of blackness in my mind, I repeated the operation on the other photographs, and then for the other position-angles.

§ 4. Reductions.

The object of the reductions is to find (1) the mean distance from the solar limb of each equal-density curve, and (2) the position of each equal-intensity curve with reference to its mean circular-intensity curve. The steps are as follow:—

(a) There is a slight difference amounting to a few thousandths of an inch between the diameters of the moon as obtained from negatives and from positives. On the negatives the lunar diameter is 0·565 of an inch, and I reduced all the measured distances to this diameter by correcting them by half the difference between this figure and the diameter appertaining to each measured distance.

(b) Reduction of the Distances from Lunar Limb to Solar Limb.—M (fig. 4) is the centre of the moon, A, B and S are respectively the centres of the sun at second and third contacts and t seconds after the second contact. The duration of totality is about 205 seconds. The diameter of the moon is D = 0·565 of an inch, and that of the sun is d = 0·540 of an inch. The angle between the second and third contacts, 156·7 degrees, is given by the first and last photographs; it equals the angle...
subtended by BA at M. The position angle, counted from the north pole of the sun, of the second contact is 104 degrees. CMS is designated by α.

A measured distance m, at position-angle P, is reduced to distance h from the sun's limb by the following formula, small quantities being neglected,

$$\tan \alpha = (1 - \frac{t}{103}) \tan 78^\circ 3, \quad h = m + 0.0125 \left[ 1 - \frac{\cos 78^\circ 3}{\cos \alpha} \cos (P + \alpha - 104^\circ 78) \right].$$

The maximum of \( h - m \) is 0.025 inch. The correction of the position-angles is inappreciable for our purpose.

(c) Curves of Equal Intensity of the Corona.—I define the mean distance of an equal-intensity curve of the corona as the mean of the distances of twenty-four points of the curve, 15 degrees apart. Equal-blackness curves coincide with equal-intensity curves on Photographs VIII. and IX., and also on Photograph I. The measured distances were first corrected for corrections (a) and (b), and then each twenty-four distances belonging to an equal-intensity (or blackness) curve were combined to a mean; the differences, \( \delta h \), (mean minus reduced distance) define the equal-intensity (or blackness) curve with reference to the circular mean curve. Finally curves were interpolated from the observed 95 curves at regular intervals of the mean distance. An extract of the results is contained in Table I. (p. 337), and graphs of some of the curves are shown in fig. 5.

(d) Reduction of the Distances of Portions of an Equal-blackness Curve to the Mean Distance of that Curve.—Though equal-blackness curves were measured on all pictures at all position angles, only portions of these curves can be used together, because the equal-blackness curves do not everywhere coincide with the equal-intensity curves of the corona. In next section it will be shown (1) that in the case of Photographs V., VI. and VII., owing to luminosity of the sky, the left and right
halves of an equal-blackness curve coincide each with an equal-intensity curve of the corona, though not with the same curve of the corona, and that on the two halves of Photographs I. to IV. an equal-blackness curve differs inappreciably from an equal-intensity curve; (2) that on account of the overlapping of the coronas belonging to neighbouring pictures the intensity and blackness curves do not coincide at certain position-angles. Therefore, if the mean distance of each equal-blackness curve be derived separately for each half of Photographs V., VI. and VII., and all measurements be excluded which belong to position-angles where there is appreciable overlapping of coronas, the mean distance will also be the mean distance of an equal-intensity curve. Each measurement belonging to a position-angle $p$, and reduced in accordance with (a) and (b), plus the correction $\delta h$ derived above (c), gives a mean distance of the equal-blackness curve, and there are as many values of this mean distance as there are measurements. Their average value $h$ is the final value, and its error can be determined from the differences from the mean. Table III. contains $h$, its error and the number of measurements $p$ which contribute to the mean value. $p = 24$ indicates that all the points of the curve, position-angles 0 to 345, were used. For $p = 21$, the points at position-angles 225, 240, 255 degrees are excluded and for $p = 19$ those at 210 and 270 degrees are omitted in addition. For Photographs Vb. to VII. the points omitted lie symmetrically round position-angles 60 degrees and 240 degrees. The quantities are given in unit of $10^{-3}$ solar diameter, those derived in inches being multiplied by 1.852 (diameter of moon on photograph 0.565 of an inch, diameters of moon and sun 994.5 and 950.7 seconds). I designate by “corresponding distances” the distances from the sun’s limb of two points on two different pictures of the corona at which there is equal blackness. In Table III. the mean corresponding distances stand on the same line. I shall show in the next section that at these tabulated distances the ratio of the intensities of the coronas is a constant for each two photographs.

§ 5. Correlative Distances on Corona. [Definition see under (d).]

(a) I employ the following notation. $I$ or $S$ is an intensity of light acting on a photographic plate, and they are the quantities of light falling on unit area of the plate, which is the area cut out in the focal plane of the camera by unit of spherical angle at the centre of the object-glass. $i$ or $s$ is an intensity of a luminous object, i.e., a quantity of light falling from unit area of object (area cut out by unit of spherical angle) on unit area of the object-glass, which unit area equals that for the plate. $\alpha$ designates the exposed area of the object-glass and $t$ the time during which the plate is illuminated. Then $I = \alpha s$ and $S = \alpha s$.

For the pattern of screens by which I reduced the aperture of the lens the loss of light due to the object-glass will be about proportional to the aperture, and it need not be taken into account, but the effects of diffraction require special investigation (see Appendix I.).
(b) Intensity and Time for Equal Blackness.—Experiments have proved that for the same photographic plate and development the intensities of light and the durations of exposure necessary to produce the same blackness on the film bear a certain relation to each other. According to Michalke this relation is independent of the degree of blackness. I have represented Michalke's observations by the formula \( tI^\alpha = \text{constant} \), where \( \alpha = 1.08 \), and further redetermined \( \alpha \) for the plates employed by me (Imperial special rapid). I used as a source of light a disc of opal glass (2 inches in diameter), illuminated from behind by an electric lamp, and I exposed directly to the light of the disc successively different portions of the same plate at distances varying from 1 to 15 metres. A Thornton-Pickard shutter recorded the duration of exposure automatically on a chronograph. My value of \( \alpha \) is \( 1.05 \pm 0.01 \).

(c) The ratio of two intensities, \( i_m : i_n \), which illuminate, through apertures \( \alpha_m, \alpha_n \) of a lens during times \( t_m, t_n \), a photographic plate placed in the focus of the same camera is a constant if they produce equal blackness on the film. By (a) and (b)

\[
\frac{i_m}{i_n} = \left( \frac{t_n}{t_m} \right)^{\frac{1}{\alpha}} = F_{mn}.
\]

\( F_{mn} \) can be calculated for the eclipse photographs. The individual exposures of Photographs VI. and VII. are uncertain to about a second (see § 6), but their sum is accurately known (100'88). I take here \( t_s = 11'00 \), and hence \( t_i = 89'88 \). The other data are given in § 1. The numerical value of \( \alpha \) is of no importance for the first five photographs.

\[
\begin{array}{cccccccc}
  m, n & 1, 2 & 1, 3 & 1, 4 & 1, 5 & 5, 6 & 6, 7. \\
  \log F_{mn} & 0.278 & 0.551 & 0.884 & 1.335 & 1.059 & 0.869.
\end{array}
\]

(d) Correlative Distances on the Corona.—If the pictures of the corona had not been overlapping, and the sky been dark, an equal-blackness curve would have coincided with an equal-intensity curve of the corona, and the ratio of the intensities of the corona belonging to two such curves on Photographs \( m \) and \( n \) would equal a constant \( F_{mn} \) [see (c)]. I shall call "correlative distances on corona" the distances of points of the corona at which the ratio of the intensities equals \( F_{mn} \).

(e) Simultaneous and Successive Exposures.—I make the following two assumptions:—(1) the degree of blackness on the film is independent of the order in which two or more exposures are made; (2) if two intensities give the same blackness for certain exposures, they do so, too, when these exposures are made on an otherwise exposed film. I have checked (1), but not (2), by experiment.

Let two intensities \( I \) and \( S \) illuminate the film together during the same time \( t \). By (b)

\[
(I+S)^t = S'(t+t') = S't + S't' \text{ for equal blackness},
\]
where \( t' \) can be determined from the equation. The formula expresses that \((I+S)\) acting on the film during \( t \) gives the same blackness as \( S \) acting during \( t \) and \( t' \), \( t' \) being, of course, after (or before) \( t \). Hence the positive sign stands for "the one exposure after the other." Each of the terms may be replaced by a term of the form \( \alpha \, b \), which equals it in value [see (2)], and \( \alpha \) expresses the intensity, \( b \) the time. The terms may be written in any order [see (1)].

(f) Elimination of the Diffused Light of the Sky.—Let \( i \) and \( I \) belong to the corona, \( s \) and \( S \) to the sky. On the second half of the \( m \)th photograph \( I_m + S_m \) illuminates the film during \( t_m \); and thereafter \( S_m + 1 \) during \( t_{m+1} \); on the first half of the \((m+1)\)th photograph \( S_m \) illuminates the film during \( t_m \), and thereafter \( I_{m+1} + S_{m+1} \) during \( t_{m+1} \). Let both produce equal blackness. By (e)

\[
(I_m + S_m)^* t_m + S_{m+1} t_{m+1} = \text{constant} = S_m t_m + (I_{m+1} + S_{m+1})^* t_{m+1}
\]

\[
I_m t_m + S_m t_{m+1} + S_{m+1} t_{m+1} = I_{m+1} t_m + S_m t_{m+1} + S_{m+1} t_{m+1}.
\]

The last two terms disappear, and therein lies the advantage introduced for Photographs V. to VIII. by the failure of the mechanism during the eclipse;

\[
I_m t_m = I_{m+1} t_{m+1}, \quad \text{where} \quad I' = I \left( \frac{S_m}{I} + 1 \right)^* - \left( \frac{S_{m+1}}{I} \right)^*.
\]

Substitute \( i \) and \( S \) [see (a)] and introduce \( F \) by (c); therefore

\[
\frac{i_m}{t_{m+1}} = F_{m, m+1}, \quad \text{where} \quad i_m = \left[ \left( \frac{S_m}{I_m} + 1 \right)^* - \left( \frac{S_{m+1}}{I_{m+1}} \right)^* \right].
\]

Equal blackness was observed at the distances \( h_m \) and \( h_{m+1} \), hence \( h_m \) and \( h_{m+1} \) are corresponding distances; they are, however, not correlative distances on the corona, because the ratio of \( i_m \) and \( i_{m+1} \), the intensities of the corona at \( h_m \) and \( h_{m+1} \), does not equal \( F_{m, m+1} \). On the other hand, the distances \( h_m + \Delta h_m \), \( h_{m+1} + \Delta h_{m+1} \), at which the intensities of the corona equal \( i_m \) and \( i_{m+1} \), are, by definition (d), correlative distances on the corona. Hence we have

\[
\Delta h_m = (\log i_m - \log i_{m+1}) \left( \frac{dh}{d \log i} \right)_m.
\]

I calculate \( \log i \) and the differential quotient by the formula derived in this paper, which gives \( i \) as a function of \( h \); further, \( \Delta i' \) for \( s = 0.6 \), and thence \( \Delta h \). The values are: \( \Delta h = 0 \) for \( h = 200 \), \( \Delta h = -3 \) for \( h = 600 \), \( \Delta h = -15 \) for \( h = 1000 \), and \( \Delta h = -35 \) for \( h = 1400 \). The measured corresponding distances are correlative distances on the corona with an error \( \Delta h \). These systematic errors are insignificant compared with the accidental errors of measurement (see Table III.) up to \( h = 800 \), and even for the most distant parts of the corona they do not reach these accidental errors. The correlative distances determine the intensity formula (see § 7), and in the equations the residuals appear under the form \( v = \Delta h_m - F_{m-1, m} \Delta h_{m-1} \). I observed on
pictures VIIa. and VII. the corresponding distances \( h_5 = 550 \), \( h_7 = 1000 \), and \( h_6 = 900 \), \( h_7 = 1400 \); hence \( v \) equals \(-10\) for \( h = 1000 \), and \(-17\) for \( h = 1400 \), while the accidental errors \( v \) are about 45 and 75, that is to say, four times as great as the systematic errors. Compared with the actual residuals \( v \) left by the equations, the systematic errors are still smaller. The result, then, is this: Let there be equal blackness on the two adjoining halves of two neighbouring pictures (Nos. \( m \) and \( m+1 \)) of the corona at distances \( h_m \) and \( h_{m+1} \), then \( h_m \) and \( h_{m+1} \) are also correlative distances on the corona at which the ratio of the intensities equals \( F_{m,m+1} \).

The result would have been different if the backgrounds of the two neighbouring pictures had not been overlapping. \( \hat{i'} = i + s \) would have been found instead of \( i \), and \( s \) could not have been separated from \( i \).

\( (g) \) The intensity of the diffused light of the sky can be disregarded on the first five photographs. To prove this, I start from the equations [see \((f)\)]

\[
(I_m + S_m)^t_m + S_{m+1} t_{m+1} \text{ = constant for equal blackness.}
\]

The lower sign belongs to the first half of the \( m \)th photograph, and the upper sign to the second half. For the first five photographs \( s \) is small compared with \( i \), hence by \((a)\), \((b)\), and \((c)\)

\[
\alpha_m^* (i_m' + \sigma_m)^* t_m = \text{constant, where } \sigma_m = s (1 + F_{m,m+1})
\]

\[
\frac{i_m'}{i_n'} = F_{m,m+1}, \text{ where } \frac{i'}{i_n} = i + \sigma
\]

\( \sigma_m \) is the intensity which produces at aperture \( a_m \) and exposure \( t_m \) the same blackness as the two superposed exposures to the diffused light. The distances belonging to the intensities \( i_m' \) and \( i_n' \) are, by definition, correlative distances on the corona. We obtain, then, in the same manner as explained in \((f)\),

\[
\Delta h_m = \sigma_m \left( \frac{dh}{dt} \right)_m
\]

and

\[
v = \Delta h_m - F^{1/4}_{m,m+1} \Delta h_1 = \Delta h_m - F_{m,m+1} \left( \frac{dh}{dt} \right)_m \left( \frac{dh}{dt} \right)_m \Delta h_1 = (\sigma_m - \sigma_1 F_{1,m}) \left( \frac{dh}{dt} \right)_m.
\]

\( \sigma_m \) is calculated by the above formula and \( s = 0.6 \), except for the first photograph and the first half of the second. The values range between 0.8 and 2.3.

A minute before the beginning of totality the cap was removed from the object-glass and during that time light must have been reflected into the camera by the shutter, which was placed about an inch from the object-glass, and illuminated the plate at the place where Photographs I. and IIa. were taken. The blackness of the background lies between that of IV. and V., and I estimate \( \sigma_1 = 10 \) and \( \sigma_2 = 5 \).

The calculated values of \( v \) do not amount to a third of the accidental errors \( v \) of measurement (Table III). It is, therefore, permissible to regard the corresponding
distances measured on pictures I. to Va. as correlative distances on the corona, just as if no diffused light had been illuminating the plate.

After the experience gained at this eclipse I should again place the pictures as they appear in the diagram, i.e. make the opening of the plate-holder twice as long on a side as the distance between the pictures. This arrangement entails no disadvantage for the short exposures, and for the long exposures the intensity of the diffused light can be eliminated. (See § 1, last section.)

(h) Overlapping of Coronas of Neighbouring Pictures.—At a point A of the mth picture the intensity of the corona is \(i_m\) at distance \(h_m\), and the intensity of the light which illuminates A for a time \(t_m\) is \(I_m = a_m(i_m)\). The same point is illuminated for a time \(t_{m \pm 1}\), also by light of intensity \(I_{m \pm 1}\) belonging to a different part of the corona in the \((m \pm 1)\)th photograph, where the corona has an intensity \(i_{m \pm 1}\) and \(I_{m \pm 1} = a_m(i_{m \pm 1})\). Point A lies on an equal-blackness curve of the mth picture, and this curve coincides with an equal-intensity curve of the corona (intensity = \(i_m\)) at all points where there is no overlapping. By (c)

\[
[a_m i_m]^a t_m = [a_m(i_m)]^a t_m + [a_{m \pm 1}(i_{m \pm 1})]^a t_{m \pm 1},
\]

or very nearly

\[i_m = (i_m) + (i_{m \pm 1}) F_{m, m \pm 1}.\]

The equal intensity curve (intensity = \(i_m\)) cuts the radial line belonging to A (distance = \(h\)) at \(A'\), and \(AA' = \Delta h\) is the distance of the two curves at A. Hence

\[
\Delta h = (i_{m \pm 1}) F_{m \pm 1} \frac{dh}{di}.
\]

I measured on a diagram the distances of a point A from the solar limbs of the following and preceding pictures, calculated \(i_{m \pm 1}\) by the formula \(i = f(h)\) and thence \(\Delta h\). In deriving the mean distance of an equal-blackness curve [preceding section (d)] I used only those measured distances for which the average value of \(\Delta h\) (including \(\Delta h = 0\)) is less than a half of the calculated error of the average distance. The number of values is given in Table III. under heading \(p\) [see preceding section (d)]. The average values of \(\Delta h\) increase with the accidental error, but they have always the same sign, so that the systematic residuals \(v\) become very small compared with the accidental errors \(e\). It would of course have been better if all the images had been further apart. (See § 1, last section.)

The outcome of the discussion given in this section is, that the mean corresponding distances given in Table III. are also mean correlative distances on the corona.

§ 6. Photographs Nos. VI. and VII.

(a) Duration of Exposure.—Owing to the failure in the driving of the plate-holder only two pictures (VI. and VII.) belong to the three exposures 9.02, 2.82, 89.04 seconds. The sum of the durations of exposure of these pictures is thus given
(100.88). It is of some importance to know the upper limit, if not the accurate durations, of the exposure belonging to Photograph VI. On Photograph No. VII, three images are eccentrically superposed (see fig. 6). The order of magnitude of the time for which they were illuminated can be found from the degree of blackness of the background which belongs to each image. In this way I find that circle (b) is due to a short exposure of the order of a second, the faint circle (c) (dotted in fig. 6) which is faintly visible within the corona is the lunar disc during a very long exposure, and semicircle (a) must belong to an exposure of about 10 seconds. Now (b) is exactly at the position on the plate, as determined by its distance from other pictures, at which the plate-holder was locked by the electromagnet of the propelling mechanism. The contacts made by the clock for unlocking and locking the plate-holder are between the contacts for exposures, and hence no part of the exposure which produced (c) can have contributed to (b). As (c) belongs to the longest exposure, (b) must be due to some portion of the 2.8-seconds exposure. The first part of this exposure must have contributed to picture VI., because the plate moved (see the instantaneous photographs of the protuberances on the lunar disc of picture VI. and in the coronas of VI. and VII.) while an exposure was going on. The exposure given to No. VI. is therefore 9.02 + 2.82 - \tau = 11.84 - \tau, and the combined exposure for abc of No. VII. is 100.88, less the exposure of No. VI. \tau may lie between 0.1 and 1 second (see above). I should add that the lunar disc on Photograph VI. is exactly round and not blurred in the least. Apart from the instantaneous pictures and trails of prominences on the lunar disc, the picture VI. is perfect.

(b) Measurement of Curve of Equal Blackness on Photograph VII.—I shall now investigate whether the three eccentrically superposed images on this photograph can be utilised in this research. Let the curves of equal intensity of the corona be circles, and let us consider the curves at some distance from the sun. Let C and A (fig. 6) be the centres of two photographs of the sun (not moon, as it was supposed in No. 6a) and MM' and NN' be circles of radius r along which the corona has an intensity \( i \). To centre C belongs the exposure \( t_1 \) and to A the exposure \( t_2 \). Along circle MM', \( i \) has been exposed during \( t_1 \) and on this is superposed an exposure to \(-\frac{di}{dr}\Delta r\) during \( t_2 \), i.e., \( i \) has been exposed during \( t_1 + t_2 \) and \(-\frac{di}{dr}\Delta r\) during \( t_2 \). This additional radiation has the same value with opposite signs at two opposite points of circle MM'. In the same way along circle NN' intensity \( i \) has acted during \( t_1 + t_2 \), and \( (\frac{di}{dr})\Delta r \) during \( t_2 \). Hence the radiation \( i \) was exposed during \( t_1 + t_2 \) along a curve which lies between the two circles MM' and NN' and in such a way that the mean of the distances (\( p \) and \( p' \)) from C of two opposite points of this curve is equal to \( r \). Along
this curve there is equal blackness on the photograph and the same blackness occurs on Photograph VI. at a point at distance $h_6$, which was illuminated by $i_6$ during $t_6$. Hence

$$i_6/i = \text{constant} = (t_1 + t_2)^{1/n}/t_6^{1/n}.$$

The mean distance of the equal-blackness curve is the average value of $\rho$ which is $r$. But $r$ is, by assumption, the distance of the point on the corona at which the intensity is $i$. Hence the mean distance of the equal-blackness curve and $h_6$ are correlative distances on the corona. The same result holds good for the three eccentrically superposed pictures $abc$ of the VII$^\text{th}$ photograph, and the constant $F_{6,7}$ is equal to $(t_1 + t_2 + t_3)^{1/n}/t_6^{1/n}$. Photograph VII. may therefore be measured and reduced in the same way as the other photographs, provided that always two opposite points of an equal-blackness curve be measured. Terms of the second order have been neglected in this derivation; they amount to only a fraction of the distance AC (0.11 diameter) and are small quantities compared with the errors of measurement.

§ 7. The Formula which gives the Intensity of the Corona as a Function of the Distance $h$.

I first tried whether the observed distances satisfied Professor Turner's formula (intensity inversely proportional to the sixth power of the distances from the sun's centre), but find inadmissible residuals. Another formula has therefore to be derived. If the distances given in columns I. to V$\alpha$, Table III., be plotted as ordinates, and the corresponding distances standing in the first column as abscissae, the points belonging to the same column lie as nearly in a straight line as can be expected from the accuracy of the observations, and all these five lines can be made to intersect in a point $-x$, $-x$.

Hence

$$h_1 + x = \gamma_n (h_n + x), \quad n = 1\text{ to }5, \quad x \text{ a constant.}$$

The intensity $i$ being a function of the distances $h$, which are counted from the sun's limb, I write $i = cf(h+x)$. Hence $i_1 = cf(h_1+x) = cf[\gamma_n(h_n+x)]$ and $i_n = cf(h_n+x)$,

$$\frac{i_1}{i_n} = \text{constant} F_{1,n} = \frac{f[\gamma_n(h_n+x)]}{f[h_n+x]},$$

as $h_1$ and $h_n$ are correlative distances on the corona. This relation is satisfied by $f(z) = z^{-y}$. Hence $i = c(h+x)^{-y} \quad \text{and} \quad F_{1,n} = \gamma_n^{-y}$. The formula is the same as Professor Turner's, with this difference, however, that $x$ need not be the radius of the sun.

Approximate values of $x$ and $y$ are found in this way. I assume $x = 0, 40, &c.,$ to 320 (solar diameter = 1000) and calculate $\gamma_n$ from $h_1, h_n, \text{and } x$. The residuals are
v = h_i + x - \gamma_n (h_n + x). \ I take the sum of the residuals irrespective of sign for n = 2 to 5. For each value of n the sum of the residuals is a minimum for x between 80 and 120, and the sum for all values of n together is a minimum for x = 110. The sum of the residuals is 50 per cent. greater for x = 20 and x = 300. x = 500 (radius of the sun) leaves inadmissible residuals.

The observed values of F_{1,n} and \gamma_n belonging to x = 110 give y = 3.4 for n = 2, 3.3 for n = 3, 3.5 for n = 4, and 3.8 for n = 5.

In the same way, if the distances obtained from Photograph No. VIa. be plotted as ordinates and those on Photograph Vb. as abscissae, a straight line represents the observations as well as any smooth curve that can be drawn, and the same remark refers to the distances obtained from Photographs Vb. and VII. The sum of the residuals is again small for values of x near 110, though the range of possible values of x is larger. The resulting value of y lies near 4.

I think this is sufficient proof that the function represents very nearly the observations. Let us assume it to be exactly correct. The method explains that x and the n constants \gamma are determined independently of the times of exposure from the condition \( h_i + x(h_n + x) = h_i' + x(h_n' + x) = \gamma_n \), and that there are n equations for the unknown y. These n equations will be rigorously satisfied, provided the correct values of F be introduced, and hence n - 1 values of F_{1,n} or n - 1 values of the time of exposure can be determined from the equations along with y.

I prefer to determine x and y together by the Method of Least Squares. Let \( x_0 + \xi, y_0 + \eta \) be the true values of x and y, and \( v_n \) be the accidental error of measurement of \( h_n \), and \( \Delta F_{mn} \) the correction of an approximate value \( F_{mn} \), which need not necessarily be the calculated value [5 (c)]. The observations must rigorously satisfy the equations

\[
\frac{h_n + v_n + x_0 + \xi}{h_m + v_m + x_0 + \xi} - (F_{mn} + \Delta F_{mn})\frac{1}{y_0 + \eta} = 0,
\]

or

\[
v_n - \frac{h_n + x_0}{h_m + x_0} v_m = - (h_n + x_0) + \xi + (F_{mn} + \Delta F_{mn})\frac{1}{y_0 + \eta} (h_m + x_0).
\]

The sum of the squares of the left side which contains the accidental errors is a minimum for the most probable values of \( \xi, \eta \), and (n - 1) values \( \Delta F_{mn} \). The solution gives these unknowns as functions of one of the \( \Delta F \), or if all the \( \Delta F \) be introduced as unknowns one of them must come out indeterminate. Instead of \( \Delta F \), I introduce the corrections of the adopted times of exposure \( \Delta t \). For the first five photographs \( \xi, \eta, \Delta t_1, \Delta t_2, \Delta t_3 \) will be found as functions of \( \Delta t_4 \) and \( \Delta t_5 \), and for Photographs Vb., VI., and VII., \( \xi, \eta, \Delta t_6 \) as functions of \( \Delta t_4 \) and \( \Delta t_5 \). Finally, all the time records can be used in determining the corrections \( \Delta t \). It will be seen that the uncertainty of the exposure of Photograph VI. is not such a serious deficiency as might be expected at first sight.
To determine by the Method of Least Squares only \( \xi \) and \( \eta \) would mean the discarding of the condition \((h_1 + x)/(h_n + x) = (h'_1 + x)/(h'_n + x)\) and must lead to erroneous results.

I calculate \( \xi, \eta, \) and \( \Delta t \) from equations which result from logarithmic differentiation of the equation given above. Let \( t_n = t_n^0 + \Delta t_n \) \((n = 1 \text{ to } 6)\), \( t_7 = 100.88 - t_6^0 - \Delta t_6 + \Delta t_7 \) (see § 6), \( \alpha = 1.05 + \Delta \alpha \), where \( t_n^0 \) \((n = 1 \text{ to } 5)\) are assumed to equal the observed values and \( t_6^0 \) is arbitrarily chosen equal to 11.00 (see § 6). The values \( F_{mn} \) are those appearing in § 5 (c), and they sufficiently approach their true values. I start from \( x_0 = 140, y_0 = 4 \), the result of a first solution. The equations of condition are

\[
\begin{align*}
n &= \alpha \xi + b \eta + c_n \Delta t_n - c_n \Delta t_n + d \Delta \alpha, \\
&= \frac{1}{4} \log F_{mn} - \log \frac{h_n + 140}{h_m + 140}, \\
\alpha &= -\text{Mod}\left(1 - F_{mn}^{-1/4}\right) \left(h_m + 140\right), \\
b &= \frac{1}{4^2} \log F_{mn}, \\
c_n &= \text{Mod}\left(4at_m\right)^{-1}, \\
&\text{and similarly for suffix } n,
\end{align*}
\]

but

\[
c_0 = \text{Mod}\left(4\alpha\right)^{-1} (t_6^{-1} - t_7^{-1}) \text{ in equations } m = 6, n = 7,
\]

\[
d = (4\alpha)^{-1} \log F_{mn} \text{ for } m = 5, n = 6 \text{ and } m = 6, n = 7.
\]

The weight \( p \) of an equation is calculated with \( r_m \) and \( r_n \) as given in Table III., 0.01 being the error of an equation of unit weight. The calculated weights served merely as a guide. The adopted weights appear in Table IV. The numerical equations are:

Photographs.

<table>
<thead>
<tr>
<th>Photographs</th>
<th>I.</th>
<th>II.</th>
<th>III.</th>
<th>IV.</th>
<th>Va.</th>
<th>Vb.</th>
<th>VIa.</th>
<th>VII.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = ( -(8.808) (h_1 + 140)^{-1} \xi + 0.0174 \eta + (9.090) \Delta t_1 - (9.111) \Delta t_2 )</td>
<td>n = ( -(9.072) (h_1 + 140)^{-1} \xi + 0.0344 \eta + (9.090) \Delta t_1 - (9.122) \Delta t_3 )</td>
<td>n = ( -(9.239) (h_1 + 140)^{-1} \xi + 0.0553 \eta + (9.090) \Delta t_1 - (9.111) \Delta t_4 )</td>
<td>n = ( -(9.367) (h_1 + 140)^{-1} \xi + 0.0834 \eta + (9.090) \Delta t_1 - (9.085) \Delta t_5 )</td>
<td>n = ( -(9.297) (h_5 + 140)^{-1} \xi + 0.0662 \eta + (9.085) \Delta t_5 - (7.973) \Delta t_6 + (9.401) \Delta x )</td>
<td>n = ( -(9.233) (h_6 + 140)^{-1} \xi + 0.0543 \eta + (8.023) \Delta t_6 - (7.061) \Delta t_7 + (9.315) \Delta x )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( n \) is entered in Table IV. The brackets indicate logarithms, −10 being omitted.

On account of the defects of Photograph VII. and the uncertainty of the exposure of VI., I have solved the equations appertaining to Photographs I to Va. separately from those belonging to Photographs Vb. to VII., and finally have discussed the whole material.

(a) Photographs I. to Va.—These determine the intensity curve from distance 60 to 520. In accordance with the above, two of the \( \Delta t \) are indeterminate. I choose \( \Delta t_4 \)
and \( \Delta t_5 \) and express the other unknowns as functions of them. The result of the solution is

\[
x = 140 + 9.2 \pm 16 - 22.2 \Delta t_4 + 21.2 \Delta t_5
\]
\[
y = 4.0 + 0.71 \pm 0.22 - 4.68 \Delta t_4 + 4.40 \Delta t_5
\]
\[
t_1 = 0.84 - 0.28 \pm 0.08 + 3.01 \Delta t_4 - 1.84 \Delta t_5
\]
\[
t_2 = 0.80 - 0.18 \pm 0.06 + 2.28 \Delta t_4 - 1.20 \Delta t_5
\]
\[
t_3 = 0.78 - 0.01 \pm 0.04 + 1.66 \Delta t_4 - 0.65 \Delta t_5
\]
\[
t_4 = 0.80 + 1 \Delta t_4
\]
\[
t_5 = 0.85 - 1 \Delta t_5
\]

The errors are mean errors. The mean error of an equation of unit weight is 0.014, as compared with the adopted value 0.010.

So far the time records have not been used (except in the calculations of the differential quotients, which is merely a matter of convenience). I determine \( \Delta t_i \) and \( \Delta t_5 \) from all the time records, introducing the condition that the values of \( t \) differ from a mean value \( t_0 \) by accidental errors \( v \). The equations are

\[
t_0 - v = 0.56 + 3.01 (\Delta t_4 - \Delta t_5) + 1.17 \Delta t_5
\]
\[
t_0 - v = 0.62 + 2.28 + 1.08
\]
\[
t_0 - v = 0.77 + 1.66 + 1.01
\]
\[
t_0 - v = 0.80 + 1.00 + 1.00
\]
\[
t_0 - v = 0.85 + 1.00
\]

The result is \( \Delta t_4 - \Delta t_5 = +0.096 - 0.05 \Delta t_5 \). The equations do not determine \( \Delta t_5 \) with any degree of accuracy. The unknowns then become

\[
x = 147 \pm 16 + 2 \Delta t_5
\]
\[
y = 4.26 \pm 0.22 - 0.05 \Delta t_5
\]
\[
t_1 = 0.85 \pm 0.08 + 0.98 \Delta t_5
\]
\[
t_2 = 0.84 \pm 0.06 + 1.07 \Delta t_5
\]
\[
t_3 = 0.93 \pm 0.04 + 0.93 \Delta t_5
\]
\[
t_4 = 0.90 + 0.95 \Delta t_5
\]
\[
t_5 = 0.85 + 1.00 \Delta t_5
\]

The value of \( \Delta t_5 \) is irrelevant for our purpose, it cannot be more than a fraction of a second and such a value changes \( x \) and \( y \) only by a small fraction of its error.

We may change \( y \) by a small quantity \( \eta \) of the order of its error and \( x \) by a corresponding quantity \( \xi \) without altering appreciably the residuals. The equations give \( \xi = (1.880) \eta \). I assume \( y = 4 \) and throw its error on \( x \). The result is

\[
(A) \quad x = 127 \pm 23, \quad y = 4.00.
\]

\( b \) Photographs \( Vb., VI. \) and \( VII. \)--The photographs furnish material for the intensity-curve from \( h = 110 \) to about 1700 (1.7 solar diameter).
Again two of the \( \Delta t \) remain indeterminate. I take \( \Delta t_7 = 0 \), which is permissible, as any reasonable error has a small effect on \( x \) and \( y \), see (c), and express the unknowns as functions of \( \Delta t_5 \). The result is

\[
x = 140 - 23 \pm 46 + 1.4 \Delta t_5
\]
\[
y = 4.00 - 0.29 \pm 0.32 - 1.05 \Delta t_5
\]
\[
t_6 = 11.0 + 1.37 \pm 0.60 + 5.45 \Delta t_5
\]

The error of an equation of unit weight is 0.021.

The time records (except \( t_6 + t_7 = 100.88 \)) have not yet been used. \( \Delta t_5 \) can be determined from the last equation.

The upper limit of \( t_6 \) [see § 6 (a)] is 11.84 - 0.1 = 11.7 and it gives \( \Delta t_5 = -0.12 \) and the lower limit of \( t_6 \) is 11.84 - 1.0 = 10.8, which gives \( \Delta t_5 = -0.29 \), both with an error of 0.11. The large value of \( \Delta t_5 \) belonging to the lower limit of \( t_6 \) is out of the question, because the pendulum of the contact clock could not possibly have been placed so much out of beat. Nevertheless, I maintain both values,

\[
\begin{align*}
t_6 &= 11.7 \\
x &= 117 \pm 46 \\
y &= 3.84 \pm 0.34 \\
t_5 &= 0.73
\end{align*}
\]
\[
\begin{align*}
t_6 &= 10.8 \\
x &= 117 \pm 46 \\
y &= 4.01 \pm 0.34 \\
t_5 &= 0.56
\end{align*}
\]

I again reduce \( x \) to \( y = 4.0 \). The normal equation gives \( \xi = (2.107) \eta \), hence

\[
\begin{align*}
\xi &= 10.8 \\
x &= 117 \pm 46 \\
y &= 4.00 \\
t_5 &= 0.73
\end{align*}
\]

The second result is not possible, as already mentioned.

(c) All the Photographs I. to VII.—In this solution I have included the unknown \( \Delta \alpha \) in order to see what effect the error of \( \alpha \) has on \( x \) and \( y \). Five corrections \( \Delta F \) can be found or five of the \( \Delta t \), leaving two, say \( \Delta t_5 \) and \( \Delta t_7 \), besides \( \Delta \alpha \), indeterminate. The result is:

\[
\begin{align*}
x &= 140 - 2 \pm 19 - 7 \Delta t_5 + 0.5 \Delta t_7 - 20 \Delta \alpha \\
y &= 4.00 - 0.15 \pm 0.14 - 1.1 \Delta t_5 + 0.009 \Delta t_7 - 4 \Delta \alpha \\
t_1 &= 0.84 + 0.21 \pm 0.08 + 1.68 \Delta t_5 - 0.006 \Delta t_7 + 2.5 \Delta \alpha \\
t_2 &= 0.80 + 0.19 \pm 0.06 + 1.46 \Delta t_5 - 0.004 \Delta t_7 + 2.0 \Delta \alpha \\
t_3 &= 0.78 + 0.27 \pm 0.05 + 1.30 \Delta t_5 - 0.003 \Delta t_7 + 1.4 \Delta \alpha \\
t_4 &= 0.80 + 0.17 \pm 0.04 + 1.16 \Delta t_5 - 0.002 \Delta t_7 + 0.8 \Delta \alpha \\
t_5 &= 0.85 + 1 \Delta \alpha \\
t_6 &= 11.00 + 1.17 \pm 0.37 + 5.5 \Delta t_5 - 0.063 \Delta t_7 + 0.25 \Delta \alpha \\
t_7 &= 100.88 - t_6 + 1 \Delta t_7
\end{align*}
\]
The mean error of an equation of unit weight is found = 0.017 as compared with
the adopted value of 0.010. Any possible error $\Delta t$, cannot alter the value of the
variables by more than a small fraction of their errors, and $a$ was deduced from
experiments with an error of $\pm 0.01$. So far the time records have not been used;
I determine $\Delta t$, as under (a) from the recorded times $t_1$ to $t_n$, neglecting $\Delta t$, and $\Delta a$.
The result is $\Delta t = -0.14 \pm 0.06$. I substitute this value and calculate the errors on
the supposition that $\Delta t = \pm 1.0$, $\Delta a = \pm 0.02$, which certainly exceed the true
errors. The result is

$$ x = 139 \pm 19, \quad y = 4.00 \pm 0.17, $$

$t_e$ becomes 11.40$-0.50$, which lies between the limits derived for $t_e$ in § 6 (a). In
this solution no use has been made of the time of exposure assigned to the sixth
photograph.

The error of $y$ may be combined with that of $x$ (see above).

$$(C) \quad x = 139 \pm 23, \quad y = 4.00.$$  

The results (A), (B), (C) agree very well; the good agreement of (A) and (B),
which rest on different material, is remarkable. Considering that all the material
contributed to (C), I might adopt it as final. I change $x$ by a unit to round off the
figure. Hence

$$(D) \quad i = c (h + 140 \pm 23)^{-4}. $$

$h$ is counted from the sun's limb in unit of $10^{-3}$ solar diameter and log $c = 12.228$
expresses the intensity in unit of the intensity of the corona at $h = 1000$. The
residuals left by (D) and calculated with the corrected values of $F$ appear in
Table IV. under heading ($v$). I employ them to derive the errors of the distances.
I divide the residuals in each column in three groups and regard the mean of the
residuals in each group as the error of log $(h_n + 140) - \log (h_m + 140)$, where $h_n$ and $h_m$
are the mean distances in each group. The errors of measurement will be about the
same on the first two photographs and they can therefore be calculated. The
calculations of the errors of $h_n$ is sufficiently evident. The result is:

<table>
<thead>
<tr>
<th>$h$</th>
<th>100.</th>
<th>200.</th>
<th>400.</th>
<th>600.</th>
<th>800.</th>
<th>1000.</th>
<th>1200.</th>
<th>1400.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Errors</td>
<td>1.4</td>
<td>5</td>
<td>15</td>
<td>27</td>
<td>47</td>
<td>70</td>
<td>100</td>
<td>130</td>
</tr>
</tbody>
</table>

These errors are almost twice as great as those in Table III. The excess must,
I think, be mainly set down to systematic errors of measurement which are different
for the several positives.

Fig. 7 shows a comparison of the intensity curve with the observations.
As the observations do not give absolute intensities, but the ratio of the
intensities at two correlative distances, I adopt at distances $h_1$, $h_{50}$, and $h_{60}$ the
intensities as calculated from the formula (D) and calculate the intensities at the
correlative distances $h_2$, $h_3$, $h_4$, $h_{50}$, $h_{60}$, $h_{70}$, from the latter and the known ratios F.
The differences between these intensities and the tabular intensities are the outstanding errors. The ratios of the intensities are calculated with 11.40 seconds for the sixth exposure and the recorded values of the times of exposure for the other...
exposures. The outstanding errors thus contain, apart from the errors of \( h \), all the systematic errors arising from erroneous records of times of exposure. The points belonging to Photographs I., Vb., VIIb. which are placed on the curve are shown by dots, while the observed correlative points are marked by circles. The systematic errors are clearly reflected in these points.

§ 8. Question whether or not the Formula (D), § 7, holds good at any Position-angle?

Table I. gives at intervals of 15° of position-angle the amount \( \delta h \) by which the distance from the sun's limb of an equal-intensity curve exceeds the mean distance of that curve. Since these quantities were obtained from measurements on Photographs I., VIII., and IX., which have a uniform background all round, systematic errors of measurement will be eliminated in the differences, and their errors are more comparable to the errors given in Table III. than to those derived in last section. At a certain point of an equal-intensity curve, which is \( h + \delta h \) from the sun's limb, the intensity is expressed by formula (D), in which \( h \) designates the mean distance of the intensity-curve. The intensity at the point may also be expressed by \((c+\delta c)(h+\delta h+140)^{-1}\), and if \( c+\delta c \) be a constant, i.e. \( \delta h/h+140 = \delta c/4c = \text{constant} \) at a series of points, the formula will hold good for these points. The values \( a = 100\delta h/h+140 \) are entered in Table II. The value of the constant \( c+\delta c \), which gives at \( h + \delta h \) a value of the intensity equal to that given by formula (D) involving \( c \) and the mean distance \( h \), is given by \( \delta \log c = 0.017 a, (0.017 = 4 \mod/100) \). According to Table II. the quantities \( a \) differ for the same position-angle, and they vary systematically with the distance. I adopt for the same position-angle the same constant at all distances, and determine it by \( \delta \log c = 0.017 a_0 \), and hence the logarithm of the calculated intensity at \( h + \delta h \) will differ by \((a_0-a) \times 0.017\) from that calculated by formula (D). I choose for \( a_0 \) the mean of the values \( a \) belonging to the same position-angle, and find that \( a_0-a \) lies between 0 and 4 for 90 per cent. of the number of points and, therefore, the difference of the intensities is from 0 to 17 (log 1.17 = 0.068) per cent. of the intensity. An error of 17 per cent. in the intensity is equivalent to an error in distance \( h \) of 9 at \( h = 100, 21 \) at \( h = 400, 44 \) at \( h = 1000 \).

The errors of \( h \) belonging to formula \( i = (c+\delta c)(h+\delta h+140)^{-1} \) are those thus derived combined with the errors given at the end of § 7. The residuals in \( h \) left by such an intensity curve would, therefore, be in excess of the errors of the observed values of \( h \).

At some position-angles \( \delta c/c \) changes little with the distance from the sun and therefore the formula represents the observations satisfactorily, and in some regions the representation would be improved if points lying on a curve be considered together. Whether these curves agree with the course of the streamers or not I have not investigated.
§ 9. *On the Number of Particles and Intensity of Light per Unit Volume of the Corona.*

I shall explain that this problem can be solved on the following assumptions:—
1. The luminosity of the corona is caused by particles, which are heated to incandescence by solar radiation, and which scatter sunlight.
2. The number \( N(r) \) of particles per unit volume is a function of the distance \( r \) from the sun's centre.
3. The apparent intensity is a known function of \( r \) [see formula (D), § 7].
4. The ratio \( g(r) \) of polarised and total light has been observed and represented as a function of \( r \).
5. The intensity of light, \( T(r) \), of a particle heated by solar radiation is correctly determined by Stefan's and the Wien-Planck formulae.*

With reference to (5) I have calculated the temperatures of particles at distances \( h = 50, 100, 200, 300, 400, 600, ..., 1600 \) from Stefan's formula (absolute temperature of the sun = 6000), and the intensities for wave-lengths 3000 to 5000. I find that their integral intensity \( T(r) \) appertaining to blue-violet light is very nearly inversely proportional to the sixth power of \( r \), the average error of the intensities between \( h = 50 \) and 1200 being only 7 per cent. of the intensity.

I adopt the following notation:—

- \( C \) = centre of sun, \( P \) = position of scattering particle, \( r \) = its distance PC (in unit of the sun's radius), \( \theta = \frac{1}{2} \pi \) = angle CP Earth, \( P(r) \cos^2 \theta \) = light polarised by a particle at \( P \) in direction \( \theta \), \( S(r) - P(r) \cos^2 \theta \) = total light scattered by a particle at \( P \) in direction \( \theta \), \( F(r) = N(r) [T(r) + S(r)] \), \( f(r) = N(r) P(r) \).

The functions are

\[
S(r) = c_2 2 \left( \frac{1}{3} - r^{-1} - 3r^{-3} \right), \quad P(r) = c_2 (r^{-1} - r^{-3}),
\]

\[
T(r) = c_3 r^{-6}.
\]

Let us find by integration the total light emitted by a channel of unit section which runs in the direction towards the earth. I designate by \( \rho \) (= \( r \cos \theta = h + 500/500 \)) the shortest distance of this channel from \( C \) and introduce

\[ g = \frac{360}{500} \rho^{-1} = \frac{360}{500} \rho^{-1} \text{sec} \theta = 360 (h + 500)^{-1}. \]

The element of volume at \( P = r \sec \theta d\theta = \frac{360}{500} g^{-1} \sec^2 \theta d\theta. \)

Unit volume at \( P \) sends light \( F(r) - f(r) \cos^2 \theta = F(g \cos \theta) - f(g \cos \theta) \cos^2 \theta. \)

The total light sent by all the particles in the channel towards the earth equals

\[
C(h+140)^{-4} = C360^{-4} \rho^4 (1-g)^{-4} = \frac{360}{500} g^{-12} \left[ \int_0^\pi F(g \cos \theta) \sec^2 \theta d\theta - \int_0^\pi f(g \cos \theta) d\theta \right].
\]

* See Arrhenius, 'Lick Observatory Bulletin,' No. 58.
The left side can be developed into a power series of \( g \)

\[
(1-g)^{-4} = \sum_{0}^{\infty} P_{n}g^{n},
\]

therefore \( F \) and \( f \) must also be power series of \( g \):

\[
F(p) = F(g) = C'g^{\infty}\sum Q_{n}g^{n},
\]

\[
f(p) = f(g) = C'g^{\infty}\sum R_{n}g^{n}, \text{ where } C' = \frac{360}{2} C.
\]

Let

\[
d_{n} = \int_{0}^{\frac{\pi}{2}} \cos^{n} \theta \, d\theta.
\]

\[
d_{2n} = \frac{1.3...2a-1}{2.4...2a} \frac{\pi}{2}, \quad d_{2a+1} = \frac{2.4...2a}{1.3...2a-1} \frac{1}{2a+1}.
\]

These substituted in (2) give

\[
\sum P_{n}g^{n} = \sum d_{n+3}Q_{n}g^{n} - \sum d_{n+5}R_{n}g^{n}
\]

or

\[
\frac{P_{n}}{d_{n+3}} = Q_{n} - R_{n} + \frac{R_{n}}{n+5}.
\]

The second integral in (2) gives the polarised light, while the left side equals the total light. Their ratio was designated by \( q(p) \); hence

\[
q(p) (1-g)^{-4} = \sum d_{n+3}R_{n}g^{n}.
\]

Provided \( q(p) \) be observed as a function of \( \rho \), i.e. of \( g \), \( R_{n} \) can be calculated by (II), and \( Q \) by (I), i.e. \( F(p) \) and \( f(p) \) become known functions. Their values are, if \( C'' = C' (360/500)^{b} \),

\[
F(p) = N(p) [T(p) + S(p)] = C'' \rho^{-5} \sum Q_{n} \left( \frac{0.72}{\rho} \right)^{n},
\]

(III)

\[
f(p) = N(p) P(p) = C'' \rho^{-5} \sum R_{n} \left( \frac{0.72}{\rho} \right)^{n}.
\]

Substitute \( T, S, \) and \( P \) and find \( N(p) \) and \( c_{1}/c_{2} \). The problem can therefore be solved if \( q(p) \) were known. I am unable to say whether the measurements of the polarised light made at the last eclipse suffice to determine this function.

With reference to (I), \( 2P_{n}/3d_{n+3} \) very nearly equal the coefficients of a binomial series, and it is not difficult to prove that

\[
(1-g)^{-4.25} > \frac{3}{2} \sum P_{n} \frac{d_{n+3}}{g^{n}} > (1-g)^{-4.5}.
\]

The exponent \( y = 4 \), of formula (D), is derived from the observations with an error of 0.3 (assuming \( x = 140 \) to be correct), hence the errors of the exponents in the
above inequality are about ten times as much as the range of the exponents, and we may write

\[ \Sigma \frac{P_n}{d_{n+3}} g^n = \frac{3}{2} (1-g)^{-4.5}. \]

(I), (4), and (5) give then, if \( C'' = 1.5 C'' \),

\[ F(\rho) - f(\rho) = C'' \rho^{-5} \left( \frac{1 - 0.72}{\rho} \right)^{-4.5} - \frac{1}{5} C' g^2 \Sigma \frac{5}{n+5} R_n g^n, \]

which stands for the light radiated and scattered at right angles to the radial direction by the particles in unit volume at distance \( \rho \) from the sun's centre. Considering that the second term is only a fraction of the polarised light and the latter a fraction of the total light, \( F(\rho) - f(\rho) \) nearly equals the first term. If there were no light scattered by the particles but only radiated, the number of particles per unit volume, \( N(\rho) \), would, by (1), be proportional to \( \rho (1-0.72 \rho^{-1})^{-4.5} \). This result differs from that derived by Arrhenius, who based his calculations on \( T(\rho) = \text{constant} \).

10. Plea for Repetition of such Observations as contained in this Paper and for Observations of the Light Polarised at Various Distances.

(a) For wave-lengths 0.3 to 0.5 the radiation of a particle at \( h = 50 \) is 355 times as great as that at \( h = 1000 \), while for wave-lengths 0.55 to 0.65 this ratio is only 70. Blue-violet radiation is almost inversely proportional to the sixth power of the distance of the particle from the sun's centre (see § 9, 5), and for red-yellow radiation the power is only 4.3.

Hence if in addition to photographs on ordinary plates a series of photographs be taken with a colour screen on a plate sensitized for red-yellow rays another formula would be found which should lead (see last section) to the same number of particles per unit volume as that belonging to blue-violet radiation. Two such series of photographs, together with observations of the light polarised at various distances, would thus decide the debated question whether the luminosity is actually caused by minute particles which are heated to luminescence by solar radiation and which scatter sunlight.

(b) Though it is a fact that the brightness of the corona undergoes changes, we are ignorant whether the intensity of the corona at a certain distance in terms of that at unit distance is a constant or not. Inferences might be drawn from data such as contained in this paper and belonging to a series of eclipses which would advance our knowledge of the constitution of the corona and give us some idea of the causes which produce it. It is, of course, necessary that the plates have on all occasions the same relative sensitiveness in the different regions of the spectrum. (I employed Imperial special rapid plates.)
I cannot finish this paper without expressing my indebtedness to the University Court of Glasgow for a grant of £100 towards the expenses of the expedition; to my companion, Mr. John Franklin Adams, who presented half of this sum to the Court and superintended the arrangements for the transport of the instruments; to Mr. Andrew Crookston, Glasgow, for his hospitality at his comfortable house at Kalaa and the help the employees of his firm extended to the expedition en route; to the Council of the Royal Dublin Society for the loan of a siderostat, and to my companion, Mr. Henry A. Mavor, M.Inst.C.E., Glasgow, who, in the capacity of physician, engineer, and adviser, took upon himself much of that work which is not mentioned, but is so important to the success of an expedition.

APPENDIX I.*

Diffraction due to the Screens.

For the first four exposures, each of about a second, the aperture of the lens is reduced by a perforated screen which has thirteen equal circular openings. The arrangement of these openings will be seen in fig. 1: there are six holes in the corners of a regular hexagon, one in the centre, and six others are equidistant from each two of them. The diffraction pattern of a star does not consist, as might be thought, of a series of detached images which lie on lines intersecting in a centre, but, as photographs of α Lyrae have proved, shows, apart from a central region, luminous rings at the same distances at which one opening produces them. On the photograph of α Lyrae rings are visible as far as 5π (linear value of π = 9) for the first screen, and on the eclipse photographs the prominences have certainly made no impression beyond 10π. Faint though the intensity of the rings be, it requires investigation whether a distant ring belonging to a point of the corona near the sun has an intensity comparable to that of a distant point on whose image the ring is superposed, or rather whether all the diffracted light together is not a negligible quantity. I shall show that it is small. The result would have been different if the exposures had been longer and more distant parts of the corona had been photographed with the screens.

Let P be a point in the focal plane and C the position of its central image. I introduce a rectangular system of co-ordinates XY in the plane of the screen, origin in centre of the central opening, and X-axis parallel to CP.

Let there be only two holes which lie diametrically opposite and whose centres have the x-co-ordinates ±x, then the state of oscillation at P is given by

\[ k\pi c^{2} \left( J_{1}(u) \right) 2 \cos (\pi x) \sin x, \]

* Postscript, added at the request of one of the Referees. The photographic experiments were subsequent to and confirmatory of the mathematical analysis.
where \( \rho \) designates the radius of the opening, \( \theta \) the angular distance of CP at the centre of the object-glass, \( \lambda \) the wave-length, \( r = \frac{2\pi}{\lambda} \sin \theta \), \( u = r\rho \), and \( J_1(u) \) Bessel's function of order 1. Let there be thirteen holes arranged as defined above and the distance between each two be equal to \( \alpha \), and let a diagonal of the hexagon and the \( x \)-axis enclose angle \( \phi \), then the state of oscillation at \( P \) is given by

\[
\sin \alpha \left\{ k\pi \rho^2 \frac{2}{u} J_1(u) \left[ 1 + 2 \cos (r\alpha \cos \phi) + 2 \cos \left( r\alpha \cos \left( \frac{\pi}{3} + \phi \right) \right) + 2 \cos \left( r\alpha \cos \left( \frac{\pi}{3} - \phi \right) \right) \right] \right. \\
+ 2 \cos (r\alpha \sqrt{3} \sin \phi) + 2 \cos \left( r\alpha \sqrt{3} \cos \left( \frac{\pi}{6} + \phi \right) \right) + 2 \cos \left( r\alpha \sqrt{3} \cos \left( \frac{\pi}{6} - \phi \right) \right) \right\}.
\]

The intensity at \( P \) is the square of the coefficient of \( \sin \alpha \). The position of point \( P \) is determined with reference to \( C \) by its linear distance \( \xi = f \sin \theta \) (\( f \) = focal-length) and its position-angle \( \phi \) counted from a line parallel to one of the diagonals of the hexagon of the screen. For same values of \( \xi \) the intensity is the same for \( \pm \phi \) and it is periodical with reference to \( \phi \), with a period of \( \pi/3 \). Hence the intensity can be developed into a cosine-series progressing by multiples of \( 6\phi \).

To find the quantity \( Q \) of light falling on a ring round \( C \) limited by radii \( \xi_1 \) and \( \xi_2 \), I multiply the intensity by the element \( \xi d\xi d\phi \) of the area in the focal plane and integrate from \( \phi = 0 \) to \( 2\pi \) and from \( \xi_1 \) to \( \xi_2 \). The integration with reference to \( \phi \) can be carried out. The result is, if \( u \) be introduced instead of \( \xi \),

\[
\xi = \frac{f \lambda}{2\rho} u, \quad u' = u \frac{\alpha}{\rho},
\]

\[
Q_{\xi_1, \xi_2} = k^2 (f\lambda)^2 (13\pi \rho^2) 2 \int_{\xi_1}^{\xi_2} \left( \frac{J_1(u)}{u} \right)^2 du \\
+ k^2 (f\lambda)^2 (\pi \rho^2) 12 \int_{\xi_1}^{\xi_2} \left( \frac{J_1(u)}{u} \right)^2 du \left[ 8J_0(u') + 5J_0(2u') + 2J_0(3u') \right. \\
+ 6J_0(\sqrt{3}u') + J_0(2\sqrt{3}u') + 4J_0(\sqrt{17}u') \right].
\]

\( J_0 \) designates Bessel's function of order zero. I transform the second integral. The values of \( J_0 \) and \( J_1 \) are with sufficient accuracy for values of \( u \) larger than \( \pi \),

\[
J_0(x) = \sqrt{\frac{2}{\pi}} \frac{1}{\sqrt{x}} \sin \left( x + \frac{\pi}{4} \right), \quad (J_1(x))^2 = \frac{1}{\pi x} (1 - \sin 2x \ldots).
\]

The terms in \([ \; ] \) have, for the first screen, respectively the periods \( 70^\circ, 35^\circ, 23^\circ, 40^\circ, 20^\circ, 26^\circ \), and owing to these short periodic terms the quantity to be integrated changes sign at small intervals of \( u \). To a given value of \( u_1 \), say, \( = n\pi \), a limit \( u_2 \) near \( (n+1)\pi \) can be found which makes the second integral zero. I have convinced myself by mechanical quadrature that this deduction is correct even for \( u_1 = 0, u_2 = \pi, \ldots, u_1 = 3\pi, u_2 = 4\pi \). For our purpose it is unnecessary to take the second part into account. Therefore, if all the light falling on the ring be considered
together the distribution is almost exactly the same as if all the light had passed through only one of the openings; and in accordance with the above, if the ring be divided into 12 parts by 6 diameters, beginning at \( \phi = 0 \), each segment contains a twelfth of the light falling on the whole ring.

The quantity of light falling on such a twelfth of a zone between \( u = n\pi \) and \((n+1)\pi\) is given by

\[
Q_n = C i \pi \rho^2 \frac{1}{12} f_n, \quad \text{where} \quad f_n = 2 \int_{u}^{(n+1)\pi} \frac{J_1(u)}{u} du.
\]

\(i\) designates the intensity outside the object-glass.

I next consider the light \( Q \) falling on unit area at a point \( C \) of the image of a luminous area. Draw circles, radii \( n\pi \), round \( C \), and divide each ring by 6 diameters into 12 equal parts. Project from centre of object-glass this system of circles and lines on the luminous area. Let the intensity \( i_{mn} \) of the source be constant within an area of the source corresponding to part \( m \) of ring \( n \); then, if there were \( x \) units in one of these parts, each unit would send \( Q_n \) (for \( i = i_{mn} \)) divided by \( x \) to unit at \( C \), i.e. the \( x \) units send \( Q_n \) to unit at \( C \). The total quantity of light falling on unit at \( C \) is therefore given by

\[
Q = C \pi \rho^2 \left[ f_0 i_0 + \sum_{n=1}^{\infty} \frac{f_n}{12} (i_{n(0)} + i_{n(2)} + \ldots + i_{n(12)}) \right]
\]

or

\[
Q = C \pi \rho^2 (i_0 + \Delta i),
\]

where

\[
\Delta i = \sum_{n=1}^{\infty} \frac{f_n}{12} (i_{n(0)} + i_{n(2)}(7) - 2i_0) + \ldots + \frac{f_n}{12} (i_{n(0)} + i_{n(12)} - 2i_0),
\]

because \( \sum \frac{f_n}{n} = 1 \). Parts 1 and 7, 2 and 8, &c., lie diametrically opposite with reference to \( C \). Hence the quantity of light at \( C \) is not changed by diffraction if the source be everywhere equally intense, or if the intensity uniformly increase along the lines drawn through \( C \). In the case of the corona the second condition is very nearly satisfied in the neighbourhood of a point, and thus the most luminous diffraction rings hardly affect the quantity of light at \( C \), there being almost as much light lost as gained.

Let \( \Delta i \) be known for each of the four screens (i.e. \( \rho \)), and at each distance \( h \). Equal blackness was observed on two photographs exposed equally long with screens \( \alpha \) and \( \beta \), at two points \( h_a \) and \( h_b \); hence \( Q_a = Q_b \), and

\[
\frac{C \pi \rho_a^2}{C \pi \rho_b^2} \frac{i_a + \Delta i_a}{i_b + \Delta i_b} = 1,
\]

or

\[
\frac{i_a + \Delta i_a}{i_b + \Delta i_b} = F_{a,b} \quad [F_{a,b}, \text{see } \S 5 (c)].
\]
The distances \( h + \Delta h \) at which the corona has the intensities \( i + \Delta i \) are correlative distances on corona [compare \$ 5 (d) and (f)], where \( \Delta h = + \Delta i \frac{dh}{di} \).

The intensity formula for the corona ought to have been derived from the observed values of \( h \) corrected by \( \Delta h \).

As to the calculation of \( \Delta h \), I obtained the intensities of the corona from a diagram. I drew six lines through \( C \) at intervals of \( 30^\circ \) and marked off points at distances \((n + \frac{1}{2}) \pi \) from \( C \). I assume that the intensity of the corona belonging to a point thus marked equals the mean intensity at all the points lying within a ring limited by circles \( n\pi \) and \((n + 1) \pi \) and up to \( 15^\circ \) from it. The intensity at the points was read off the diagram and multiplied by \( f /12 \). The linear value of \( \pi \) is, in unit of \( 10^{-3} \) solar diameter, \( 9.1 \) for screen 1, \( 6.5 \) for screen 2, \( 4.7 \) for screen 3, \( 3.2 \) for screen 4, \( 0.55 \) for full aperture. For screens 3 and 4 several rings were treated together. In some directions the calculation had to extend as far as ring \( 80\pi \). I calculated \( f \) by the following formula

\[
2 \int_0^{n\pi} \left[ \frac{J_1(u)}{u} \right]^2 du = 1 - \frac{[J_0(n\pi)]^2 - [J_1(n\pi)]^2}{1 - r_n},
\]

\[
J_0(n\pi) = \frac{1}{\sqrt{n\pi}} \left( 1 - \frac{1}{8n\pi} \right) \quad J_1(n\pi) = \frac{1}{\sqrt{n\pi}} \left( 1 - \frac{3}{4n\pi} \right) \quad \text{for large } n,
\]

\[
f_n = r_{n+1} - r_n.
\]

For small values of \( n \) I interpolated the value of the integral from the table given in MUELLER's 'Photometrie der Gestirne,' p. 166.

The result of the calculation is—

<table>
<thead>
<tr>
<th>Screen</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( h )</td>
<td>65</td>
<td>110</td>
<td>160</td>
<td>98</td>
</tr>
<tr>
<td>( \Delta h )</td>
<td>+0.7</td>
<td>-0.4</td>
<td>-0.9</td>
<td>-0.3</td>
</tr>
<tr>
<td>( n )</td>
<td>1.2</td>
<td>1.7</td>
<td>3.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The systematic errors \( \Delta h \) due to diffraction, and still more their functions \( u \) [see \$ 5 (f)], are so small compared with the accidental errors \( n \) of measurement, as calculated from the residuals, that they can be neglected, and hence formula (D), \$ 7, gives the relative intensities of the corona.

APPENDIX II.

Comparison of Corona and Moon.

The results contained in this section are not to be considered as an attempt to standardise my eclipse plates, but they originated in a desire to give future observers some ideas of the intensities with which they have to deal.
After my return to the Observatory I photographed the moon on three nights with the eclipse apparatus and approximately at the same zenith distance the sun had at the eclipse. The atmosphere was exceptionally transparent for Glasgow on the first and third nights. I used plates returned from Kalaa and I developed them in the same way and at the same temperature as the eclipse photographs.

(a) Brightness of Corona.—The plates show, just as the eclipse photographs, a background due to diffused light. I compared the intensity of the background of the lunar photographs with those on the eclipse negatives, picking out those exposures which showed the same density of background in both. The durations of exposure give then the ratio of the light of the sky when illuminated by the corona and that when illuminated by the moon, and this equals the ratio of the total light emitted by the corona and the moon, provided the diffused light at the eclipse is exclusively due to the corona and the relative intensities of the two spectra are the same. Assuming Zöllner’s observations of the luminosity of lunar phases in terms of that of full moon, I find from 17 comparisons that the total light of the corona equals seven full moons. The comparison belongs to blue-violet rays.

(b) The Intensity of the Corona in Terms of Lunar Intensity.—Let \( i_a \) be the intensity of the region of the moon which lies north and south of Grimaldi and close to the edge of the moon. I compared the blackness of this region on the photograph with that of the corona on that photograph which was equally long exposed and through the same aperture, and measured the distances of points of the corona at which both showed the same degree of blackness. With the reduced distances I calculate, by formula (D), \( i/c \), which equals \( i_a/c \). Instead of \( i_a \), which belongs to phase angle \( \alpha \), I introduce \( i_r \), the intensity of the Grimaldi region at mean full moon, and find \( \log i/c \) equal to 2·543 from nine photographs on October 18, 2·578 from three photographs on November 14, and 2·532 from 17 photographs on November 15. The mean 2·551 belongs to \( h = 122 \), and at this distance from the sun’s limb the intensity of the corona equals that of the Grimaldi region at mean full moon. Therefore the constant of formula (D) is \( \log c = 12·228 - 2·551 + \log i_r = 9·677 + \log i_r \).

For want of suitable apparatus I am unable to measure \( i_r \) in terms of the average intensity of full moon, but I am led to expect by integration of the intensity formula and comparison with the total light of the corona (seven full moons) that \( i_r \) is about 4. \( i_r = 4 \) would make the intensity of the corona at a distance of 0·23 diameter equal to that of full moon, a result which is quite at variance with that cited by Langley.*

* ‘The 1900 Solar Eclipse Expedition.’
TABLE I.—[See § 4 (c.)] Equal-intensity Curves of the Corona.

<table>
<thead>
<tr>
<th>Mean distance</th>
<th>50</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position-angle from N. of sun.</td>
<td>Observed minus mean distances, Unit = 0.001 solar diameter.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>+6</td>
<td>+46</td>
<td>+78</td>
<td>+53</td>
<td>-7</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>+4</td>
<td>+15</td>
<td>+43</td>
<td>+42</td>
<td>+62</td>
<td>+13</td>
</tr>
<tr>
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<td>+6</td>
<td>+13</td>
<td>+37</td>
<td>+26</td>
<td>+4</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>+7</td>
<td>+11</td>
<td>+39</td>
<td>+43</td>
<td>+44</td>
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Table III.—[See § 4 (d).] Mean Corresponding Distances ($h$) from the Sun’s Limb of Points of the Corona at which the Photographs show Equal Blackness.

(Unit = 0.001 Solar Diameter.)

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Table IV.—(See § 7.) Weights \((p)\) and Residuals \((n, v)\) of Equations.

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Blue-Violet Light in the Solar Corona on August 30, 1905.
IX. On the Surface-Tension of Liquids Investigated by the Method of Jet Vibration.*

By P. O. Pedersen.

Communicated by Lord Rayleigh, O.M., Pres.R.S.

Received June 11,—Read June 27, 1907.

[Plates 2–4.]

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* Abstracted from a response to Det Kongl. Danske Videnskabernes Selskabs (The Royal Danish Scientific Society's) problem in Physics for 1905; delivered October 30, 1906; awarded the Society's gold medal.
INTRODUCTION.

Among the large number of methods available for the determination of the surface-tension of liquids that proposed by Lord Rayleigh* stands out with great fundamental advantages. The principle is as follows:—A jet of liquid issuing from a not circular aperture is executing transverse vibrations about its cylindrical configuration of equilibrium. Since the phase of vibration depends upon the time elapsed, it is always the same at the same point in space, and thus the motion is steady and the boundary of the jet a fixed surface showing stationary waves.

Measurements of the corresponding wave-length (λ), the velocity (V), and cross-section (A) of the jet, together with the density (ρ) of the liquid afford the necessary constants for the calculation of the capillary-tension (T) according to Lord Rayleigh's theory of jet-vibration.

The method is free from every supposition respecting the angle of contact. This advantage, however, it has in common with several other methods, especially the following:—

The method of reflection proposed by R. Eötvös† and also used by D. Pekár‡ and G. Zemplén.§

The method of ripples|| that has been used very much in recent times.

The method of maximum pressure of small air-bubbles proposed by M. Cantor* and further developed by R. Feustel.**

Another advantage of Lord Rayleigh's method is that the surface in use is continually renewed. In this manner the capillary-tension can be determined before the surface is \( \frac{1}{100} \) second old. This circumstance is of very great importance, as the

---


main reason of the great discrepancies the different determinations of the surface-
tension show in relation to each other is certainly to be found in the variable 
condition of the tested surface. These irregularities could arise from impurities, for 
example, fat, oil, or similar substances, even the smallest portion of which is able to 
produce a great alteration in the surface-tension. Thus Lord Rayleigh\(^*\) has proved 
that a film of oil not thicker than \(2 \times 10^{-6}\) mm. reduces the surface-tension of 
water about 28 per cent., and the same author has later\(^†\) proved that an oil film of 
even \(1 \times 10^{-6}\) mm. produces a noticeable reduction in the capillary-tension of water. 
W. C. Röntgen’s\(^‡\) experiments show that even an oil film of only \(0.5 \times 10^{-6}\) mm. is 
able to appreciably alter the condition of the surface. A. Oberbeck\(^§\) has been able to 
detect the existence of a film of oil that was only \(0.3 \times 10^{-6}\) mm. thick.

Apart from contamination, the surface can undergo different changes of a chemical 
and physical nature. In this manner the fluid with which the surface is in contact 
can cause a chemical change in it. If the liquid under examination is a mixture or a 
solution the concentration at the surface will in many cases be different from that in 
the interior.

From the above it is clear that the surface-tension of a liquid is, as a rule, not 
constant, but varies with the time that has elapsed from the formation of the surface. 
The value of the capillary-tension, immediately after the formation of the surface, I 
propose to call the “initial value,” while the value of the capillary-tension, when the 
surface is sufficiently old, is called the “stationary value.” Most of the methods for 
determination of the surface-tension give values differing from these two limiting 
values, but it is just these two limiting values that have the greatest interest. Of 
these the stationary value is of importance in many practical cases, but from a 
thetical standpoint the initial value is, without doubt, of the greater interest, as it 
must stand in a more simple relation to the properties of the liquid than the 
stationary value, which is dependent upon alien conditions.

With the other methods of measuring, attempts have also been made to work with 
quite fresh surfaces. Grunmach, Brümmer and Loewenfeld have adopted a 
method of obtaining pure liquid surfaces originally proposed by Röntgen.\(||\) The 
principle of the method is, that the liquid is conducted from below through the neck 
of a funnel over the upper horizontal edge of which the liquid flows. This method, 
however, does not appear to be applicable to all cases (see Grunmach, ‘Wiss. Abh. 
d. K. Norm.-Aich.-Komm.,’ Heft III., “Experiments with Mercury”), and has at 
least two faults, firstly, that when the surface renewal takes place somewhat quickly, 

(‘Papers III.,’ p. 383).


it so easily causes inconvenient currents in the liquid; secondly, the renewal is slowest in the middle of the surface, just at the place which is the subject of the measurement.

Feustel* asserts that the method of maximum pressure of small air-bubbles also gives the tension of a surface that is continually renewed. To this, however, may be replied that the renewal takes place, and must take place, very slowly. If the air-bubbles are produced quickly, the maximum pressure becomes dependent upon the speed with which they are produced.

It will be seen that the surface renewal takes place by Lord Rayleigh's method in a much more effective manner than is possible with the other methods.

Notwithstanding the undoubted fundamental advantages of this method, it has been used in very few cases, for besides Lord Rayleigh† it has only been applied by F. Piccard‡ and G. Meyer.§ Of these Piccard has made use of the method for the determination of the relative values of the surface-tension of ether, water, alcohol and mercury, but his measurements were carried out with so great an amplitude of vibration (see the plates of his paper, especially Plate VIII., figs. 14, 28 and 29, and Plate X., Photographs 10 and 11) that his results are of very insignificant importance. Meyer has only measured the relative values of the surface-tension of mercury under various conditions.

The explanation of the little use that has been made of this method is to be found in the great difficulties connected with adequate exact determination of the wavelength and cross-section or velocity of the jet. It may be at once remarked here that none of the methods previously used for the determination of these quantities can be taken as satisfactory. It has, therefore, been of the first importance to work out really good methods for the measurements of these quantities.

All the following measurements described here are carried out at ordinary laboratory temperatures.

Even if this method is not so convenient in practice as some of the other methods, that is no great drawback. What is needed in this field of investigation is not any further accumulation of many different measurements, but some more reliable results. Similar reasons have caused the method of ripples, which is just as complicated, to be used a great deal of late.

**Theory of the Vibration of a Jet about its Cylindrical Form of Equilibrium.**

§1. Before entering into the description of the experimental part of this work it is necessary to set forth a few preliminary remarks on the theory of jet vibrations.

* Feustel, *loc. cit.*
It will be convenient to set out together the meaning of the symbols employed:—

\[ V = \text{velocity of the jet (cm./sec.)} \]
\[ A = \text{cross-section of the jet (cm.}^2\text{)} \]
\[ \rho = \text{density of liquid (gm./cm.}^3\text{)} \]
\[ T = \text{surface-tension (dyne/cm.)} \]
\[ Q = VA = \text{discharge of the jet (cm.}^3\text{/sec.)} \]
\[ \lambda_n = 2\pi/k = \text{wave-length corresponding to the vibration determined by formula (1) (cm.)} \]
\[ I_n(x) = \sum_{s=0}^{\infty} \frac{x^{n+2s}}{2^{n+2s} \Pi(s) \Pi(n+s)} \quad I'_n(x) = \frac{dI_n(x)}{dx} \]

Let us suppose that the polar equation of the surface of the jet is

\[ r = a + b_n \cos n\phi, \cos kz \quad \ldots \ldots \ldots \quad (1) \]

\( n \) is an integer greater than 1. The jet is here and in the sequel regarded as horizontal and the plane \( \phi = 0 \) is also horizontal. According to Lord Rayleigh's* theory the surface-tension is determined by

\[ T = \frac{4\sqrt{\pi}}{a^2k^2 + n^2 - 1} \cdot \frac{I_n(ak)}{akI'_n(ak)} \cdot \rho \cdot \frac{V^2A^{3/2}}{\lambda_n^2} = \mu_n(ak) \cdot \rho \cdot \frac{Q^2}{A^{1/2} \lambda_n^2} \quad \ldots \ldots \quad (2) \]

where

\[ \mu_n(ak) = \frac{4\sqrt{\pi}}{a^2k^2 + n^2 - 1} \cdot \frac{I_n(ak)}{akI'_n(ak)} \quad \ldots \ldots \ldots \quad (3) \]

Vibrations corresponding to different values of \( n \) in (1) will be independent of each other.

The development of Lord Rayleigh's theory rests upon certain suppositions, viz.:—

1. That the deviations from the circular-cylinder form are exceedingly small.
2. That the vibrations are executed without any loss of energy.
3. That the original velocity of the jet is the same over the whole cross-section.
4. That the surface-tension is constant.

Each of these hypotheses will now be viewed somewhat closer individually:—

1. This hypothesis is, in practice, impossible to carry out, as it is precisely on the basis of the divergence from a cylindrical form that it is possible to determine the wave-length, and the smaller the divergence the more difficult the determination becomes. To reduce the uncertainty resulting from this, I have investigated a jet of the same liquid partly with large, and partly with proportionally small deviation from

the cylinder form, and I have similarly used a method for the measurement of the wave-lengths that even permits of a really good determination for small divergences. This matter is more fully considered later.

2. This hypothesis is also of great importance for the development of the theory, but, on the other hand, not satisfactory in practice. The liquid has always some viscosity even though, as in many cases, it is only small. It is, however, possible for the most part to determine the influence of viscosity on the time of vibration, and in this manner to correct the errors caused by it.

The calculation of this correction rests upon the following supposition, which will be very nearly true as long as the viscosity is small:

The harmonic vibration of the jet corresponding to the normal co-ordinate \( b_n \) is changed by the viscosity to a damped harmonic vibration.

Let the logarithmic decrement of the vibration be \( \delta \); we have then

\[
N_1 = N + \sqrt{(1 + \delta^2/4\pi^2)},
\]

where \( N_1 \) is the frequency of vibration with damping, \( N \) is the frequency without it.

For the determination of the surface-tension we have instead of (2) the following equation

\[
T = \left(1 + \frac{\delta^2}{4\pi^2}\right) \cdot \mu_n(\alpha k) \cdot \rho \cdot \frac{Q^2}{A^{1/2} \lambda^2}. \ldots \ldots \ldots \ldots (4).
\]

The experimental determination of \( \delta \) is described later.

3. The velocity of the thin jets investigated in this work will certainly be nearly the same over the whole cross-section, and correspond to that calculated from the cross-section and the discharge of the jet.

4. The surface-tension is in many cases dependent upon whether the surface extends or contracts (compare, for example, the damping action of oil films on waves); but with the fresh surfaces as used here the surface-tension is certainly very nearly constant.

**Calculation of the Coefficients \( \mu_n(x) \).**

\( \S \) 2. The use of the formula \([(2), \S 1]\) for the determination of the surface-tension demands the calculation of the coefficients \( \mu_n(x) \) determined by the formula \([(3), \S 1]\), or

\[
\mu_n(x) = \frac{4\sqrt{\pi}}{x^2 + n^2 - 1} \cdot \frac{I_n(x)}{x \cdot I'_n(x)}. \ldots \ldots \ldots \ldots (1).
\]

Here

\[
I_n(x) = i^{-n} J_n(ix),
\]

where \( J_n \) is the Bessel's function of the \( n^{th} \) order.
INVESTIGATED BY THE METHOD OF JET VIBRATION.

Similarly \( I'_n(x) = \frac{dI_n(x)}{dx} \). In accordance with the theory of Bessel's functions we have

\[
I'_n = \frac{n}{x} I_n + I_{n+1}, \quad I'_n = I_{n-1} - \frac{n}{x} I_n, \quad I_{n+1} + \frac{2n}{x} I_n - I_{n-1} = 0 . \quad (2).
\]

Accordingly we have

\[
\mu_n(x) = \frac{4\sqrt{\pi}}{x^2 + n^2-1} I_n \frac{1}{x I_{n-1} - n I_n} . \quad (3).
\]

By use of the last formula (2) the values of \( I_2 \) and \( I_3 \), &c., can be calculated from \( I_0 \), \( I_1 \), and by substituting these in formula (3) we have \( \mu_n(x) \).

In order to facilitate the use of this method for the determination of surface-tension I have calculated a table of the values of \( \mu_n(x) \) most commonly used. This table will be found at the end of this paper, and contains the values of \( \log_{10} \mu_n(x) \) for \( n = 2, 3, 4, \) and \( 6 \) and for \( x = 0:00 \) to \( x = 1:00 \).

The details of the calculation of this table are given in my original paper.

Calculation of the Vibration of a Jet.

§ 3. In accordance with Lord Rayleigh's theory the vibration of a jet can now be determined when the velocity and original cross-section is known, although, as previously emphasised, the theory is only available for small deviations from the circular form.

The circumference at the original cross-section is determined by

\[
r = a_0 + F(\phi) . \quad (1).
\]

By help of Fourier's series this equation can be written as

\[
r = a_0 + \sum_{n=2}^{\infty} b_n \cos(n\phi + \epsilon_n) . \quad (2),
\]

when, if necessary, the value of \( a_0 \) is changed so that \( b_0 \) vanishes, and the origin of co-ordinates is changed so that \( b_1 \) becomes zero.

Each term in (2) can be taken alone and the resulting vibration of the jet can be calculated as the sum of all the vibrations corresponding to the different values of \( n \) in (2).

Thus it is only necessary to consider

\[
r = a_0 + b_n \cos(n\phi + \epsilon_n) . \quad (3).
\]

The wave-length \( \lambda_n \) corresponding to the vibration (3) is, according to [(2), § 1],

\[
\lambda_n = C \sqrt{\mu_n(a_0 \rho)} . \quad (4),
\]

where

\[
C = \rho^{1/2} A^{3/4} \cdot V \cdot T^{-1/2} . \quad (5)
\]

is independent of \( n \).
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PEDERSEN ON THE SURFACE-TENSION OF LIQUIDS

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The equation of the jet becomes then

\[ r = 0.7746 \cdot 0.1647 \left( 1.1318 + 0.1440 \cos 2\phi \cdot \cos \frac{2\pi z}{3.932} + 0.0138 \cos 4\phi \cdot \cos \frac{2\pi z}{1.227} + \ldots \right) \]

\[ = 0.1444 + 0.01837 \cos 2\phi \cdot \cos \frac{2\pi z}{3.932} + 0.001760 \cos 4\phi \cdot \cos \frac{2\pi z}{1.227} \]

\[ + 0.0001913 \cos 6\phi \cdot \cos \frac{2\pi z}{0.646} + \ldots \quad (10) \]

from which the co-ordinates for every point of the surface of the jet can be calculated. The profile line resulting from \( \phi = 0 \) in (10) has special interest. This line is shown in fig. 1. In order better to judge the form of the curves the height is enlarged fifty times in relation to the length. It can be seen that the form of the curve is mainly determined by the original vibration corresponding to \( n = 2 \), but that at the same time also the other vibrations cause perceptible deviations.

In the measurements made by Lord Rayleigh, Piccard, and Meyer the wavelength \( \lambda_z \) is determined as the length between two successive summits of the profile line of the jet. It can be seen in fig. 1, that this length can vary and deviate somewhat from the wave-length \( \lambda \). In order to illustrate the size of these deviations for the jet corresponding to (10), drawings of the summits of the profile line are shown in fig. 2. By calculation it is found that \( r \) is maximum for \( z = 0, z = 3.932 + 0.109 \text{ cm}, z = 2.3.932 + 0.171 \text{ cm}, \) and \( z = 3.3.932 + 0.211 \text{ cm} \).

As above stated, \( \lambda_z = 3.932 \text{ cm} \).

The wave-lengths measured in this manner are

\[ \lambda^0-I = 3.823 \text{ cm} \quad \lambda^I-I = 3.870 \text{ cm} \quad \lambda^{II-III} = 4.314 \text{ cm} \]

The errors stated in per cent. of \( \lambda_z \) are respectively \(-2.6, -1.6, \) and \(+9.7\).

The error can be reduced by taking the mean value of several lengths. On the other hand, the amplitudes of the supplementary vibrations have been greater in proportion to the fundamental vibration with almost all the measurements up to now than in the instance mentioned here.

Even with relative measurements as those made by Meyer* these reasons can

* Meyer, loc. cit.
have weight, as the wave-lengths \( \lambda_2 \), \( \lambda_3 \), and \( \lambda_4 \) are dependent upon the surface-tension, and a slight variation, for example in \( \lambda_2/\lambda_4 \), can to some extent alter the wave-lengths measured.

\[ \text{Fig. 2.} \]

**Preliminary Investigations.**

*Arrangement for Keeping the Pressure Constant.*

§ 4. Before I begin the description of the different measurements I will mention a method for the production of a constant pressure by use of ordinary tap-water, as I have used this means in almost all the preliminary investigations.

It has hitherto always been an inconvenience in experiments with jets that the pressure varies continuously as the fluid runs out. To avoid this variation it is not advisable to use the simple method of renewing the quantity of discharge by a corresponding inflow of fluid, as this arrangement produces disturbances in the fluid mass, causing irregularities in the jet. All those who have worked with jets know how great is the demand for rest in the reservoir, and how exceedingly sensitive the jets are to external influence.

Lord *Rayleigh* states: "The jet is exceedingly sensitive to disturbances in the reservoir, and no arrangement hitherto tried for maintaining the level of the water has been successful."

After a number of experiments I have come to the conclusion that the following arrangement for this special use is perfectly satisfactory:

From the tap the water is conducted direct through a rubber tube to the spout of the funnel \( T \) (fig. 3), which is fastened with sealing-wax to the neck of the bottle \( F \). This rests through a wooden frame \( R \) on a metal plate \( P \), which is provided with three adjustable screws \( S \). The whole is borne on a bracket \( K \), placed on an outer wall. The bottle \( F \) is open above and is provided with an outlet from below as shown in the figure. By help of the adjustable screws the upper edge of \( T \) is kept horizontal.

The water coming from the supply pipe will run over the edge of the funnel in the form of a thin layer, and the height of the surface of water in the funnel will only be very slightly dependent upon the speed of the supply, so that the unavoidable variations in the pressure of the supply pipe will practically have no influence.

The water in the funnel \( T \) is in connection with the water in the reservoir \( B \) through a syphon made of glass tubes \( r_1, r_2, r_3 \) and rubber tubes \( g_1 \) and \( g_2 \); the surface in \( B \) will keep the same height as the surface of water in \( T \). \( B \) is provided below with a tubulure that serves for the introduction of one branch of a \( T \)-tube, the other two branches of which are provided with rubber tubes, the one serving the jet apparatus, whilst the other is only used for filling or emptying the reservoir.

It follows from the above that when the quantity of water supplied to \( T \) from the supply pipe is greater than that used in the jet apparatus, the surface of water
in B will keep itself practically constant, independently of the quantity used in the jet apparatus. This is, of course, on the understanding that the diameter of the syphon is sufficiently large.

Experiments have shown that with this arrangement, and for jets not exceeding 2 mm. in diameter, the water surface in B will vary at most 0.2 mm., and the apparatus can stand and operate by itself day and night.

The above-mentioned arrangement is especially convenient for investigation of a jet produced from ordinary tap-water, and was used in practically all the preliminary investigations for judging the exactness and practicability of the methods of measuring. As these investigations take, as a rule, a long time, it is very important that the pressure be kept constant.

For other fluids that are available only in limited quantities this method cannot, of course, be used. In these cases the author has, as a rule, employed the usual modus operandi with decreasing pressure. This will be more fully explained under the description of the experiments.

**Determination of the Cross-section of the Jet.**

§ 5. When using the present method for determination of the surface-tension it is necessary besides the wave-length to know two of the three following quantities: velocity of the jet, the sectional area of the jet, and the discharge. This last named is easiest to determine with sufficient exactness, and will, therefore, in every case be measured. The choice then remains between measuring the velocity of the jet or the cross-sectional area, but before making this choice I will give a short summary of the methods that are available at this moment to determine the velocity and sectional area of a jet.

The velocity V can be determined by use of Torricelli's formula $V = \alpha \sqrt{(2gH)}$, where H is the pressure, g the acceleration of gravity and $\alpha$ a coefficient. Many experiments have been made to investigate the exactness of Torricelli's formula. The results of these investigations are, mainly: for fluids with little viscosity, with not too high pressure, and, lastly, with holes the diameter of which exceeds 5 mm., the formula is practically correct, as the coefficient $\alpha$ is very nearly equal to 1; for water $\alpha = 0.97$ to 0.99. Special reference can be made here to Th. Vautier's* careful investigations on this subject.

With this in view, it was the author's original intention to determine the velocity of the jet in this manner; it, however, soon appeared that, just in the circumstances which have especial interest in the present instance, the deviations from Torricelli's formula are very important. It is for this reason that, so as not to use too great a quantity of fluid, it is necessary to use thin jets, for example with a diameter of

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1 millimetre. Several influences result from this which with a greater diameter of jet have only secondary importance, but here take a prominent part. I shall quite superficially treat these influences here, as I hope later to have an opportunity to give a more exhaustive account of this subject.

In Torricelli's formula \( H \) indicates the pressure measured from the jet to the fluid's surface; but this in reality must be reduced by the pressure produced by the surface-tension in the interior of the jet. Let \( d \) cm. be the diameter of the jet, \( \rho \) the density, and \( T \) dyne/cm. the surface-tension, then will the pressure produced by the surface-tension correspond to a head of liquid, the height of which, \( h \) cm., is determined by

\[
h = \frac{2T}{d\rho}
\]

If we take, for example, for water \( d = 0.1 \) cm., \( \rho = 1 \), \( T = 73.5 \) dyne/cm., we have \( h = \text{circa} 1.5 \) cm. As can be seen, it is a correction which is not quite infinitesimal, though but little attention has been given to it. C. Christiansen* is probably the first who has commenced the investigation with special regard to the conditions under discussion. Some experiments of M. Isarn† also confirm the above view. He determined the time that elapsed for 141 cm³ of fluid to run through a circular hole of a diameter of 0.8 mm. with the pressure varying from 11.8 cm. to 9.0 cm. and found

for water 290 seconds,

alcohol 270

These two measurements will now be calculated with reference to the correction mentioned before (1), it being supposed that the diameter of the jet in both instances was \( d = 0.07 \) cm.

For water we take \( \rho = 1 \), \( T = 73.5 \) dyne/cm.; for alcohol we take \( \rho = 0.8 \), \( T = 22.0 \) dyne/cm.

In accordance with this the above correction will be for water \( h = 2.14 \) cm., for alcohol \( h = 0.80 \) cm.

The effective pressure will according to this be

For water \( H = \frac{1}{4} (\sqrt{11.8 - 2.14} + \sqrt{9.0 - 2.14})^2 = 8.20 \) cm.

alcohol \( H = \frac{1}{4} (\sqrt{11.8 - 0.80} + \sqrt{9.0 - 0.80})^2 = 9.53 \) cm.

The total discharge will be

For water \( \pi \cdot \frac{0.07^2}{4} \cdot \sqrt{2.981 \cdot 8.2} \cdot 290 = 141.3 \) cm³.

alcohol \( \pi \cdot \frac{0.07^2}{4} \cdot \sqrt{2.981 \cdot 9.53} \cdot 270 = 141.8 \) cm³.

Thus the difference shown in the time of outflow is wholly explained in this manner.

Isarn himself explains the difference mentioned as originating from different contractions, and calculates on the basis of such measurements the coefficient of contraction. There can be no doubt, however, that this is incorrect, as the influence of the surface-tension on the coefficient of contraction certainly is not great, as will be shown later.

If this reduction of the velocity on account of the capillary-pressure in the jet were the only deviation from Torricelli's formula, it could be corrected and the velocity accordingly calculated; but as the diameter of the jet becomes smaller the value of $\alpha$ is also reduced and this coefficient becomes to a great degree dependent upon the nature of the edge of the hole, so that in every case it is necessary to determine the value of $\alpha$, or, in other words, determine the velocity of the jet in another manner.

Lord Rayleigh*, who used this method to determine the velocity of the jet, says with regard to it: "The pressure at any moment of the outflow could be measured by a water manometer read with a scale of millimeters. Some little uncertainty necessarily attended the determination of the zero point; it was usually taken to be the reading of the scale at which the jet ceased to clear itself from the plate on the running out of the water."

According to the above, this method can not be taken as a satisfactory solution of the question.

Direct measurement of the velocity of the jet can be made in several manners. Th. Vautier† added small drops of another fluid and determined the velocity of the drops by taking photographs on a plate moving with a known speed. The method seems to be good so long as the diameter of the jet is not too small (in Vautier's experiments the diameter of the hole was 5.76 mm.), but with small diameters the method is useless on account of the risk of noticeable change both in the surface-tension and in the coefficient $\alpha$ on account of the additional alien liquid.

Another and simpler method‡ is to determine the velocity by help of the geometric form of the jet. This method can also give satisfactory results for thick jets, but for thin ones it is of no value.

Besides the previously mentioned reduction of velocity on account of the capillary pressure in the jet, the surface-tension produces other differences in the velocity. The presence of the jet is inseparably connected with a continual production of new fluid surface, and the requisite energy is essentially taken from the kinetic energy of the jet as its horizontal velocity reduces. The loss of pressure, $h_1$, corresponding to this reduction is easily found to be

$$h_1 = \frac{4T}{d\rho g} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2).$$

† Th. Vautier, loc. cit.
This reduction is thus seen to be double that originating from the capillary-pressure for a water jet with a diameter of 1 mm. becomes \( h_t = \text{circa 3'0 cm.} \)

This fact has also been the subject of but little attention, though A. Dupré* has undertaken some interesting experiments about the height to which a jet can rise.

A closer examination of how the reduction of velocity corresponding to \( h_t \) spreads itself over the jet I am obliged to leave to another opportunity, only a particular characteristic fact being named here. If the pressure is reduced more and more so that it comes near to the value \( h_t + h \), the jet can be observed to deviate more and more from a parabola, the curvature of the jet just outside the hole becoming much too great. If the pressure is reduced almost to \( h_t + h \), the jet first runs a short distance horizontally and then falls vertically down. If we determine the discharge and cross-section of the jet, the velocity in the horizontal part of the jet can be calculated, and it will be observed that this velocity is almost equal to that corresponding to the pressure \( h_t \). It is very difficult to maintain the jet in the above position; the slightest disturbance will cause the jet to cease.

It is also possible to determine the velocity of a jet by measuring the pressure it produces by normal impact on a sufficiently large plane surface. Measurements in this manner have been made, for example, by Buff,† who worked with a jet with diameter from 5 to 7 mm. This method seems to give quite reliable results and may most probably be available even for much smaller jet thicknesses, but the difficulties connected with its use will be, in consequence, considerably greater. The balance used must, in such a case, be made very sensitive, and it will probably then be difficult to keep the sensitiveness constant. In the use of this method there must also be taken into consideration a correction resulting from the surface-tension. The pressure measured must be reduced by the capillary-pressure in the jet multiplied by the area of its cross-section, in other words, by

\[
\frac{2T}{d} \cdot \frac{\pi}{4} \cdot d^2 = \frac{\pi}{2} Td.
\]

At the same time the surface-tension along the jet's circumference, or \( T_{\pi d} \), must be added to the pressure measured. The final correction will accordingly be \( +\frac{1}{2} \pi Td \).

The cross-section of a jet has hitherto, as a rule, been determined by direct geometrical measurements, which ordinarily take place in such a manner that the points of some micrometer screws are brought exactly to touch the surface of the jet. In this manner a sufficient exactness can be reached, as a rule, with thick jets. The condition is quite the reverse when the diameter of the jet is only about 1 millimetre. In this case it will most probably be impossible to get even a moderately satisfactory exactness. In this respect a great progress has been made by the elegant method

proposed by K. Prytz* and based on the optical contact between a microscope and a reflecting surface. It is possible in this manner to determine the diameter of a circular jet with great exactness, but with not circular jets the method, unfortunately, becomes impracticable.

§ 6. As none of the known methods for the determination of the velocity and cross-section of thin jets are quite satisfactory, I have worked out a new method for the determination of the cross-sectional area of a jet.

The principle of it is the following: A definite length of a jet is taken and weighed, and on the basis of the weight and the density of the liquid the sectional area of the jet is calculated.

The taking of this definite length of the jet is accomplished by help of a "jet-catcher," shown in figs. 4-7. It consists of two cylindrical vessels $K_1$ and $K_2$, the
ends of which are the steel plates $P_1$ and $P_2$. The edges of these steel plates, $k$, are knife-formed and effect the cutting of the jet, as described later.

The "jet-catcher" itself is, as is shown in figs. 5–6, arranged on a pendulum $C$, turning about the axis $p-p$. In order to vary the height of the pendulum the stands $A$ are furnished with a number of holes for the screws $S$, as shown in the figure. The "jet-catcher" is fastened to the pendulum through the cross-piece $t$ by means of the screws $s$ (see fig. 4). The exact position is secured by means of two cones $i$, which fit in the corresponding holes in the cross-piece $t$.

The axis of the pendulum is arranged perpendicularly over, and parallel to, the horizontal jet at such a height that the position of the jet in relation to the "jet-catcher" is about as shown in fig. 6, where $S$ indicates the jet.

If the pendulum is caused to swing, the "jet-catcher," every time it passes the jet, will cut out a portion of it. If the jet is perpendicular to the edges $k$, and parallel to the plane through corresponding edges, the length of the piece that is cut out of the jet each time is equal to the distance between the edges $k$. With a complete swing (both forwards and backwards) the total length $L$ of the portions of the jet cut off (see fig. 7) is

$$L = L_1 + L_2 . . . . . . . . . . . . . . . . . (1).$$
INVESTIGATED BY THE METHOD OF JET VIBRATION.

If the jet is parallel to the plane through the edges, but makes an angle of $90^\circ - \phi$ with these, then the total length of the portions cut off during a complete swing will become

$$L = \frac{1}{\cos \phi} (L_1 + L_2) \quad \ldots \quad (2).$$

If the jet is at right angles to the edges, but makes the angle $\omega$ with the plane through the edges (see fig. 7), the conditions are a little more complicated. In the figure the jet is drawn in two positions, $S_1$ and $S_2$. The one position, $S_1$, gives a picture of what takes place with the "jet-catcher" moving in one direction, $S_2$ gives a corresponding picture of the movement in the opposite direction. $V$ is the velocity of the jet. With regard to the other symbols, reference is made to the figure.

We have

$$L'_1 = L_1 \sec \omega + y_1, \quad y_1 = V/v_1 \cdot x_1, \quad x_1 = L_1 \tan \omega,$$

also

$$L'_1 = L_1 (\sec \omega + V/v_1 \cdot \tan \omega) \quad \ldots \quad (3).$$

In the same manner we get

$$L'_2 = L_2 (\sec \omega - V/v_2 \cdot \tan \omega) \quad \ldots \quad (4).$$

By the addition of (3) and (4) we get

$$L = L'_1 + L'_2 = (L_1 + L_2) [\sec \omega + \frac{1}{2} V \tan \omega (1/v_1 - 1/v_2)] \quad \ldots \quad (5);$$

as the last term is so small that we can take $L_1 = L_2$ without any appreciable error.

If $v_1 = v_2$,

$$L = (L_1 + L_2) \cdot \sec \omega \quad \ldots \quad (6).$$

In practice $v_1$ and $v_2$ will have almost the same value, although the velocity will naturally be somewhat smaller each time the "jet-catcher" passes the jet. To investigate the influence of this difference in velocity we take $v_2 = 0.9v_1$, $V = v_1$.

The equation (5) then becomes

$$L = (L_1 + L_2) \cdot (\sec \omega - 0.0555 \tan \omega) \quad \ldots \quad (7).$$

By $v_1 = 0.9v_2$ and $V = v_2$, equation (5) becomes

$$L = (L_1 + L_2) \cdot (\sec \omega + 0.0555 \tan \omega) \quad \ldots \quad (8).$$

To judge the influence of the angle $\omega$ the Table I. is available, which also contains the corresponding values for $v_2 = 0.95v_1$ and $v_1 = 0.95v_2$.

In practice the ratio between $v_1$ and $v_2$ will still more approach to 1. As can be seen, no especially great exactness is required in the adjustment of the "jet-catcher" relatively to the jet.
In these evolutions it is supposed that \( l_1 = l_2 \) (see fig. 7), a condition easy to satisfy with great exactness.

It can easily be seen that all the foregoing continues to be true in the main, even if the velocity of the jet is not the same over the whole cross-section. With use of the method on jets that are not cylindrical there are some complications. Reference will only be made here to the jets investigated in this paper, the equation of which is \( r = a + b \cos n \phi \cos k z \).

When \( n \) is an even number, the oblique sections produced by the edges \( k \) can, without appreciably altering the volume of the piece cut out, be replaced by the normal sections through the points where the axis meets the oblique sections. If \( n \) is uneven, this will not be the case, but the deviation will be small for all the jets investigated in this work. The only error to be considered will thus result from the circumstance that the volume of the jet which is cut off by two normal sections, at a constant distance from each other, will vary a little with the position in relation to the stationary waves of the jet. To investigate the amount of this error the volume of the jet \( V_0 \) between the planes \( z = 0 \) and \( z = L \) is determined:

\[
V_0 = \int_{\phi=0}^{\phi=2\pi} \int_{z=0}^{z=L} L^2 d\phi = \pi L \left( \alpha^2 + \frac{b^2}{4} \right) + \pi \frac{b^2}{8k} \sin 2kL \quad . . . \quad (9).
\]

If \( \lambda \) is the wave-length, then \( k = 2\pi/\lambda \) and

\[
V_0 = \pi \cdot L \left( \alpha^2 + \frac{b^2}{4} \right) + \frac{b^2}{16} \lambda \sin \frac{4\pi}{\lambda} L \quad . . . \quad (10).
\]

If \( \lambda \) is equal to the distance between the edges (this distance is always greater, the actual error consequently smaller than that calculated), then equation (10) shows that the greatest volume that can be cut out is

\[
V_1 = \lambda \pi \left( \alpha^2 + \frac{1}{2} b^2 \right) + \frac{1}{4} \lambda b^2,
\]

whilst the average value is

\[
V_0 = \lambda \pi \left( \alpha^2 + \frac{1}{4} b^2 \right).
\]
The greatest error is, expressed in per cent.,

\[ \Delta = 100 \cdot \frac{b^2}{a^3 + b^3}. \]

For \[ b/a = 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \]

\[ \Delta = 0.04 \quad 0.16 \quad 0.35 \quad 0.65. \]

For the values of \( b/a \) here used this error is without importance.

For the "jet-catcher" used here

\[ L_1 = 2.97985 \text{ cm.,} \quad L_2 = 2.99225 \text{ cm.,} \quad L = L_1 + L_2 = 5.9721 \text{ cm.} \]

The whole of the "jet-catcher," with the exception of the before-mentioned steel plates, is made of magnalium, which is both light and keeps in good condition. Before use the "jet-catcher" is dipped in melted paraffin, so that it is covered with a thin layer, removed only from the edges of the knives, \( k \).

In order to prevent evaporation during weighing it is necessary to cover the openings of the "jet-catcher"; this is done by the help of two indiarubber plates fastened to two metal rods, pressed against the two openings by help of springs. It is also necessary to introduce a correction for evaporation during the cutting off, as described below.

The measuring itself takes place in the following manner: The fluid contained in the "jet-catcher" from a previous measurement is completely removed and the apparatus is carefully cleaned. The indiarubber coverings are set and the "jet-catcher" is weighed and arranged on the pendulum, whereupon the rubber covers are removed and the pendulum carried up to a horizontal position, released and allowed to complete five whole swings, after which it is caught again. As soon as this takes place the rubber covers are put on, the "jet-catcher" is taken from the pendulum and all outside drops removed, after which the weighing takes place. After the conclusion of the remaining measurements, which takes place in the course of a few minutes, the jet is stopped and the "jet-catcher" again arranged on the pendulum. The rubber covers are removed and the pendulum is allowed again to complete five whole swings, beginning with the same height as with the "cutting off," after which the rubber plates are replaced and the "jet-catcher" weighed again. If we call the weight of the liquid contained in the "jet-catcher" by the first weighing \( P \) mg, and by the second \( P - p \) mg, then the loss by evaporation during these swingings is \( p \) mg. The whole weight of the quantity of the liquid cut off the jet is then \( P + \alpha \cdot P \) mg, as the loss by evaporation during the cutting off is \( \alpha P \) mg.

The determination of the coefficient \( \alpha \) takes place as follows: Two cuts are made, the pendulum completing only one whole swing. The quantity of liquid "cut off" is determined in the ordinary manner, after which the loss of weight, \( p_n \), for five whole swings of the pendulum is determined as explained above. Next four cuts are made,
the pendulum completing two whole swings, the corresponding loss, \( p_2 \), being determined in the same manner as above. In a similar manner \( p_3 \), \( p_4 \), and \( p_5 \) are determined. We have then

\[
\alpha = \frac{3p_1 + p_2 + p_3 + p_4 + p_5}{5p_5}.
\]

In Table II. are arranged the results of these determinations for water and alcohol (98·04 per cent.).

**Table II.**

<table>
<thead>
<tr>
<th></th>
<th>Water.</th>
<th>Alcohol, 98·04 per cent.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg.</td>
<td>mg.</td>
</tr>
<tr>
<td>( p_1 )</td>
<td>1·75</td>
<td>17·0</td>
</tr>
<tr>
<td>( p_2 )</td>
<td>2·30</td>
<td>22·0</td>
</tr>
<tr>
<td>( p_3 )</td>
<td>2·35</td>
<td>23·4</td>
</tr>
<tr>
<td>( p_4 )</td>
<td>2·40</td>
<td>23·6</td>
</tr>
<tr>
<td>( p_5 )</td>
<td>2·45</td>
<td>24·0</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0·882</td>
<td>0·881</td>
</tr>
</tbody>
</table>

In the following it is always assumed that \( \alpha = 0·88 \). A small error in the determination of \( \alpha \) is of no great importance. If the worst case in this paper is taken, \( P \) is almost equal to 230 mg. and \( p_5 = 25 \) mg.; we have then \( P + \alpha p_5 = 252 \) mg. An error in \( \alpha \) of 0·04 will give an error in the concluding weight of 1 mg. or of 0·4 per cent. The corresponding error in the surface-tension is about 0·2 per cent.

As the determination of \( p_5 \) always takes place under the same conditions—temperature, humidity, and air pressure—as those under which the "cutting off" takes place, the determination of this correction is quite certain and cannot cause great errors.

In Table III. are shown some of the values found for \( \alpha p_5 \) corresponding to orifice No. III. All the weighings are corrected for the buoyancy of the air.

Besides the sources of error investigated there are several other circumstances that possibly could cause irregularities in the exactness of the measurements. Thus it is necessary that the vessels \( K \) of the "jet-catcher" have a certain shape, so that they can without loss receive and hold the portions of the jet cut off. With the form shown in fig. 6 I have never noticed any loss of liquid.

It is further obvious that if the speed of the "jet-catcher" when passing the jet is too slow, the disturbance in the jet produced by the first knife will have time to reach the second knife before it has cut the jet through. It is also possible that the movement in the air resulting from the movement of the pendulum and the "jet-catcher"
INVESTIGATED BY THE METHOD OF JET VIBRATION.

TABLE III.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\alpha p_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg.</td>
</tr>
<tr>
<td>Water</td>
<td>1.8</td>
</tr>
<tr>
<td>Alcohol, 3.09 per cent. by weight</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>16.5</td>
</tr>
<tr>
<td></td>
<td>21.1</td>
</tr>
<tr>
<td>Aniline</td>
<td>0.6</td>
</tr>
<tr>
<td>Ammonia, density $\rho_{15/4} = 0.9903$</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>7.9</td>
</tr>
</tbody>
</table>

might have influence upon it. It is clear that both these influences are dependent upon the velocity of the "jet-catcher."

In order to investigate these questions I have made several series of experiments, one of which is given in Table IV. The result is, as can be seen, within wide limits, independent of the velocity of the "jet-catcher."

Further, I have compared the "jet-catcher" used here with another for which $L = L_1 + L_2 = 7.9030$ cm. The difference between the results of a series of experiments on the same jet was only 0.06 per cent.

TABLE IV.—Water Jet. Velocity 273.1 cm./sec. Diameter 1.3415 mm.

<table>
<thead>
<tr>
<th>Mean velocity of the &quot;jet-catcher.&quot;</th>
<th>Weight for five complete oscillations of the &quot;jet-catcher.&quot;</th>
<th>Deviation from mean value.</th>
<th>Deviation.</th>
<th>Corresponding deviation of the radius of the jet.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm./sec.</td>
<td>mg.</td>
<td>mg.</td>
<td>per cent.</td>
<td>mm.</td>
</tr>
<tr>
<td>651</td>
<td>422.15</td>
<td>+0.83</td>
<td>+0.20</td>
<td>+0.00067</td>
</tr>
<tr>
<td>586</td>
<td>421.04</td>
<td>-0.28</td>
<td>-0.07</td>
<td>-0.00024</td>
</tr>
<tr>
<td>530</td>
<td>421.43</td>
<td>+0.11</td>
<td>+0.03</td>
<td>+0.00010</td>
</tr>
<tr>
<td>463</td>
<td>420.80</td>
<td>-0.52</td>
<td>-0.12</td>
<td>-0.00040</td>
</tr>
<tr>
<td>382</td>
<td>421.97</td>
<td>+0.65</td>
<td>+0.15</td>
<td>+0.00050</td>
</tr>
<tr>
<td>280</td>
<td>420.52</td>
<td>-0.80</td>
<td>-0.19</td>
<td>-0.00064</td>
</tr>
<tr>
<td>Mean value.</td>
<td>421.32</td>
<td>Mean error .</td>
<td>$\pm 0.14$</td>
<td>$\pm 0.00047$</td>
</tr>
</tbody>
</table>

§ 7. After the above there can hardly be any doubt that this method for the determination of the sectional area of a thin jet gives very trustworthy results, and that by this means we have a convenient method of carrying out several investi-
gations on such jets with an exactness that hitherto has been difficult or impossible to reach.

I will mention only very briefly some measurements of the influence of the pressure on the sectional area of a jet, keeping myself within the limits where the question is of interest for this investigation. The measurements comprise two circular apertures, No. 1 with diameter 1.514 mm. and No. 2 with diameter 0.8043 mm., both arranged as shown in fig. 10, where B is the perforated plate. For these I have determined the sectional area of water jets for heads between 50 and 100 cm. The results are shown in fig. 8, where the value $a-b$ corresponds to aperture No. 1 and $c-d$ to No. 2. The values measured are shown by a cross; it can be seen that they very nearly fall on the straight lines $a-b$ and $c-d$.

For aperture No. 1 the sectional area decreases 4.98 per cent., while the head increases from 50-100 cm.
For aperture No. 2 the sectional area decreases 5·03 per cent., while the head increases from 50–100 cm.

The apertures used in this investigation have diameters between No. 1 and No. 2. For these, without making any great error, it can be calculated that the sectional area decreases 1 per cent. for each 10 cm. the head increases.

The determination of the discharge takes place in the usual manner and needs no comment.

Production of the desired Deviation from the Cylindrical Form of a Jet.

§ 8. In § 3 is shown the importance of the jet executing one single vibration, in other words, that its surface is determined approximately by

$$r = a + b \cos n\phi \cos \left(\frac{2\pi z}{\lambda_n}\right) \ldots \ldots \ldots \ldots \ldots (1),$$

as in the contrary case the determination of the wave-length $\lambda_n$ causes difficulty and becomes inaccurate. By the measurements that up to now have been made with this method only little attention has been paid to this condition. Lord Rayleigh* writes as follows: "... The first set of observations here given refers to a somewhat elongated orifice of rectangular form; ... refers to an aperture in the form of an ellipse of moderate eccentricity; ... relate to an orifice in the form of an equilateral triangle with slightly rounded corners. ..." PICCARD† says: "Le liquide s'écoule par un tube aplati. ..." MEYER‡ expresses himself in the following manner on this question: "Die elliptische Oeffnung ist mittelst einer Stopfnadel durchgeschlagen, welche auf einem Oelstein solange geschliffen wurde bis eine in ein Probestück des Membran geschlagene Oeffnung die gewünschte Form und Grösse hatte. ... Um eine grössere Genauigkeit zu erzielen, wäre vor allem auf eine schwärere Beobachtungs-metode und die Herstellung einer genau elliptischen Oeffnung Bedacht zu nehmen."

Apart from the last-mentioned reference—which according to § 3 is incorrect—the importance of, and the means for, giving the jet a single vibration has been wholly neglected.

I have endeavoured to solve this question by making the aperture as exact as possible after the formula

$$r = a + b \cos n\phi \ldots \ldots \ldots \ldots \ldots (2).$$

As the dimensions must be small, for example $a = 0·65$ mm., so as not to use too great a quantity of liquid, the work is consequently accompanied with some difficulty. The following method, however, proved itself to be good. The aperture is first drawn enlarged, fig. 9, ABCD, after which I chose a fine round file, the radius $r$

† PICCARD, loc. cit.
‡ MEYER, loc. cit.
of which is somewhat smaller than the smallest radius of the curvature of the aperture. On the drawing is constructed the curve $abcd$, described by the centre of a circle with radius $r$ rolling inside the curve $ABCD$. The values of the radius vector for the curve $abcd$ corresponding to $\phi = 0^\circ, 6^\circ, 12^\circ, \&c.$, are determined on the drawing. By help of these values and by using a small milling machine, with the above-mentioned little file as cutter, the orifice can be cut in the correct form $ABCD$. Further particulars are given in the original paper.

The plate B is in most cases of platinum iridium (90 Pt+10 Ir) and has the form of a circular plate, about 17 mm. in diameter and about 0.5 mm. thick. In the middle of each plate the thickness is reduced to about 0.25 mm. Fig. 10 shows the ordinary arrangement of aperture and conducting tube. A represents a glass tube, B a perforated plate, and C a ring of indiarubber. Some few apertures are made in
brass. Microphotographs of some of the orifices used are shown on Plate 2; below each photograph is denoted the length of the largest diameter of the corresponding orifice. Further particulars will be given later.

It proved, however, that even with the best of the apertures produced in this manner the jet was not quite free from alien vibrations. That is due partly to deviations from the correct form of the aperture, but also to the fact that the cross-section of the jet is not strictly similar to the form of the aperture. This last-mentioned inconvenience would be got rid of by allowing the jet to flow out of a tube which had the correct form of cross-section. This solution is, however, for several reasons inconvenient. When the jet flows out of a tube the velocity will be less at the surface than in the axis; and, finally, the production of such a tube would be very difficult.

I have also tried to produce the deviation of the jet in another manner, namely, by using a circular orifice and a non-circular conducting tube (see fig. 11); but generally I prefer the other method.

With regard to the purity of the vibrations obtained, the jet-photographs on Plates 3 and 4 will give good information. The production of these jet-photographs will be described in the next section.

_Determination of the Wave-length._

§ 9. Of all the quantities on which the surface-tension according to equation [(2), § 1] depends, \( \lambda_a \) is undoubtedly the most difficult to determine. In all the previous measurements, as mentioned before, \( \lambda_a \) is determined as the distance between the summits of the jet, and the determination has taken place by direct measurement either on the jet itself or on a photograph of it. As the amplitude of the vibrations must be small, this method is very unsatisfactory and cannot give good results.

An exact determination of \( \lambda_a \) can be made in many ways, but they will most probably have it in common that the jet itself is used as an optical, image-forming system. Of the methods I have endeavoured to use I will only describe the following two.
The first method is illustrated by fig. 12. Here \( abba \) represents one of the profile lines of the jet (seen from above). \( L \) is a Nernst-lamp (1 amp. 220 volts), the linear filament being vertical. The rays coming from \( L \) are reflected by the mirror \( S \) and unite after reflection from the surface of the jet in the image \( L_n \). When the profile line is a sinusoid the distance between the images \( L' \) and \( L_n \) will be equal to the wave-length. This distance can be determined with great accuracy, and if the jet were perfectly free from alien vibrations this method would be able to give very exact results. Unfortunately it has not been possible for me to produce a jet so regular that I could make use of this method with real advantage. Even very small deviations from the desired jet-form change the position of the images very
considerably. The execution of a measurement also demands much time, and this is probably the greatest drawback of the method.

The other method is as follows:

The rays from a horizontal linear incandescent lamp L₁ (about 23 cm. long, 25 candle-power, 110 volts) is reflected from the mirror S perpendicularly down on the jet s (see fig. 13). Close beside the jet is arranged a vertical photographic plate P, upon which an image is formed, the approximate form of which is shown by the line m–n on fig. 14. The lamp L₁ is enclosed in a shield ABC.

The part BC of this shield has the form shown in fig. 15, making the illumination of the jet the same for its entire length. In series with the lamp L₁ another lamp, L₂, is inserted, the power of which can be regulated by the help of a rheostat placed parallel to it. L₂ is arranged at the same height as the jet, and the light from it produces a homogeneous fog on the plate P which is only interrupted by the shadows s₁–s₂ of the jet and T₁–T₂ of the wire T which is arranged horizontally in front of the plate.

The manner in which the image m–n (fig. 14) is formed will be explained only very briefly. In fig. 16 is shown the circular cross-section of a horizontal jet. L is a vertical ray; its direction is after two refractions and one reflection changed to L₁. The angle between L and L₁ is denoted by y and the refractive index of the liquid by n₀. With the symbols of the figure

\[ y = 4b - 2i. \]
It is easily shown that \( y \) is maximum when
\[
\sin i = \sqrt{\frac{4 - n_o}{3}}.
\]

In order to illustrate the positions of the emergent rays, fig. 17 is drawn. The ray for which \( y \) is maximum cut the plate \( P \) in \( B \), and at that point the intensity of illumination will be maximum. All the points \( B \), collectively, form the image \( m-n \) (fig. 14).*

Let the maximum value of \( y \) corresponding to \( z^* \) be denoted by \( y_\star \), then \( y - y_\star \) has the same sign as \( b_n \cos k\zeta \). The wave form of the image \( m-n \) is produced in this manner.

As the amplitude of the curve \( m-n \) is much greater than that of the jet, it is much easier to determine the wave-length by measuring on the image \( m-n \) than on the jet itself.

The measuring of the wave-length takes place in the following manner (fig. 14): The distance \( L \) between two homologous suitable points on the image \( m-n \) is determined. By dividing this length by the number \( v \) of waves between the points

* For further information about this question see J. M. Pernther 'Meteorologische Optik' (Wien and Leipzig, 1902), p. 482.
† In \( r = a + b_n \cos n\phi \cos k\zeta \ldots [(1), \S 1]. \)
measured, we have \( \lambda_n \). This would be perfectly correct if the jet were horizontal over the whole length, in other words, parallel to \( T_1-T_2 \), and perpendicular to the light incident on the jet. As this is not the case, the following correction is necessary: \( L \) represents the distance between the homologous points in the image, but what is in reality necessary to be known is the distance between the corresponding points \( p \) and \( q \) on the jet itself. With the symbols used in the figure, this correction for the point \( p \) will be with sufficient exactness: 
\[
x = \frac{e}{d} (ab + ac - (a_1b_1 + a_1c_1)).
\]

Here \( e \) is the distance from the point on the image to the point \( Q \) (see fig. 17) where the ray of minimum deflection is reflected. This correction is calculated for both the two points \( p \) and \( q \), and the distance \( L_n \) between these points is \( L_n = L - x - x_1 \).

This formula is not quite correct, as \( e \) as a rule will have different values at the two ends, but the corresponding error is only small, and will be neglected here. \( L_n \) is here determined as the distance between the points \( p \) and \( q \), although in reality it is the length of the portion \( p-q \) of the jet that is needed; but this error is only small for the jets examined here.

The wave-length is therefore determined by \( \lambda_n = L_n/\nu \).

In the following, the wave-length is always determined by the last-mentioned method, although perhaps it is not so exact as the first, in principle; it has nevertheless great advantages compared with it. Among these advantages is the comprehensive view of the whole jet, tending to prevent mistakes, and the much shorter time needed for the determination, inasmuch as the actual measuring work can be done afterwards on the finished plate. Finally, the exactness that is reached is certainly as great as is possible, so long as it is not feasible to obtain absolutely pure jet-vibrations. One fault, however, with this method is that it is only available for transparent liquids.

During exposure the plate \( P \) is arranged in a plate-holder which is fixed in a vertical frame. This can be laid down in a horizontal position by turning the pivots below. The frame is arranged on a horizontal slide that can move in a direction at right angles to the jet. The movement of the slide towards the jet is stopped by an adjustable stop leaving a distance of about 4 mm. between the plate and the jet.

On Plates 3 and 4 are shown some photographs of jets taken in this manner; further details will be given later.

By the use of nearly monochromatic illumination still better jet-images may be obtained.

**Investigations on the Influence of the Amplitude of Vibration.**

§ 10. If the jet's cross-section is determined by the equation

\[
r = a + b \cos n\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),
\]

then \( r_{\text{max}} = a + b \) and \( r_{\text{min}} = a - b \).
In the following the amplitude of the jet will be denoted by \( \delta \), determined by

\[
\delta = 100 \cdot \frac{r_{\text{max}} - r_{\text{min}}}{r_{\text{max}} + r_{\text{min}}} \quad (2)
\]
or, according to equation (1),

\[
\delta = 100 \cdot \frac{b}{a} \quad (2').
\]

The same notation will be used for the orifices.

In §1 the necessity of an investigation respecting the influence of the amplitude on the period of vibration has been already emphasized. The only material that is available in this case consists of the measurements made by Lord Rayleigh* and recorded in his original paper. For some of these I have calculated the surface-tension according to formula [(2), §1], and arranged Table V. in order of decreasing amplitude.

**Table V.**

<table>
<thead>
<tr>
<th>Orifice.</th>
<th>T.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triangle with slightly rounded corners. (Table V., by Rayleigh)</td>
<td>57·4 dyne/cm.</td>
</tr>
<tr>
<td>Square. (Table VII., by Rayleigh)</td>
<td>64·6</td>
</tr>
<tr>
<td>Ellipse of moderate eccentricity (( \delta &gt; 9 )). (Table II., by Rayleigh)</td>
<td>69·5</td>
</tr>
<tr>
<td>Ellipse (( \delta = 9 )). (Table IV., by Rayleigh)</td>
<td>72·9</td>
</tr>
</tbody>
</table>

From the values of T it is evident that the amplitude for the three jets has been too great. How far this is also the case with the jet corresponding to the orifice for which \( \delta = 9 \) cannot be determined on the basis of the investigations mentioned. In the measurements of Meyer† and Piccard‡ the amplitudes in accordance with the above have been much too great.

In order to decide this question, I have made a series of measurements with jets of water; the orifices used for these are recorded in Table VI.

The results of these experiments are found in Table VII., where the orifices are arranged with decreasing amplitudes. In the table, T indicates the surface-tension calculated upon the supposition that the amplitudes could be considered as extremely small.

† Meyer, loc. cit.
‡ Piccard, loc. cit.
INVESTIGATED BY THE METHOD OF JET VIBRATION.

TABLE VI.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Largest.</td>
<td>Smallest.</td>
<td>$\delta$.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mm.</td>
<td>mm.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I.</td>
<td>1.671</td>
<td>1.009</td>
<td>2</td>
<td>24.7</td>
</tr>
<tr>
<td>II.</td>
<td>1.545</td>
<td>1.281</td>
<td>2</td>
<td>9.3</td>
</tr>
<tr>
<td>III.</td>
<td>1.424</td>
<td>1.303</td>
<td>2</td>
<td>4.4</td>
</tr>
<tr>
<td>IV.</td>
<td>0.830</td>
<td>0.820</td>
<td>2</td>
<td>0.61</td>
</tr>
<tr>
<td>V.</td>
<td>1.386</td>
<td>1.384</td>
<td>2</td>
<td>0.14</td>
</tr>
<tr>
<td>VII.</td>
<td>1.556</td>
<td>1.530</td>
<td>2</td>
<td>0.86</td>
</tr>
<tr>
<td>A</td>
<td>2.202</td>
<td>—</td>
<td>3</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>2.372</td>
<td>2.128</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>C</td>
<td>2.398</td>
<td>2.318</td>
<td>6</td>
<td>—</td>
</tr>
</tbody>
</table>

Table VII.—Ordinary Tap-Water.

$$\rho_{18/4} = 0.99913, \quad \frac{dT}{dt} = -0.151.$$

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>I.</td>
<td>2</td>
<td>24.7</td>
<td>2.9508</td>
<td>0.01060</td>
<td>1.2100</td>
<td>65.63</td>
<td>16.4</td>
</tr>
<tr>
<td>17</td>
<td>II.</td>
<td>2</td>
<td>9.3</td>
<td>3.1864</td>
<td>0.01149</td>
<td>1.2306</td>
<td>70.99</td>
<td>17.0</td>
</tr>
<tr>
<td>28</td>
<td>II.</td>
<td>2</td>
<td>9.3</td>
<td>4.6535</td>
<td>0.01097</td>
<td>1.8210</td>
<td>72.38</td>
<td>14.3</td>
</tr>
<tr>
<td>19</td>
<td>III.</td>
<td>2</td>
<td>4.4</td>
<td>2.9942</td>
<td>0.01073</td>
<td>1.1506</td>
<td>74.02</td>
<td>14.6</td>
</tr>
<tr>
<td>29</td>
<td>III.</td>
<td>2</td>
<td>4.4</td>
<td>4.3291</td>
<td>0.01020</td>
<td>1.7041</td>
<td>74.07</td>
<td>14.4</td>
</tr>
<tr>
<td>37</td>
<td>III.</td>
<td>2</td>
<td>4.4</td>
<td>3.8649</td>
<td>0.01043</td>
<td>1.5095</td>
<td>73.99</td>
<td>14.5</td>
</tr>
<tr>
<td>38</td>
<td>III.</td>
<td>2</td>
<td>4.4</td>
<td>3.8327</td>
<td>0.01043</td>
<td>1.4932</td>
<td>74.33</td>
<td>15.1</td>
</tr>
<tr>
<td>39</td>
<td>III.</td>
<td>2</td>
<td>4.4</td>
<td>3.8597</td>
<td>0.01049</td>
<td>1.5053</td>
<td>74.18</td>
<td>15.4</td>
</tr>
<tr>
<td>23</td>
<td>VII.</td>
<td>2</td>
<td>0.86</td>
<td>3.8745</td>
<td>0.01394</td>
<td>1.3945</td>
<td>74.40</td>
<td>15.2</td>
</tr>
<tr>
<td>22</td>
<td>VII.</td>
<td>2</td>
<td>0.86</td>
<td>5.6274</td>
<td>0.01334</td>
<td>2.0675</td>
<td>74.53</td>
<td>14.5</td>
</tr>
<tr>
<td>20</td>
<td>IV.</td>
<td>2</td>
<td>0.61</td>
<td>1.2580</td>
<td>0.004728</td>
<td>0.5800</td>
<td>75.03</td>
<td>14.8</td>
</tr>
<tr>
<td>30</td>
<td>IV.</td>
<td>2</td>
<td>0.61</td>
<td>1.8440</td>
<td>0.004551</td>
<td>0.8815</td>
<td>74.29</td>
<td>14.3</td>
</tr>
<tr>
<td>21</td>
<td>V.</td>
<td>2</td>
<td>0.14</td>
<td>3.0412</td>
<td>0.01097</td>
<td>1.1612</td>
<td>74.12</td>
<td>14.9</td>
</tr>
<tr>
<td>31</td>
<td>V.</td>
<td>2</td>
<td>0.14</td>
<td>4.4577</td>
<td>0.01060</td>
<td>1.7387</td>
<td>74.03</td>
<td>14.0</td>
</tr>
<tr>
<td>24</td>
<td>A</td>
<td>3</td>
<td>—</td>
<td>8.2429</td>
<td>0.02912</td>
<td>1.2620</td>
<td>71.03</td>
<td>15.0</td>
</tr>
<tr>
<td>25</td>
<td>B</td>
<td>4</td>
<td>—</td>
<td>8.8476</td>
<td>0.03113</td>
<td>0.8222</td>
<td>73.40</td>
<td>14.9</td>
</tr>
<tr>
<td>26</td>
<td>C</td>
<td>6</td>
<td>—</td>
<td>9.3313</td>
<td>0.03312</td>
<td>0.4457</td>
<td>74.83</td>
<td>14.2</td>
</tr>
</tbody>
</table>

The values of $T$ for the orifices A, B, and C agree very well with those for the apertures for which $n = 2$, when due regard is taken to the amount of the amplitude.

In the following, notice is only taken of those orifices for which $n = 2$. 
In Table VIII. are given the mean values of $T_{15}$ corresponding to each aperture. It is evident that the orifices I. and II. have too great amplitudes. For the orifice III. it cannot with certainty be determined on the basis of Table VIII.; if the amplitude has any influence on the period it can only be said that the influence must be small. The amplitude for the next orifice, VII., is only one-fifth of that of orifice III., and there can therefore be no doubt that the amplitude of orifice VII. is sufficiently minute. That is still more certain for the orifices IV. and V. In Table VIII. is also inserted the mean value of $T_{15}$ for holes VII., IV., and V. taken together. This mean value is 74.34. The fourth column contains the values of $74.34 - T_{15}$ and the fifth column contains the values of $\frac{74.34 - T_{15}}{\delta^2}$ for the orifices I., II., and III. Finally in the last column the values of 0.02 $\delta^2$ are given for all the orifices. The numbers in the last two columns must naturally be taken with all possible reserve, but still they serve to explain, and at the same time also prove, the correctness of the above result, namely, that the amplitudes for holes VII., IV., and V. are so small that their values have no appreciable influence on the determination of the surface-tension.

Reference has only been made in the above to the amplitude of the aperture and

**Table IX.**

<table>
<thead>
<tr>
<th>Orifice</th>
<th>Pressure</th>
<th>$\delta$ measured on the jet</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>95 cm</td>
<td>37.6</td>
</tr>
<tr>
<td>I</td>
<td>43 cm</td>
<td>29.2</td>
</tr>
<tr>
<td>II</td>
<td>95 cm</td>
<td>16.3</td>
</tr>
<tr>
<td>III</td>
<td>43 cm</td>
<td>4.9</td>
</tr>
<tr>
<td>VII</td>
<td>43 cm</td>
<td>1.06</td>
</tr>
<tr>
<td>IV</td>
<td>43 cm</td>
<td>0.88</td>
</tr>
</tbody>
</table>
not to the jet itself. To get an idea of the size of the amplitude of the jet I have taken photographs of different jets, and afterwards by help of an object-micrometer measured the largest and smallest diameters at a distance of 3 to 4 cm. from the apertures. The results of these determinations are given in Table IX.; it appears that the amplitude of the jet is somewhat greater than the amplitude of the orifice, and that it increases with the pressure.

Therefore the above conclusion respecting the permissible amplitude will not always hold good. The pressure, about 70 cm., used by the measurements made here, lies, however, within the limits investigated in Table VII. (about 42 up to 97 cm. pressure).

The nature of the liquid may also play a part; but that has hardly any great influence as far as these investigations are concerned.

In order to attain greater certainty on this point I have determined the surface-tension of some other liquids by measurements with orifices III., V., and VII.; the results obtained are shown in Table X. This is calculated as follows: In the same manner as in Table VII., $T_{18}$ is determined for each individual orifice, and for each of these the mean value is taken. The mean value for all the measurements with apertures VII. and V. is taken as the correct value of the surface-tension for the liquid in question. Table X. contains the deviations from the mean value found in this manner, with reference to the orifices in question, shown as a percentage of the surface-tension.

**Table X.**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Orifice III.</th>
<th>Orifice V.</th>
<th>Orifice VII.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>per cent.</td>
<td>per cent.</td>
<td>per cent.</td>
</tr>
<tr>
<td>Ordinary tap-water</td>
<td>$-0.23$</td>
<td>$-0.31$</td>
<td>$+0.30$</td>
</tr>
<tr>
<td>Distilled water</td>
<td>$-0.34$</td>
<td>$-0.17$</td>
<td>$+0.19$</td>
</tr>
<tr>
<td>CuSO$_4$ + Ag; $p = 1.0506$</td>
<td>$+0.90$</td>
<td>$+0.07$</td>
<td>$+0.00$</td>
</tr>
<tr>
<td>5.79 per cent. alcohol + 94.21 per cent. water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean value</td>
<td>$-0.50$</td>
<td>$-0.25$</td>
<td>$+0.23$</td>
</tr>
</tbody>
</table>

It appears that the results for orifice VII. are generally a little larger than for orifice V. The difference lies, however, within the limit of error, as the determination for orifice V. is difficult. It proves, however, that under the present conditions the amplitude for orifice VII. is sufficiently small. On the other hand, however, it also appears that the values for orifice III. are, as a rule, a little too small. It would therefore be natural to carry out the measurements with orifices VII. and V. The determination is, however, in reality made with orifices VII. and III., for the following reason: The amplitude for orifice V. is so small that the determination of the wave-length is difficult and uncertain, especially for liquids with small surface-tension, or, in other words, large wave-lengths. On the other hand,
the measurements of the wave-length for orifice III. are carried out with great exactness and easiness, just as the determination with orifice VII. is, as a rule, quite good. I have therefore chosen these two orifices and corrected for the too great amplitude of orifice III. by adding 0·5 per cent. to the results, a correction obtained from Table X. In the following this correction is represented by [8].

Execution of Observations.

§ 11. All the experiments to No. 37 are made with ordinary tap-water under constant pressure, produced in the manner explained in § 4. In all the other experiments the pressure diminished as the liquid ran out. This variation was, however, only small, as the cross-section of the reservoir used was about 400 cm², and the quantity of liquid used about 1000 cm³. The pressure for all the experiments after No. 40 was about 70 cm.

The measurements themselves took place in the following manner:—

The orifice is closed by a wooden plug. The requisite quantity of liquid is poured into the reservoir, care being taken to fill both the conducting tube and the jet tube completely, the plug is withdrawn and the jet started. Then the jet is adjusted so as to be parallel to the plate-holder and to have the height suitable for the "jet-catcher." The last adjustment is easily controlled by the shadow of the jet on a ground glass placed in the frame and furnished with marks, between which the shadow must fall. At the same time the jet tube is moved until the image (m–n, fig. 14) of the jet is as sharp and clear as possible. In order to enable these adjustments to be made easily, the jet tube is arranged in a bridge that can be moved in all directions by help of screws.

As the direction of the "jet-catcher" once and for all is parallel to the frame, the jet by the above adjustments is brought into the required position and the measuring of its cross-section can take place. Immediately afterwards the measurements of the discharge begin, after which the plate-holder with an unexposed plate is placed in the frame, which is lying down. The light is then shut off, the shutter removed from the plate-holder and the slide moved into its position, whereupon the frame is brought up to its vertical position and the lamps L₄ and L₅ lighted. After exposing for about 15 seconds the lamps are turned out, the slide brought back and the shutter replaced in the plate-holder. The entire photographing process takes about 40 seconds. Before finishing the measurement of the discharge another photograph is taken in the same manner.

Finally the necessary weighing takes place and the evaporation is determined as explained in § 6.

In changing from one liquid to another the whole apparatus is cleaned very carefully and finally washed out with distilled water, after which it stands for some time to dry. Before use it is washed out with some of the liquid to be tested.
§ 12. On account of the pressure not being constant, it is necessary to investigate the influence of its variations.

According to § 7 the cross-section of the jet increases about 1 per cent. for every 10 cm. the pressure decreases. The cross-section ought, then, to be measured at mean pressure, but is in fact determined at the commencement of the experiment. If the liquid pressure has diminished $h$ cm. during the experiment, the mean cross-section is

$$A + \frac{h}{2000},$$

where $A$ is the measured cross-section. The corresponding correction $[\epsilon]$ in the surface-tension $T$ is, then, with sufficient exactness

$$[\epsilon] = T \cdot \frac{h}{4000} \ldots \ldots \ldots \ldots \ldots \ (1).$$

This correction is always negative.

Influence of the Variation of Pressure on the Wave-Length and Discharge.—If the effective pressure reduces from $H$ cm. to $H-h$ cm., the first photograph of the jet will correspond to the pressure $H-y$ cm. and the last with sufficient exactness to the pressure $H-h+y$ cm. The corresponding velocities are

$$V_a = \sqrt{2g(H-y)}; \quad V_b = \sqrt{2g(H-h+y)}.$$

The mean value is

$$V_{ab} = \frac{1}{2} [\sqrt{2g(H-y)} + \sqrt{2g(H-h+y)}] \ldots \ldots \ldots \ldots \ldots \ (2).$$

As $y$ and $h$ are small compared with $H$, this expression can without any appreciable error be reduced to

$$V_{ab} = \frac{1}{2} [\sqrt{2gH} + \sqrt{2g(H-h)}] \ldots \ldots \ldots \ldots \ldots \ (2').$$

As the wave-length is determined as the mean of the results from the two plates, $V_{ab}$ is the velocity corresponding to the wave-length measured. The average velocity $V_o$ that determines the discharge $Q$ is, as is known, similarly determined by

$$V_o = \frac{1}{2} [\sqrt{2gH} + \sqrt{2g(H-h)}].$$

In this manner no correction is demanded on account of variable pressure in the determination of the wave-length and the discharge.

The curvature of the jet produces a small error since the cross-section is determined for the highest part of the jet. The average cross-sectional area will therefore be a little smaller than that measured. Under the conditions used here this error will only be insignificant.
The influence of the viscosity is, according to equation [(4), § 1], determined by the coefficient

$$ g = 1 + \frac{\delta^2}{4\pi^2} \ldots \ldots \ldots \ldots \ldots (3), $$

where \( \delta \) is the logarithmic decrement of the vibration. The determination of \( \delta \) is made by measuring on the image \((m-n, \text{fig. 14})\) of the jet, making the supposition that the amplitudes of the image are proportionate to those of the jet. The results are—

For water:

\( \delta = 0.074 \); \( g = 1.00014 \);
\( \text{,, 98} : 04 \text{ per cent. alcohol + 1.96 per cent. water} \): \( \delta = 0.173 \); \( g = 1.00076 \);
\( \text{,, 46} : 34 \text{ per cent. alcohol + 53} : 66 \text{ per cent. water} \): \( \delta = 0.210 \); \( g = 1.00110 \);
\( \text{,, aniline} \): \( \delta = 0.265 \); \( g = 1.0018 \).

The numbers given are only approximate, but they show that \( g \), in all cases considered here, is almost equal to 1, and as the determination of \( \delta \) is uncertain, no correction is introduced. An exact investigation of the influence of the viscosity on the form of the jet image cannot be made until the theory of this image is further developed.

**Remarks on the Jet Photographs.**

§ 13. On Plates 3 and 4 are shown fifteen jet photographs. In each photograph the number of the orifice and the nature of the liquid are denoted.

The photographs are arranged according to the orifices, in the same order as in Table VII., and the remarks concerning them are given in the same order.

Plate 3, figs. 6, 7 and 8, shows clearly the influence of viscosity on the damping of the vibration. Fig. 6 is a water jet: this has only a very small damping. Fig. 8 is an alcohol jet: with this the damping is a little larger. Fig. 7 is a jet of a mixture of water and alcohol \((46:34 \text{ per cent. alcohol + 53} : 66 \text{ per cent. water})\): with this the damping is much greater than for the other two. The viscosity has about the following values in these three cases (Th. Gray, 'Physical Tables,' Table 151, 1897):

\( 0.012 \text{ by } 15^\circ \text{C.} ; \quad 0.036 \text{ by } 15^\circ \text{C.} ; \quad 0.014 \text{ by } 15^\circ \text{C.} \)

As the logarithmic decrement is the same for all vibrations, the fundamental vibration will be purer at some distance from the orifice than immediately after the jet has been formed, as is also shown on several of the photographs.

It appears from these photographs that the jet image is very well adapted to investigation of the jet vibrations. Similarly, they show that it is possible to make orifices which for all practical purposes are correct. In further investigations by this method it will be possible to go still farther in this direction.

All the jet photographs commence about 1.5 cm. from the orifice.
INVESTIGATED BY THE METHOD OF JET VIBRATION.

RESULTS.

Water.

§ 14. For the determination of the surface-tension of water I have made three series of measurements, the results of which are shown in the Tables XI., XII., and XIII.

The first table refers to ordinary tap-water, and gives a mean value

\[ T_{15} = 74.33 \text{ dyne/cm.} \]

The second table is for freshly distilled water, and gives

\[ T_{15} = 74.31 \text{ dyne/cm.} \]

The third table is for distilled water that has been kept for about a year in a stoppered bottle: the result is

\[ T_{15} = 74.23 \text{ dyne/cm.} \]

The greatest value found is in experiment No. 44 (Table XIII.):

\[ T_{15} = 74.80 \text{ dyne/cm.} \]

The least is in experiment No. 41 (Table XIII.), namely:

\[ T_{15} = 73.40 \text{ dyne/cm.} \]

The greatest deviation in the 18 experiments recorded in the Tables XI.-XIII. is thus about 1.9 per cent.

TABLE XI.—Ordinary Tap-Water.

\[ \rho_{15/4} = 0.99913, \quad \frac{d\rho}{dt} = -0.151. \]

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Orifice</th>
<th>Discharge of the jet.</th>
<th>Sectional area of the jet.</th>
<th>Wavelength.</th>
<th>( T_{15} )</th>
<th>( t )</th>
<th>([\epsilon])</th>
<th>([\delta])</th>
<th>( T_{15} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>III</td>
<td>2.9942</td>
<td>0.01073</td>
<td>1.1506</td>
<td>74.02</td>
<td>14.6</td>
<td>0.00</td>
<td>0.37</td>
<td>74.33</td>
</tr>
<tr>
<td>29</td>
<td>III</td>
<td>4.3291</td>
<td>0.01020</td>
<td>1.7041</td>
<td>74.07</td>
<td>14.4</td>
<td>0.00</td>
<td>0.37</td>
<td>74.35</td>
</tr>
<tr>
<td>37</td>
<td>III</td>
<td>3.8649</td>
<td>0.01043</td>
<td>1.5095</td>
<td>73.99</td>
<td>14.5</td>
<td>0.06</td>
<td>0.37</td>
<td>74.22</td>
</tr>
<tr>
<td>38</td>
<td>III</td>
<td>3.8327</td>
<td>0.01043</td>
<td>1.4932</td>
<td>73.33</td>
<td>15.1</td>
<td>0.07</td>
<td>0.37</td>
<td>74.54</td>
</tr>
<tr>
<td>39</td>
<td>III</td>
<td>3.8597</td>
<td>0.01049</td>
<td>1.5053</td>
<td>74.18</td>
<td>15.4</td>
<td>0.07</td>
<td>0.37</td>
<td>74.54</td>
</tr>
<tr>
<td>23</td>
<td>VII</td>
<td>3.9745</td>
<td>0.01384</td>
<td>1.3945</td>
<td>74.40</td>
<td>15.2</td>
<td>0.00</td>
<td>—</td>
<td>74.43</td>
</tr>
<tr>
<td>33</td>
<td>VII</td>
<td>5.6274</td>
<td>0.01334</td>
<td>2.0675</td>
<td>74.53</td>
<td>14.5</td>
<td>0.00</td>
<td>—</td>
<td>74.47</td>
</tr>
<tr>
<td>21</td>
<td>V</td>
<td>3.0412</td>
<td>0.01097</td>
<td>1.1612</td>
<td>74.12</td>
<td>14.9</td>
<td>0.00</td>
<td>—</td>
<td>74.12</td>
</tr>
<tr>
<td>31</td>
<td>V</td>
<td>4.4577</td>
<td>0.01060</td>
<td>1.7387</td>
<td>74.03</td>
<td>14.0</td>
<td>0.00</td>
<td>—</td>
<td>73.88</td>
</tr>
</tbody>
</table>

Mean value of orifice III.

Mean value of orifice VII.

Mean value of orifice V.

Mean value of all experiments.
Table XII.—Distilled Water.

Tested about two days after the distillation.

\[ \rho_{15/4} = 0.99913, \quad \frac{dT}{dt} = -0.151. \]

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Orifice</th>
<th>Discharge of the jet.</th>
<th>Sectional area of the jet.</th>
<th>Wavelength.</th>
<th>T&lt;sub&gt;t&lt;/sub&gt;</th>
<th>t.</th>
<th>[\epsilon].</th>
<th>[\delta].</th>
<th>T&lt;sub&gt;15&lt;/sub&gt;.</th>
</tr>
</thead>
<tbody>
<tr>
<td>129</td>
<td>III</td>
<td>3.8514</td>
<td>0.01042</td>
<td>1.5038</td>
<td>74.07</td>
<td>13.3</td>
<td>0.06</td>
<td>0.37</td>
<td>74.12</td>
</tr>
<tr>
<td>130</td>
<td>III</td>
<td>3.8516</td>
<td>0.01043</td>
<td>1.5000</td>
<td>74.41</td>
<td>13.6</td>
<td>0.06</td>
<td>0.37</td>
<td>74.51</td>
</tr>
<tr>
<td>131</td>
<td>VII</td>
<td>5.0647</td>
<td>0.01381</td>
<td>1.8424</td>
<td>74.36</td>
<td>14.0</td>
<td>0.06</td>
<td>—</td>
<td>74.15</td>
</tr>
<tr>
<td>132</td>
<td>VII</td>
<td>5.0696</td>
<td>0.01380</td>
<td>1.8408</td>
<td>74.64</td>
<td>14.2</td>
<td>0.06</td>
<td>—</td>
<td>74.45</td>
</tr>
</tbody>
</table>

Mean value of orifice III  
" " VII  
" " all experiments

74.32  
74.30  
74.31

Table XIII.—Distilled Water.

Tested about one year after the distillation. In the meantime kept in a corked vessel.

\[ \rho_{15/4} = 0.99913, \quad \frac{dT}{dt} = -0.151. \]

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Orifice</th>
<th>Discharge of the jet.</th>
<th>Sectional area of the jet.</th>
<th>Wavelength.</th>
<th>T&lt;sub&gt;t&lt;/sub&gt;</th>
<th>t.</th>
<th>[\epsilon].</th>
<th>[\delta].</th>
<th>T&lt;sub&gt;15&lt;/sub&gt;.</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>III</td>
<td>3.7997</td>
<td>0.01037</td>
<td>1.4869</td>
<td>73.83</td>
<td>19.0</td>
<td>0.06</td>
<td>0.37</td>
<td>74.74</td>
</tr>
<tr>
<td>41</td>
<td>III</td>
<td>3.7450</td>
<td>0.01032</td>
<td>1.4808</td>
<td>72.50</td>
<td>18.9</td>
<td>0.06</td>
<td>0.37</td>
<td>73.40</td>
</tr>
<tr>
<td>42</td>
<td>V.</td>
<td>3.9079</td>
<td>0.01079</td>
<td>1.5224</td>
<td>73.05</td>
<td>18.6</td>
<td>0.06</td>
<td>—</td>
<td>73.53</td>
</tr>
<tr>
<td>43</td>
<td>V.</td>
<td>3.8899</td>
<td>0.01074</td>
<td>1.5068</td>
<td>74.03</td>
<td>18.2</td>
<td>0.06</td>
<td>—</td>
<td>74.45</td>
</tr>
<tr>
<td>44</td>
<td>VII</td>
<td>4.9599</td>
<td>0.01354</td>
<td>1.8226</td>
<td>74.39</td>
<td>18.1</td>
<td>0.06</td>
<td>—</td>
<td>74.80</td>
</tr>
<tr>
<td>45</td>
<td>VII</td>
<td>4.9532</td>
<td>0.01358</td>
<td>1.8115</td>
<td>74.10</td>
<td>18.0</td>
<td>0.06</td>
<td>—</td>
<td>74.49</td>
</tr>
</tbody>
</table>

Mean value of orifice III  
" " V  
" " VII  
" " all experiments

74.07  
73.99  
74.64  
74.23

That the results are almost the same for the three kinds of water is not surprising, as Dupré* and Lord Rayleigh† have shown that even very considerable impurities

* Dupré, 'Théorie mécanique de la chaleur,' p. 376, Paris, 1869.
do not appreciably alter the surface-tension, as far as quite fresh surfaces are concerned.

As the result of my experiments I fix the initial value of the surface-tension of water as

\[ T_{15} = 74.30 \text{ dyne/cm.} \]

The surface-tension of water has been so often determined, and in so many manners, that even a moderately exhaustive representation of the results is impossible and, besides, without great interest, as many of the measurements have but little value. In Table XIV. are shown the results of a few determinations by the capillary-tube method, and Table XV. contains most of the results obtained by the method of capillary ripples.

With respect to the values found by the capillary-tube method, it appears that, with the exception of Quincke's values, they are all smaller than those found here. This is quite natural, because it is the stationary value of the surface-tension that is measured by the capillary-tube method. Under the given conditions this value must be smaller than the initial value.

The values found by the method of capillary ripples in most cases agree well with the value found here. They are as follows:—Lord Rayleigh, 74.35 dyne/cm.; Dorsey, 73.72; Watson, 74.76; and Kalähne, 74.22 dyne/cm. The mean value for all four is

\[ T_{15} = 74.26 \text{ dyne/cm.} \]

An exception from this, however, is made by Grunmach's measurements (Brümmern and Loewenfeld, who worked exactly in the same manner as Grunmach, are not mentioned here).

Grunmach's measurements divide themselves into two groups, the surface of the liquid being either the same during the investigation or continually renewed. Table XV. shows that Grunmach's value for distilled water in the first case is

\[ T_{15} = 78.41 \text{ dyne/cm.}, \]

and in the other

\[ T_{15} = 75.89 \text{ dyne/cm.} \]

These results are very extraordinary, for two reasons. Firstly, it would be expected that the former value would agree with the values found with the same method by other investigators. This, however, is far from being the case, as Grunmach's value, 78.41 dyne/cm., is 5.6 per cent. larger than the corresponding mean value, 74.26 dyne/cm., of the other measurements.

Secondly, it would be supposed that the surface-tension for the continually renewed surface would be the greater. Grunmach, however, came to the opposite result and found a value 3.3 per cent. lower in this case.

A satisfactory explanation of this circumstance will certainly demand fresh investigations, and before these are finished it will be difficult to judge of the value of
Table XIV.—The Surface-tension of Water. Method of Measurement, Capillary Tubes.

<table>
<thead>
<tr>
<th>Authority</th>
<th>Publication.</th>
<th>The surface in contact with</th>
<th>t</th>
<th>T₁₅</th>
<th>T₁₂₅</th>
<th>Remarks.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volkmann</td>
<td>'Wied. Ann.,' 56, p. 457, 1895</td>
<td>Damp air</td>
<td>15·0</td>
<td>73·26</td>
<td>73·26</td>
<td>Volkmann's values for temperatures from 0° to 40° C. are generally accepted as the most exact by this method of measurement.</td>
</tr>
<tr>
<td>Quincke</td>
<td>'Wied. Ann.,' 52, p. 1, 1894</td>
<td>Damp air</td>
<td>18</td>
<td>72·4 to 76·9</td>
<td>72·9 to 77·4</td>
<td>Of Quincke's many publications I have here only quoted that containing his latest determinations.</td>
</tr>
<tr>
<td>Domke</td>
<td>'Wiss. Abh. d. K. Norm.-Aich.-Komm.,' Heft III, 1902</td>
<td>Damp air</td>
<td>18·2</td>
<td>72·98</td>
<td>73·46</td>
<td></td>
</tr>
<tr>
<td>Weinstein</td>
<td>'Metronomische Beiträge,' No. 6, 1889</td>
<td>Damp air</td>
<td>20·0</td>
<td>71·1</td>
<td>71·86</td>
<td></td>
</tr>
<tr>
<td>Ramsay and Shields</td>
<td>'Zeitschr. phys. Chem.,' 12, p. 471, 1893</td>
<td>Saturated vapour</td>
<td>20·0</td>
<td>70·6</td>
<td>71·36</td>
<td>The water was tested in sealed glass tubes.</td>
</tr>
<tr>
<td>Sentis</td>
<td>'Journ. d. Phys.,' 6, p. 183, 1897</td>
<td>Damp air</td>
<td>20·0</td>
<td>73·0</td>
<td>73·76</td>
<td></td>
</tr>
<tr>
<td>Rodenbeck</td>
<td>'Diss.,' Bonn, 1879, Beibl. 4, p. 104</td>
<td>Damp air</td>
<td>17·5</td>
<td>71·7</td>
<td>72·08</td>
<td></td>
</tr>
<tr>
<td>Rother</td>
<td>'Wied. Ann.,' 21, p. 576, 1884</td>
<td>Damp air</td>
<td>15·0</td>
<td>72·02</td>
<td>72·02</td>
<td>Tested by tubes of elliptical cross-section.</td>
</tr>
<tr>
<td>Goldstein</td>
<td>'Zeitschr. phys. Chem.,' 5, p. 233, 1890</td>
<td>Damp air</td>
<td>22·0</td>
<td>72·2</td>
<td>73·26</td>
<td></td>
</tr>
<tr>
<td>Authority</td>
<td>Publication</td>
<td>The surface in contact with</td>
<td>( t )</td>
<td>( T_p )</td>
<td>( T_{12} )</td>
<td>Remarks</td>
</tr>
<tr>
<td>--------------------</td>
<td>---------------------------------------</td>
<td>-----------------------------</td>
<td>--------</td>
<td>----------</td>
<td>-----------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Rayleigh</td>
<td>'Phil. Mag.,' 30, p. 386, 1890 ('Papers III,' 391)</td>
<td>Damp air</td>
<td>18</td>
<td>73.9</td>
<td>74.35</td>
<td>Distilled water and ordinary tap-water without appreciable difference.</td>
</tr>
<tr>
<td>Dorsey</td>
<td>'Phil. Mag.,' 44, pp. 134, 369, 1897</td>
<td>Damp air</td>
<td>18</td>
<td>73.17</td>
<td>73.72</td>
<td></td>
</tr>
<tr>
<td>Watson</td>
<td>'Phys. Rev.,' 12, p. 257, 1901</td>
<td>Damp air</td>
<td>20</td>
<td>74.0</td>
<td>74.76</td>
<td></td>
</tr>
<tr>
<td>A. Kalähne</td>
<td>'Ann. d. Phys.,' 7, p. 440, 1902</td>
<td>Damp air</td>
<td>18</td>
<td>73.81</td>
<td>74.26</td>
<td>Water in a glass dish filled to overflowing.</td>
</tr>
<tr>
<td>A. Kalähne</td>
<td>'Ann. d. Phys.,' 7, p. 440, 1902</td>
<td>Damp air</td>
<td>18</td>
<td>73.77</td>
<td>74.22</td>
<td>Kalähne's mean value.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Grunmach's values differ up to 16 per cent. from each other (see Experiments 30 IV. and 7 V., p. 152).</td>
</tr>
<tr>
<td>A. Brümmer</td>
<td>'Diss.,' Rostock, 1903</td>
<td>Damp air</td>
<td>15</td>
<td>74.92</td>
<td>74.92</td>
<td>Distilled water with surface renewal. Greatest deviation between his results is 3.9 per cent.</td>
</tr>
<tr>
<td>Kolowrat-Tscherwinski</td>
<td>'J. d. russ. phys. chem. Ges.,' 36, 1904</td>
<td>Damp air</td>
<td>0</td>
<td>75.02</td>
<td>72.77</td>
<td>Grunmach's method with surface renewal.</td>
</tr>
<tr>
<td>K. Loewenfeld</td>
<td>'Diss.,' Berlin, 1905</td>
<td>Damp air</td>
<td>15</td>
<td>75.30</td>
<td>75.30</td>
<td>Grunmach's method with surface renewal.</td>
</tr>
</tbody>
</table>
Grunmach's results. I cannot, however, omit to draw attention to the fact that the mutual agreement between Grunmach's values is only small. Within the first group of measurements the deviation amounts up to 16 per cent., and for the last to 3·9 per cent.

The lowest of Grunmach's values in the two cases are

$$T_{15} = 70·4 \text{ dyne/cm.} \quad \text{and} \quad T_{15} = 74·2 \text{ dyne/cm.}$$

Both are lower than the values found here.

**Toluol.**

The value found according to Table XVI. is

$$T_{15} = 28·76 \text{ dyne/cm.,}$$

in complete agreement with Volkmann's results, namely,

$$T_{15} = 28·79 \text{ dyne/cm.}$$

This was to be expected, as in this case the initial and the stationary value of the surface-tension must be very nearly equal.

**Aniline.**

The liquid used was marked "pure," but was, however, a little coloured.

The result of the measurements is shown in Table XVI. The value is

$$T_{15} = 43·00 \text{ dyne/cm.}$$

The corresponding value by Volkmann is

$$T_{15} = 44·30 \text{ dyne/cm.,}$$

also considerably larger. To this may be remarked that Volkmann himself estimates his determination as somewhat uncertain, and, further, that aniline is somewhat soluble in water, so that there has possibly been formed a layer of water on its surface. Using the method of the maximum pressure of small air bubbles, Feustel* found

$$T_{15} = 46·6 \text{ dyne/cm.}$$

**Aqueous Solutions of Ammonia.**

Measurements were made on three solutions of ammonia. The values are (see Table XVI.),

For $\rho_{15/4} = 0·99030, \quad T_{15} = 71·25 \text{ dyne/cm.,}$

$\rho_{15/4} = 0·97921, \quad T_{15} = 68·02 \text{ dyne/cm.,}$

$\rho_{15/4} = 0·95801, \quad T_{15} = 64·69 \text{ dyne/cm.}$

* Feustel, loc. cit.
INVESTIGATED BY THE METHOD OF JET VIBRATION.

TABLE XVI.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Density $\rho_{15/4}$</th>
<th>Number of measurements</th>
<th>Greatest deviation from the mean value</th>
<th>Mean value $T_{15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluol</td>
<td>0.86736</td>
<td>2</td>
<td>0.07 0.50</td>
<td>dyne/cm. 28.76</td>
</tr>
<tr>
<td>Aniline</td>
<td>1.0250</td>
<td>5</td>
<td>0.66 0.75</td>
<td>43.00</td>
</tr>
<tr>
<td>Aqueous solution of ammonia</td>
<td>0.99030</td>
<td>4</td>
<td>0.50 0.66</td>
<td>71.25</td>
</tr>
<tr>
<td>Solution of copper sulphate</td>
<td>1.05030</td>
<td>6</td>
<td>0.53 0.53</td>
<td>74.27</td>
</tr>
<tr>
<td>Diluted sulphuric acid</td>
<td>1.08130</td>
<td>4</td>
<td>1.30 0.89</td>
<td>74.89</td>
</tr>
<tr>
<td>Aqueous ethyl alcohol—</td>
<td>1.14316</td>
<td>4</td>
<td>0.89 0.89</td>
<td>74.44</td>
</tr>
</tbody>
</table>

For comparison I will take the values found by Domke* by the capillary-tube method. The values of Domke and those of the author agree fairly well, as the last, as could be expected, are all a little larger than the first. If we compare Domke's values augmented with the difference between the author's and Domke's results for distilled water (namely, $74.30 - 73.00 = 1.30$ dyne/cm.), it appears that the difference between the two sets of values is not great (see Table XVII).

Loewenfeld† has determined the surface-tension of ammonia by the method of capillary ripples with surface renewal. His results differ rather much from the author's.

---

† Loewenfeld, 'Diss.,' Berlin, 1905.
Solution of Copper Sulphate.

\[ \rho_{15/4} = 1.0503. \]

The mean value of the determination of the surface-tension of this solution is found in Table XVI,

\[ T_{15} = 74.27 \text{ dyne/cm}. \]

The value is practically the same as for water.

Diluted Sulphuric Acid.

Of diluted sulphuric acid two different concentrations were investigated. The mean values are (see Table XVI.)

For \( \rho_{15} = 1.0813 \), \( T_{15} = 74.89 \text{ dyne/cm} \),

\[ T_{15} = 74.44 \text{ dyne/cm}. \]

The corresponding values, according to GRUNMACH (with capillary-wave method with renewed surface), are

\[ T_{15} = 76.5 \text{ dyne/cm.} \quad \text{and} \quad T_{15} = 77.8 \text{ dyne/cm}. \]

Aqueous Ethyl Alcohol.

DOMKE* has given a table of the results obtained by different authors for the surface-tension of absolute alcohol. The results are reduced to a temperature of 15° by the use of \( dT/dt = -0.08 \). The mean value of the fifteen values considered is

\[ T_{15} = 23.1 \text{ dyne/cm}. \]

The lowest value is \( T_{15} = 22.2 \text{ dyne/cm} \), the highest is \( T_{15} = 24.3 \text{ dyne/cm} \).

DOMKE himself found by the capillary-tube method,

\[ T_{15} = 23.0 \text{ dyne/cm}. \]

Grunmach* found by the method of capillary ripples:

For absolute alcohol that has not been in contact with the air and for a continually renewed surface. \[ T_{18} = 19.6 \text{ dyne/cm.} \]
For absolute alcohol the surface of which had been in contact with the air for one half-hour. \[ T_{18} = 21.2 \text{ dyne/cm.} \]
For absolute alcohol that had for some time been continually in contact with the air. \[ T_{18} = 26.3 \text{ dyne/cm.} \]

The author determined the surface-tension of several mixtures of alcohol and water. The mixtures investigated and the results obtained are shown in Table XVI. The value of \( dT/dt \) used by the calculation of the table is determined by the following formula:

\[
\frac{dT}{dt} = -(0.151 - p \cdot 0.0007),
\]

where \( p \) is the percentage of alcohol by weight.

The results are shown in Plate 2, fig. 1, where also the results found by B. Weinstein† are shown.

With regard to the surface-tension of absolute alcohol it can pretty certainly be taken that the value determined by this method will very approximately be

\[ T_{18} = 22.5 \text{ dyne/cm.} \]

in complete disagreement with the value found by Grunmach, \( T_{18} = 19.6 \text{ dyne/cm.} \), in the case of continuous surface renewal.

How this great difference is produced must be determined by further investigations on the subject.

Concluding Remarks.

§ 15. In the use of Lord Rayleigh’s method for the determination of the surface-tension of liquids it is necessary to pay attention to the following remarks:

It is necessary to determine either the velocity or the cross-section of the jet by direct measurement, as the calculation of the velocity from Torricelli’s formula may lead to great errors.

The greatest care must be taken to obtain jets executing one vibration only, corresponding to only one value of \( n \).

The amplitude of vibrations must be very small.

The determination of the wave-length must be performed by suitable optical

* Grunmach, loc. cit.
† Weinstein, 'Metronomische Beiträge,' No. 6, Berlin, 1889.
methods, as the smallness of the amplitudes renders the direct measurement impossible.

With due consideration of the above remarks, Lord Rayleigh's method is a very good one, and is highly deserving of use in the future on account of its great fundamental advantages.

With regard to the results obtained in this investigation, the author desires to call attention to the remarkable discrepancies between his results and those of Grunmach, who used the method of capillary ripples with renewal of the surface (see p. 343 above). It was to be expected that the difference between the two sets of values should be small, and further, that Grunmach's values should be intermediate between the author's values and those obtained by the capillary-tube method. But that is very far from being the case: the differences are rather great, and of a sign opposite to that expected.

In further application of this method the author would propose to use apertures with amplitudes between 4·0 and 0·5; for instance, the following set:

\[
\delta = 4·0, \delta = 2·0, \delta = 1·0, \text{ and } \delta = 0·5.
\]

**Table XVIII.**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Experiment No.</th>
<th>T₁₅</th>
<th>H</th>
<th>μ₁₅</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluol</td>
<td>156</td>
<td>28·75</td>
<td>67·4</td>
<td>0·0064</td>
<td>0·00994</td>
</tr>
<tr>
<td>Water</td>
<td>129</td>
<td>74·12</td>
<td>69·6</td>
<td>0·0114</td>
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Table XVIII contains a few results compiled from the above measurements, illustrating the relation between the cross-section of the jet (A) and the coefficient of viscosity (μ). The table is calculated for orifice III.; H is the effective head. The table shows that the cross-section increases with the viscosity.
INVESTIGATED BY THE METHOD OF JET VIBRATION.

Table of \( \log \mu_n(x) + 10 \).

\( n = 2, 3, 4, 6 \). \( 0 \leq x \leq 1 \).

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X. The Normal Weston Cadmium Cell.

By F. E. Smith, A.R.C.Sc.

(From the National Physical Laboratory.)

Communicated by R. T. Glazebrook, F.R.S.

Received July 13,—Read November 21, 1907.

The experimental investigations described in this communication had as their primary object the improvement of the Clark and Weston Cadmium Cells as standards of electromotive force.

The older investigations of Rayleigh,† Kahlé,‡ and Glazebrook and Skinner§ proved the Clark cell to be very trustworthy, and only within the last few years has any serious attempt been made to displace it from the premier position in which it was placed in 1894. In 1892 Weston§ introduced the cell bearing his name. This cell contains a solution of cadmium sulphate instead of zinc sulphate, as in the Clark, and an alloy of cadmium and mercury forms the negative pole. As originally specified, the solution was saturated at 4° C., and no crystals of cadmium sulphate were inserted in the cell; under normal conditions there was therefore no change in the concentration for small variations in temperature. When the solution is saturated at all temperatures, i.e., when solid cadmium sulphate is always present in the cell, the name “Cadmium Cell” has been frequently assigned to it in order to distinguish it from the original form. In this communication the latter cell is the type experimented with, and since it is referred to as the Weston Cadmium Cell in the reports of the International Conference the same name has been adopted by the author.

* Lord Rayleigh, ‘Phil. Trans.,’ 175, p. 412, 1884, and 176, p. 781, 1886.
MR. F. E. SMITH ON THE NORMAL WESTON CADMIUM CELL.

Lord Rayleigh* was the first to point out that the quality of the mercurous sulphate used as the depolariser in Clark cells was a cause of variation in E.M.F.; and Mr. Swinburne† arrived at the same conclusion in 1891. Later Jaeger and Lindeck‡ attributed similar variations in the Weston cadmium cell to the same salt.

In 1902 some experiments at the National Physical Laboratory§ plainly indicated that the mercurous sulphate might produce variations in the E.M.F. as great as 0·002 volt, or 1 part in 700 of the voltage of the Clark cell. A new specification of the mode of manufacture of the depolariser was thought to be desirable, and experiments were immediately made with this end in view.

Almost simultaneously Carhart and Hulett,‖ at the University of Michigan, and Wolff,¶ at the National Bureau of Standards, Washington, attacked the same problem, and a little later H. v. Steinwehr,** at the Physikalisch-Technische Reichsanstalt, made a special study of the change of E.M.F. produced by varying the size of the crystals of the depolariser. While it must be admitted that the chemistry of the standard cell is still incomplete, an analysis of results shows that different observers can set up cells of almost identical E.M.F., and that their constancy is many times that of the standards used ten years ago.

Preparation of the Materials.

Mercury.

In all our work the commercial mercury was cleaned with dilute nitric acid, washed with distilled water, and distilled twice in vacuo.

The Depolariser.

At the National Physical Laboratory the mercurous sulphate has been prepared in four ways: (1) Electrolytically; (2) by chemical precipitation, mercurous nitrate being added to sulphuric acid; (3) by the re-crystallisation of purchased samples of mercurous sulphate from strong sulphuric acid; and (4) by the action of fuming sulphuric acid on mercury.

The first of these methods was developed in 1904 by Carhart and Hulett‖ and also independently by Wolff.¶ The mercurous sulphate is formed at a mercury

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* Lord Rayleigh, 'Phil. Trans.,' 175, p. 412, 1884, and 176, p. 781, 1886.
† J. Swinburne, 'British Association Report,' Section A, 1891.
‡ W. Jaeger and St. Lindeck, 'Zeitschr. f. Instrumentenk.,' 21, p. 33, 1901.
§ F. E. Smith, 'British Association Report,' Section A, 1904.
anode in dilute sulphuric acid, the latter, in the experiments made at the National Physical Laboratory, consisting of 1 volume of strong sulphuric acid (density 1·84) to 5 volumes of water; its strength was, therefore, about 3·0 molecular. The anode surface was kept well exposed by a glass stirrer, and the current density was from 1 to 5 amperes per 100 sq. centims. of anode surface. In the second method purchased protonitrate of mercury was sometimes used, but more often it was made from mercury and nitric acid. About 15 cub. centims. of concentrated nitric acid was added to 100 grammes of mercury, and when the action was over, or nearly over, the resulting solution was added to 200 cub. centims. of dilute nitric acid (1 of acid to 40 of water). The acid solution of mercurous nitrate thus formed was run as a very fine stream from the narrow orifice of a pipette into 1000 cub. centims. of hot dilute sulphuric acid (1 to 6), the liquid being well stirred during the mixing. Mercurous sulphate was precipitated. It was washed two or three times by decantation with dilute sulphuric acid (1 to 6) and filtered. The third method of manufacture is more costly. A purchased sample of the salt is heated with concentrated sulphuric acid to a temperature of about 150° C. and the hot clear acid carefully poured into dilute sulphuric acid (1 to 6), when precipitation of pure mercurous sulphate results. The fourth method, as originally employed, is troublesome. Fuming sulphuric acid is added to pure distilled mercury and stirred well until the action between the two is practically at an end. Mercurous sulphate is thus formed in the cold and appears in the crystalline form after a few minutes. Equally satisfactory results are obtained, however, if sufficient mercury is placed in a crystallising dish to cover the base and the fuming sulphuric acid added to a depth of 2 or 3 millims. The dish is covered with a clock glass and placed in a dark room for one or two weeks.

In all the methods of production the resulting mercurous sulphate was washed two or three times by decantation with dilute sulphuric acid (1 to 6) and afterwards introduced into a Buchener funnel for the removal of the acid as completely as possible by exhaustion with a filter pump. The sides of the funnel were washed down with neutral saturated cadmium sulphate solution and the salt washed 5 or 6 times with more of the same solution. About 5 cub. centims. was needed for each washing. In a few instances the sulphate was straightway employed for the manufacture of the depolarising paste, but in the majority of cases it was transferred together with a little of the cadmium sulphate solution to a small stock bottle. After a week or ten days the solution was always slightly acid to congo red paper and the mercurous sulphate was therefore washed once more before using.

In much of the earlier work absolute alcohol which had been specially distilled was employed for washing the mercurous sulphate, and the salt was stored in contact with more of the same liquid. We cannot, however, recommend this procedure, as we believe slight hydrolysis results, owing to the absorption of moisture by the alcohol.
Cadmium Amalgam.

The amalgam has been prepared in two ways, (1) by depositing cadmium electrolytically in a weighed quantity of pure mercury, the electrolyte being an acid solution of cadmium sulphate, (2) by heating together pure cadmium and mercury, the resulting mass being washed with dilute sulphuric acid to remove the surface dross. The amalgams used have been one part of cadmium to seven parts of mercury (12 1/2 per cent.) or one part of cadmium to nine parts of mercury (10 per cent.). We have employed amalgams of other concentrations, but not in the cells discussed in this paper. The investigations of Dearlove,* Kerp and Boettger,† Bijl,‡ Puschin,§ and Jaeger|| have shown that attention must be paid to the percentage of cadmium in the amalgam. It appears probable that in an amalgam containing between 6 and 14 per cent. of cadmium, there is at normal temperatures a solid and a liquid phase, of which the former is an isomorphous mixture of mercury and cadmium. The E.M.F. of the amalgam towards a cadmium sulphate solution does not depend on the relative amounts of the two phases, and on adding cadmium to the amalgam no change in E.M.F. occurs therefore until the liquid phase disappears. Similarly, if cadmium is extracted from the mixture the E.M.F. is constant until the solid phase disappears. A rise in temperature increases the liquid and diminishes the solid phase: for any particular amalgam there are, therefore, limits of temperature between which the two phases are always present. Jaeger has shown that for all amalgams in which the two phases exist the E.M.F. towards a cadmium sulphate solution is constant for a given temperature. Dearlove first proposed a 12 1/2 per cent. amalgam; this is satisfactory at all ordinary temperatures and has been generally employed.

The Cadmium Sulphate.

We have usually ground the purchased crystals and made a saturated or nearly saturated solution by agitation and warmth. This was filtered to clear and placed in crystallising dishes to slowly evaporate. The resulting crystals were well washed several times with water and the final solution tested for acidity with congo red paper.

A saturated solution of cadmium sulphate yields crystals of the composition CdSO₄·nH₂O at all temperatures up to 74° C., when CdSO₄·6H₂O separates instead. Kohnstamm and Cohen¶ believed that they had discovered a transition point at

about 17° C., but the irregularities were afterwards traced by Cohen* to a transition which the 14.3 per cent. amalgam which was used undergoes at 23° C. The solution has also been investigated by H. v. Steinwehr,† who failed to confirm any transition point at about 17° C. Cadmium sulphate is very soluble and increases very little in solubility over the ordinary range of temperature. As purchased, the crystals are generally acid, and in all cases it appears necessary to purify by recrystallisation.

Setting up of the Cell.

We have employed the Rayleigh H form of cell in nearly all our work. A platinum wire was fused into the lower end of each limb, and the parts of the wire inside the vessel were amalgamated by passing an electric current from a platinum anode through an acid solution of mercurous nitrate to each of the wires in turn. The vessel was washed out twice with dilute nitric acid, and several times with distilled water; it was dried in an oven. A small pipette was used for the introduction of the amalgam, and a small thistle funnel for the insertion of the mercurous sulphate paste and cadmium sulphate crystals. The main stock of amalgam was flooded with very dilute sulphuric acid, and melted over a water bath; a little was then introduced into one of the limbs of the H vessel. After the amalgam had solidified the limb containing it was washed out several times with distilled water, care being taken not to wet the interior of the other limb. A little distilled water was then added, and the amalgam again melted by immersing the H vessel in hot water; after solidification it was washed once more. Into the other limb of the vessel sufficient mercury was added to cover the amalgamated platinum wire and then the mercurous sulphate paste was introduced. The paste consisted of mercurous sulphate mixed with about one-fourth its volume of powdered recrystallised cadmium sulphate, and about one tenth its volume of pure mercury. (The latter was not added when the mercurous sulphate was prepared electrolytically or by means of fuming sulphuric acid.) To this mixture sufficient saturated cadmium sulphate solution was added, so that when well mixed the whole formed a thin paste. After the introduction of some of this paste into the limb containing the mercury, powdered crystals of cadmium sulphate were added to the contents of each limb, and after an interval of one hour sufficient saturated cadmium sulphate solution was inserted to fill the vessel to the top of the cross-connecting-tube. The cells were hermetically sealed with the aid of a blow-pipe. For the comparison of their electromotive forces the cells were immersed in paraffin oil and were maintained at an approximately constant temperature of 17° C. The comparisons were made by means

of a high-resistance (15,000 ohms) potentiometer made by O. Wolff, of Berlin, and a Broca galvanometer of 1000 ohms resistance made in the workshops of the National Physical Laboratory. It was quite easy to read to one hundred-thousandth of a volt, and, if necessary, one-tenth of this could be estimated with considerable accuracy.

When testing samples of mercurous sulphate we have often used a four-limb vessel similar to two Rayleigh H-form vessels crossed. Cadmium amalgam was placed in one limb, and in the other three mercury and the depolarisers were inserted. The electrolyte was a saturated solution of cadmium sulphate.

Unit of Electromotive Force.

In a recent communication to the Royal Society, Professor Ayrton, Mr. Mather, and the author* have given the E.M.F. of some of the cells included in Table I. in terms of the ampere \((10^{-1}\text{ C.G.S.})\) and the international ohm. While it must be admitted that this E.M.F. is possibly different from the true E.M.F. in volts \((10^{-8}\text{ C.G.S.})\) by 2 or perhaps 3 parts in 10,000, it is probably the most accurate value known, and has the further advantage of being the mean of values the observations of which extended over 19 months. A further deduction is that the E.M.F. of most of the cells under observation did not change in this period by more than 0.000001 volt. We have therefore given the E.M.F. of cells in Table I. in terms of the ampere \((10^{-1}\text{ C.G.S.})\) and the international ohm.

It is impossible to give all the observations over the period 1904–1907; those given are at approximately equal intervals of time. In cases where considerable changes in the E.M.F. have resulted, more extensive observations are given in subsequent tables. The values for the period May, 1904, to October, 1905, have been deduced from intercomparisons of cells, as no value in terms of the ampere and international ohm could be assigned until the later date.

Table I. gives the results of the observations on 60 cells. Since 1904 more than 200 cells have been set up, and a few of those which seem to be most valuable from the point of view of results obtained are included in the table. For the 60 cells in Table I., 16 samples of mercurous sulphate have been used, 6 of cadmium amalgam and 5 of cadmium sulphate. In some cases the mercurous sulphate was washed with alcohol; the letter A is then inserted in column 5 of the table. The approximate depth of the paste is given in column 6, and the numbers in column 7 indicate the range of the dimensions of the mercurous sulphate crystals in thousandths of a millimetre. Particulars of the cadmium amalgam are given in columns 8 and 9; E indicates that the amalgam was prepared by the electro-deposition of cadmium, and F by the fusion of cadmium and mercury. The mercurous sulphate was usually prepared two weeks in advance of its use as a depolariser in a cell.

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<td>N 25</td>
<td>&quot;</td>
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</table>
Table I. (continued).

<table>
<thead>
<tr>
<th>Cell.</th>
<th>Date of manufacture</th>
<th>Depolariser.</th>
<th>Cadmium amalgam.</th>
<th>Electromotive force at 17° C.</th>
<th>Mean E.M.F., June, 1907.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 41</td>
<td>Mar., 1906</td>
<td>II.</td>
<td>6</td>
<td>6</td>
<td>5 to 30</td>
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<td></td>
<td></td>
<td>III.</td>
<td>4</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>HA 7</td>
<td>Nov., 1906</td>
<td>II.</td>
<td>12</td>
<td>6</td>
<td>5 to 30</td>
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<tr>
<td>P 410</td>
<td>Mar., 1907</td>
<td></td>
<td>14</td>
<td>5</td>
<td>12 1/2</td>
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<tr>
<td>AB 1</td>
<td>Jan., 1905</td>
<td>IV.</td>
<td>3</td>
<td>8</td>
<td>12 1/2</td>
</tr>
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<td></td>
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<tr>
<td>D 1</td>
<td></td>
<td>I.</td>
<td>4</td>
<td>7</td>
<td>12 1/2</td>
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<td></td>
</tr>
<tr>
<td>M 6</td>
<td>Feb., 1906</td>
<td></td>
<td>6</td>
<td>7</td>
<td>10</td>
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</tbody>
</table>
Discussion of the Results.

Effect of Various Amalgams.

The E.M.F.'s of the cells set up with amalgams prepared at different times agree under otherwise equal conditions within 1 part in 100,000. The amalgam prepared by the electrodeposition of cadmium in mercury is perhaps preferable for the cells of standardising institutions, but our observations do not show any certain difference between it and that prepared by the fusion of cadmium and mercury, when the latter amalgam is freed from dross.

Effect of the Cadmium Sulphate.

We have obtained our cadmium sulphate from various sources, but after one crystallisation and thorough washing of the crystals with water no certain difference in the behaviour of the solutions has been detected.

Effect of the Depolariser.

The mean value of the cells set up with the electrolytic mercurous sulphate is 1.01828 volts; that of the cells containing the salt prepared by chemical precipitation (Method II.) is 1.01830 volts; when mercurous sulphate was employed which had been precipitated from hot strong sulphuric acid, 1.01832 volts is the mean; and the salt prepared with fuming sulphuric acid gives 1.01831 volts.

We conclude that the mode of manufacture of the mercurous sulphate is immaterial, provided that certain conditions are observed, and our guiding principle in the manufacture of the salt and the preparation of the paste is to prevent hydrolysis by keeping the salt in contact with dilute sulphuric acid (1 to 6), or with saturated cadmium sulphate solution. This is in accordance with Hulett's investigations.

Carhart and Hulett* have examined Weston cadmium cells containing electrolytic and chemically prepared sulphate (Method II.), and conclude that there is no appreciable difference in E.M.F. Later, Hulett† constructed two other cells containing the chemical sulphate, and found them about 0.00015 volt higher than cells containing the electrolytic salt. He concludes that the electrolytic sulphate is the most reliable preparation. Dr. F. A. Wolff and C. E. Waters‡ have examined many more specimens, and conclude that the four methods dealt with in this communication give practically identical results. They have also examined samples of mercurous sulphate prepared by the action of sulphuric acid containing a small percentage of nitric acid on mercury (Lunge reaction): by the reduction of mercuric sulphate by mercury, and by digesting commercially pure samples of mercurous

‡ F. A. Wolff and C. E. Waters, 'Electrical World,' 49, pp. 100, 101, January 12, 1907.
sulphate with sulphuric acid. The last method gave the largest difference, but this was of the order of 5 parts in 100,000 only.

Mr. J. A. Sadd, A.C.G.I., a student demonstrator of the Central Technical College, has constructed some cadmium cells in accordance with a specification published by the author* in 1905. These cells contain mercurous sulphate prepared electrolytically, and were forwarded to the National Physical Laboratory for comparison with our standards. There are ten cells in all, and their values at 17° C. are as follows:—

1'01832 volts. 1'01839 volts.

<table>
<thead>
<tr>
<th></th>
<th>34</th>
<th>39</th>
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<tbody>
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<td></td>
<td>35</td>
<td>40</td>
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<tr>
<td></td>
<td>37</td>
<td>42</td>
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<tr>
<td></td>
<td>38</td>
<td>43</td>
</tr>
</tbody>
</table>

Mr. H. Tinsley, of Beckenham, Kent, has also prepared some cadmium cells in accordance with the specification mentioned above. In this case the depolariser was prepared with mercurous sulphate precipitated by adding mercurous nitrate to sulphuric acid (Method II.). Most of Mr. Tinsley’s cells are also greater in E.M.F. than the N.P.L. standards, the difference being about 1 part in 10,000.

In May, 1907, 12 cadmium cells prepared by Dr. F. A. Wolff of the National Bureau of Standards, Washington, were brought to England by Dr. Burgess, and a direct comparison between the cells of the two institutions was thus rendered possible. Cells which were believed to nearly represent the normal cell were chosen to compare with those from Washington, and the following differences were observed:—

**Table II.**

<table>
<thead>
<tr>
<th>National Bureau of Standards</th>
<th>National Physical Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>cadmium cells.</td>
<td>cadmium cells.</td>
</tr>
<tr>
<td><strong>Cell.</strong></td>
<td>E.M.F. of cell minus mean E.M.F. of all microvolts.</td>
</tr>
<tr>
<td>WP 8</td>
<td>+ 1</td>
</tr>
<tr>
<td></td>
<td>9</td>
</tr>
<tr>
<td>W 10</td>
<td>0</td>
</tr>
<tr>
<td>105</td>
<td>- 11</td>
</tr>
<tr>
<td>182</td>
<td>0</td>
</tr>
<tr>
<td>184</td>
<td>+ 1</td>
</tr>
<tr>
<td>186</td>
<td>- 1</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* F. E. Smith, ‘British Association Report,’ Section A, 1905
The mean E.M.F. of the 12 "National Bureau of Standards" cells is less than the mean E.M.F. of the 12 N.P.L. cells by 3 microvolts.

P 52, P 53, P 54, and P 55 were set up in November, 1906,
C 12, C 17, C 19, and C 117 " June ",
H 26, H 28, and H 29 " February, 1907,
P 210 " March ",

The mean E.M.F. of the 12 N.P.L. cells is not quite the mean of all the N.P.L. cadmium cells, which are believed to be normal; the latter cells have the higher mean by about 2 parts in 100,000.

Eleven of the twelve cadmium cells from Washington contain electrolytic mercurous sulphate; the twelfth, W 105, contains mercurous sulphate prepared by the Lunge reaction. The depth of the pastes in these cells is about 1·5 centims. The twelve cells of the National Physical Laboratory contain mercurous sulphate prepared chemically (Method II.), and the depth of the paste is about 0·5 centim. The nett result of these comparisons with other observers is that mercurous sulphate of sufficiently uniform properties can be prepared in several ways, provided that certain conditions are observed. The possibility of an approximately constant size of mercurous sulphate crystal resulting from all the methods must not, however, be overlooked, and as the size of the crystal has not been stipulated by us, it is necessary to examine the evidence on this point.

H. v. Steinwehr* was the first to call attention to the part played by the size of the crystal, and our method of investigation is very similar to that employed by him.

Effect of the Size of the Crystals of Mercurous Sulphate.

Twenty samples of mercurous sulphate have been examined under the microscope, and in twelve cases microphotographs have been taken, the magnification being 250. Of these, eleven are reproduced on Plate 5. It will be seen from these micro-photographs that not only do the crystals vary considerably in size, but that each method of preparation produces its own particular type of crystal. The electrolytic method, as employed by us, gives small crystals, somewhat imperfect in shape, and varying in size from 2 to 8 microns (0·002 to 0·008 millim.). The crystals resulting from the chemical precipitation method are very much rounded, like pebbles; they have the appearance of being formed from perfect crystals, the edges of which have been rounded by the solvent action of the hot dilute sulphuric acid. The uniformity in the size of the crystals is more marked in the samples produced by this method than in the specimens made in any other way tried by us. The size of most of the crystals in figs. 2 to 4 varies from 5 to 30 microns. The mercurous sulphate produced

by the action of fuming sulphuric acid on mercury is evidently in the form of large crystals, but most of these appear to get broken in the washing processes, with the result that the size of the grain is considerably diminished. Figs. 9 and 10 show these fragments of crystals, which vary in size from 5 to 25 microns.

We have not taken any microphotographs of crystals produced by Method III., as this method is only of interest as an independent means of obtaining mercurous sulphate; it is far too troublesome to be generally employed. We have, however, prepared some very large crystals by a method suggested by H. v. Steinwehr.* A dilute acid solution of mercurous nitrate was allowed to flow very slowly indeed from a burette into dilute sulphuric acid (1 to 4) heated to 100° C. over a water-bath. Small crystals of mercurous sulphate were at first formed, which grew, however, in the slightly super-saturated solution of mercurous sulphate until many of them attained a length of a few millimetres. The crystals were washed with dilute sulphuric acid (1 to 6) and the finer particles were removed by agitation with the acid and rapid decantation. The resulting product was undoubtedly of large grain, and there were numerous particles present of the size shown in fig. 5. The length of this crystal is about 400 microns.

In September, 1906, three cells were set up which contained these large crystals of mercurous sulphate as a depolariser. Table III. gives the results of observations on these cells from October, 1906, to May, 1907.

**Table III.**

<table>
<thead>
<tr>
<th>Cell</th>
<th>1906</th>
<th>1907</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>October</td>
<td>November</td>
</tr>
<tr>
<td>S 1</td>
<td>1·01843</td>
<td>42</td>
</tr>
<tr>
<td>S 2</td>
<td>36</td>
<td>35</td>
</tr>
<tr>
<td>S 3</td>
<td>40</td>
<td>38</td>
</tr>
</tbody>
</table>

The cells are not in very good agreement and the mean E.M.F. is about 8 in 100,000 higher than the E.M.F. of the normal cells in Table I. Recently we have set up more cells with a second sample of large-grained mercurous sulphate, and they also have E.M.F.'s higher than 1·01830 volts. In order that there should be no doubt about the size of the crystals in S 1, S 2, and S 3, they were unsealed in June, 1907, the pastes washed with dilute sulphuric acid to remove the cadmium sulphate crystals and the residue examined microscopically. It was apparent that during the preparation of the depolarising paste and its insertion in the cell many of the large crystals

were broken, with the result that the mean size of the crystals was diminished, but the fragments were still much larger than the crystals prepared by any of the other methods. Figs. 1 and 8 (Plate 5) are microphotographs of some of the crystals of mercurous sulphate after their removal from the cells S 1, S 2, and S 3. It was observed that in all cases there was a small number of comparatively small crystals, or fragments of crystals, associated with the large ones, but we found this unavoidable. In one instance we took very great pains to eliminate small particles, and succeeded in doing so to a considerable extent, but subsequent examination of the crystals after the manufacture of the depolarising paste and its insertion in a cell showed that their size had been appreciably reduced.

Table IV, enables a comparison to be made between cells set up with crystals of various sizes.

**Table IV.**

<table>
<thead>
<tr>
<th>Cells</th>
<th>Mercurous sulphate.</th>
<th>Size of most of the crystals in microns</th>
<th>Mean E.M.F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>E 62, &amp;c.</td>
<td>Electrolytic I.</td>
<td>5 to 15</td>
<td>1.01828</td>
</tr>
<tr>
<td>E 80,</td>
<td>&quot; I.</td>
<td>3 to 15</td>
<td>28.2</td>
</tr>
<tr>
<td>HA 1,</td>
<td>Chemical II.</td>
<td>5 to 30</td>
<td>30.3</td>
</tr>
<tr>
<td>B 41,</td>
<td>&quot; II.</td>
<td>5 to 30</td>
<td>30</td>
</tr>
<tr>
<td>HA 7,</td>
<td>&quot; II.</td>
<td>5 to 30</td>
<td>30</td>
</tr>
<tr>
<td>P 410,</td>
<td>Fuming acid IV.</td>
<td>5 to 20</td>
<td>31</td>
</tr>
<tr>
<td>N 23,</td>
<td>STEINWEHR’s method</td>
<td>about 10 per cent., 20</td>
<td>37</td>
</tr>
<tr>
<td>S 1, S 2, S 3</td>
<td></td>
<td>30 to 60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&quot; 40 &quot; 100</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>about 20 per cent., greater than 100</td>
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</table>

The higher E.M.F. of the cells S 1, S 2, S 3 is probably due to slight impurities in the mercurous sulphate, and not to the large size of the crystals. During the preparation of these crystals the sulphuric acid was not stirred, and the only agitation of the liquid was that produced by the mixing and by convection currents. It is possible for slight hydrolysis to result under such circumstances, and also possible for mercurous nitrate to be imprisoned in some of the large crystals which are formed. The latter appears to be not improbable in our case.

If we exclude from Table IV, those cells set up with the very large crystals, we have as the limits of the dimensions of the others 3 to 30 microns, and we conclude that if the size of the crystals be within these limits they will have very nearly the same solubility and practically give the same E.M.F. in a standard cell.

This conclusion is not in accordance with observations made by STEINWEHR, who first called attention to the possible effect of the size of the crystals, and claims that it is a principal cause of the variations observed in standard cells. Lord KELVIN has shown that the saturation pressure of small drops of water is greater than that of
large drops; similarly the solubility of small particles is greater than that of large ones, and therefore the saturated solution will show a greater E.M.F. than the saturated solution of the large crystals. With fluctuating temperatures the tendency is for the small crystals to disappear and the mean size of the crystals to increase; this lowers the concentration and with it the E.M.F. It is only for very small crystals that the change in solubility is appreciable, and at present it is not possible to calculate the change in E.M.F. produced by the variation in size.

Steinwehr* examined several samples of purchased mercurous sulphate; two such salts from Kahlbaum and MERck respectively gave a difference in E.M.F. of 5 parts in 10,000, and it was found that the dimensions of the crystals of the salt K giving the higher E.M.F. were of the order of 1 micron, while the crystalline structure could be seen in a number of particles of the other salt (M). The crystals of M were about 10 to 20 microns long. By grinding the M salt the difference was reduced to 1 or 2 parts in 10,000. Very large crystals were prepared by a method very similar to that afterwards used by ourselves (p. 404), and the E.M.F. of a cell containing these very large crystals was lower than that of a cell containing the K salt by 0'7 to 0'8 millivolt. By grinding some of the large crystals and setting up a cell with the small particles as a depolariser the E.M.F. was increased by 0'6 millivolt, and was therefore comparable with the K cell.

We also have set up cells with Kahlbaum's mercurous sulphate which was washed with water and is therefore hydrolysed. The E.M.F. of these cells is at present 1'0186 volts and is constant; indeed, from the point of view of constancy of E.M.F., these cells are as good as any of those dealt with in Table I.; fig. 11 (Plate 5) is a microphotograph of the salt used. The average size of the crystals is from 2 to 10 microns. The salt from Kahlbaum, used by Steinwehr, was smaller than this, the particles being from 1 to 2 microns in length at the most. The difference of 0'3 millivolt found by us between cells set up with Kahlbaum's salt and those set up with mercurous sulphate prepared by ourselves appears to be due not to a difference in size of grain, but to the hydrolysis of the former salt.

Hulettr† has also measured the size of mercurous sulphate crystals prepared electrolytically and found the particles to vary in length from 2 microns to 130 microns, but has found no difference in the E.M.F. of cells set up with these crystals.

It is, of course, always possible that in an occasional preparation a very large number of exceedingly fine crystals may be produced, and in such a case the change of E.M.F. described by Steinwehr will result, but unless there are numerous small crystals in all of our preparations—and this is highly improbable—the large crystals of mercurous sulphate which are sufficiently soluble to act as an efficient depolariser cannot give an E.M.F. appreciably lower than those which are from 5 to 30 microns

in length. The question is an interesting one, and we hope to extend our investigation, but at present there appears to be no necessity to stipulate the size of the crystals. We would, however, draw attention to the uniformity of the size of the crystals of the chemically precipitated salt, and as Method II. is the easiest of any of the methods of preparation used by us, we strongly recommend it, or one founded on it, as a standard method of preparation.

**Constancy of the Cell.**

The results recorded in Table I. indicate remarkable constancy of most of the cells. Eighty per cent. of the first fifty cells have apparently varied by not more than 2 parts in 100,000 since the first month of their preparation. Of the remainder, four have varied from 3 to 5 parts, one 6 parts and one 16 parts in 100,000. There are four others which belong to the N group of cells; these were low at first, but rose to the normal value 3 months after preparation. Further remarks on these four cells appear on p. 410. The last eight cells in Table I. are anomalous. In 12 months the three M cells have fallen 10, 16 and 21 parts in 100,000 respectively, and the five D cells have values about 30 parts in 100,000 lower than the normal. Of the approximately constant cells, twelve have been set up for 2½ years, twenty-three for more than 18 months, and thirty-six for more than 12 months. It is important to note that the comparatively new cells, i.e., those set up in March and April, 1907, are practically identical in E.M.F. with the cells set up in 1904.

Of the abnormal cells it is noteworthy that, with the exception of E 67, they belong to three groups and that the change in them has been practically continuous from the time of their construction. The cells were prepared in a manner apparently the same as that of the normal cells, and we are unable to offer a complete explanation of their remarkable behaviour. Examination of the solutions shows that they are not appreciably acid, and tests on the amalgams indicate that they give the same E.M.F. as those used in the new cells. The depolarisers are, however, at fault. This we have proved by connecting one of the cells with a new cell by means of a syphon and measuring the E.M.F. between the negative pole of the new cell and the positive pole of the abnormal cell. The same low E.M.F. was recorded. Something may have happened during the preparation of the depolarisers for these abnormal cells, but we are not aware of any departure from our usual proceeding.

There is, however, another indication that the depolarisers have changed, and we wish to draw particular attention to this, as it may lead to the discovery of the cause of the disturbance. In nearly all of the cells which have fallen by as much as 0.0002 volt many of the small crystals of cadmium sulphate have changed in colour, and in some cases the colour of the depolariser has also changed. The cadmium sulphate crystals in these cells of low E.M.F. are of a yellowish-brown tint and the mercurous sulphate in places is slightly yellow, or, in a few instances, green. This change has also been noted in cells set up with some samples of purchased mercurous sulphate, but these
cells are high in E.M.F. and approximately constant. In the normal cadmium cells the appearance of the mercurous sulphate is the same as when freshly prepared. An interesting question is whether the change in colour of the paste is the result of association with the other ingredients of the standard cell or not, and whether a charging or discharging current produces or accelerates the change. The first part of this question may be answered so far as association with the cadmium amalgam is concerned, for we have kept many samples of the paste together with saturated cadmium sulphate solution and mercury in stock bottles. In two of these pastes green patches have appeared and the dimensions of the patches are slowly increasing. The change is therefore independent of the presence of free cadmium or cadmium amalgam. The probable acceleration of the change due to a charging or discharging current is discussed on pp. 413-415.

A number of anomalous cells were closely examined in order to detect any other peculiarities besides that of the coloration of the depolariser and crystals of cadmium sulphate. In one of the cells a small bubble of air was imprisoned between the glass and the paste, and the paste in contact with the bubble and to a depth of 1 millim. from it was of a yellow tint, the remaining portion of the depolariser being normal in colour. From these colour observations it appears probable that the change is of the nature of a hydrolysis, but at present we have no reason to think that all the pastes will, with time, similarly change, and that, as suggested by Hulet,* the cathode leg of the cadmium cell is a system in unstable equilibrium. Instead we are inclined to believe that something abnormal occurred in the preparation of the pastes.

Two cells which were low in E.M.F. by 0.0001 volt, but very constant, were opened, and the solution in them was found to be very slightly acid. We regard this as an indication of insufficient washing of the mercurous sulphate. Cell No. 2 was employed in a potentiometer circuit during the estimation of current in absolute measure by the Ayrton-Jones Balance. It was used from October, 1905, to June, 1907, and could not have fallen by more than 1 part in 100,000 during this period. Its low initial E.M.F. is probably due to the presence of acid.

Hulet concludes that many of his cells have fallen 11 parts in 100,000 in a little over two years, but that Clark cells have remained constant. In 1904 the author pointed out that some cadmium cells made in 1902 had apparently fallen 0.00007 volt; these, however, were prepared in the old way with purchased mercurous sulphate washed with water, and since 1904 there is every reason to believe that they have remained constant.

Drs. K. E. Guthe and C. L. v. Ende† record the following results:—Three cadmium cells were prepared by them on Nov. 2, 1906; by the 17th of the same month each had fallen about 50 microvolts below the normal value; by Dec. 13, 1906,  

the mean fall was 100 microvolts, and there was evidence that they were still falling. These three cells contained pastes prepared by Dr. Guthe. On Nov. 10, 1906, four other cadmium cells were prepared, and contained mercurous sulphate supplied by Dr. Hulett. By Jan. 19, 1907, the mean fall of these cells was 0.00049 volt; on the same date their average E.M.F. was about 0.00023 volt lower than that of the three cells previously considered.

Dr. Guthe also gives the values of some Clark and cadmium cells set up with electrolytic and chemically prepared pastes by Professors Carhart and Hulett. The Clark cells appear to have remained constant since their construction in 1904, but some of the cadmium cells have fallen by 3 to 4 parts in 10,000. In some cases more than half of this change took place during the first year.

The results obtained at the National Physical Laboratory are, on the whole, decidedly in favour of the constancy of the cell, and tend to show that the fall in E.M.F. of certain N.P.L. cells is due to the mercurous sulphate in them being somewhat abnormal when they were set up. An investigation of the pastes of abnormal cells appears to be desirable, and may possibly lead to some explanation of the want of constancy which the foregoing statement shows has been noted by some observers.

**E.M.F. of freshly prepared Cells.**

When mercurous sulphate is freshly prepared and apparently free from acid, if cells are set up with it as a depolariser on the same day as that of the precipitation they do not usually take up their normal value immediately. They are sometimes high at first, but fall rapidly in E.M.F., sometimes attaining their normal value within a few hundred thousandths of a volt in a few hours, but more often an interval of several days is required. An example of this is afforded in the case of B151. This was completed at 2.15 p.m. on the same day as the depolariser was manufactured; it was inserted in a constant temperature bath, and observations of the E.M.F. were immediately made. At the same time another cell, B149, was completed; in this the depolariser was mercurous sulphate which had been prepared three weeks previously and had since remained in contact with saturated cadmium sulphate solution. This cell attained its normal value almost immediately.

**Table V.**

<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td>2.20 p.m. 2.33 2.37 2.45 3.0 3.10 3.30 4.0 5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B151</td>
<td>1.01861 56 55 53 51 50 49 48 47</td>
<td>39</td>
<td>36</td>
</tr>
<tr>
<td>B149</td>
<td>1.01837 36 36 35 34 34 33 33 32</td>
<td>32</td>
<td>32</td>
</tr>
</tbody>
</table>

**Vol. CCVII.—A.**
"Ageing" of Cells.

Lord Rayleigh observed that the electromotive force of Clark cells when originally set up was invariably high, and in some cases the fall in E.M.F. in a few weeks was 0.02 volt. This fall in E.M.F. immediately after manufacture has been confirmed by numerous observers, and in consequence Clark cells were supposed to require "ageing." The same is true of Weston cadmium cells if set up with pastes prepared similarly to those used by Lord Rayleigh, but such extreme changes as 2 per cent. have not come under the author's notice. The mercurous sulphate prepared by any of the four methods described in this communication does not require "ageing," or to a very small extent only.

Washing with Alcohol.

The group of cells, of which N 23 to N 26 are types, were abnormal in their behaviour. The E.M.F. was at first 3 parts in 10,000 low, but gradually increased until it was normal, and since then it has remained approximately constant. The mercurous sulphate for these cells was washed with absolute alcohol to free the salt from acid, but no attempt was made to remove the alcohol by further washing the sulphate with saturated cadmium sulphate solution. The salt was removed from the filter and immediately made into paste. Table VI. gives the observations from the

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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N 23</td>
<td>1·018000</td>
<td>06</td>
<td>11</td>
<td>19</td>
<td>22</td>
<td>23</td>
<td>25</td>
<td>27</td>
<td>29</td>
<td>32</td>
</tr>
<tr>
<td>&quot; 24</td>
<td>63</td>
<td>10</td>
<td>14</td>
<td>18</td>
<td>23</td>
<td>25</td>
<td>27</td>
<td>28</td>
<td>30</td>
<td>33</td>
</tr>
<tr>
<td>&quot; 25</td>
<td>00</td>
<td>04</td>
<td>08</td>
<td>12</td>
<td>17</td>
<td>21</td>
<td>24</td>
<td>26</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>&quot; 26</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>19</td>
<td>22</td>
<td>25</td>
<td>28</td>
<td>29</td>
<td>31</td>
<td>32</td>
</tr>
<tr>
<td>&quot; 17</td>
<td>37</td>
<td>35</td>
<td>33</td>
<td>33</td>
<td>32</td>
<td>33</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
</tr>
</tbody>
</table>

* Guthe and v. Ende* prepared some mercurous sulphate which was not thoroughly free from alcohol and found the E.M.F. of some Clark cells 0·00040 volt lower than normal when set up with this, and there was no appreciable change in the course of time. Their observations extended over three months.

---

The Temperature Coefficient and "Lag."

In experimental work involving the use of the Clark cell, temperature corrections have invariably to be introduced owing to the high value of the temperature coefficient. This is the most serious objection to its use. The temperature coefficient of the cadmium cell is much smaller and has been determined by Jaeger and Kahle, who give the following equation connecting temperature and E.M.F.:

\[ E_t = 1.0186 - 0.00038 (t-20) - 0.0000065 (t-20)^2. \]

At the National Physical Laboratory six cells were chosen and their temperatures were varied very slowly from 10° C. to 30° C. The maximum rate of change of temperature was 1° C. per hour, and before making an observation at any particular temperature the oil bath in which the cells were immersed was kept at that temperature for at least an hour, a toluene thermostat capable of maintaining a constant temperature to 0°.01 C. being employed. The cycle of temperature was repeated three times. The agreement between the cells was excellent, and the mean values of the E.M.F.'s were taken to obtain the temperature coefficient by the method of least squares. The resulting temperature formula is

\[ E_t = E_17 - 0.0000348 (t-17) - 0.00000066 (t-17)^2. \]

This is in very good agreement with Jaeger and Kahle's formula. The changes in E.M.F. from 10° C. to 15° C., 10° C. to 20° C., and 10° C. to 30° C., as deduced from the two formulæ, are given below.

<table>
<thead>
<tr>
<th>°C.</th>
<th>Jaeger and Kahle</th>
<th>N.P.L.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 to 15</td>
<td>0.00015, volt.</td>
<td>0.00014, volt.</td>
</tr>
<tr>
<td>10 ,, 20</td>
<td>0.00032, ,,</td>
<td>0.00031, ,,</td>
</tr>
<tr>
<td>10 ,, 30</td>
<td>0.00077, ,,</td>
<td>0.00076, ,,</td>
</tr>
</tbody>
</table>

The lag of E.M.F. with respect to temperature changes was shown by Ayrton and Cooper* to be much greater in the Board of Trade tube form of cell than in the H form. They concluded that there is a "simple lag," which may be removed by a comparatively short interval of constant temperature, and a "semi-permanent lag," which requires many hours of steady temperature for its complete removal. We have made similar observations on the Weston cadmium cell and find evidence of the same lag in it. The effect is, however, very small when the temperature changes are slow and the range of temperature only a few degrees, as in the experiments of Ayrton and Cooper on the Clark cell. When the range of temperature is about 15° C. and the change of temperature very rapid, a difference in E.M.F. of about 30 microvolts is often observed after the normal temperature of the cell has been restored for 4 or

5 hours. Much, however, depends on the construction of the cell. An extreme case is illustrated in fig. 12. Here a cell was maintained at a temperature of 55° C. for 12 hours and was then plunged into a bath of paraffin oil at 17° C. The oil was stirred, and observations of the E.M.F. were frequently made. At 11.20 A.M. (see fig. 12) the cell was at a temperature of 55° C. and was then immersed in the oil at 17° C. Twenty minutes afterwards the E.M.F. was normal to 1 part in 4000; after a total interval of 40 minutes it was right to 1 in 10,000, and after 1 hour to about 7 parts in 100,000. Fourteen days elapsed, however, before the cell was within 2 parts in 100,000.

Recovery after Short-circuiting.

In order to test the recuperative power of the Weston cadmium cell, one of the cells was short-circuited for 1 minute, another for 5 minutes, a third for 5 hours,
and a fourth for 5 days. The recovery of the first two cells is illustrated in figs. 13 and 14. It will be observed that the cell which was short-circuited for 1 minute was right within a ten-thousandth of a volt 1 minute afterwards, but 40 minutes were occupied in its recovery to 1 part in 100,000. The cell which was short-

circuited for 5 minutes was nearly 1 in 1000 low 1 minute afterwards; at the end of the second minute it was 1 in 2000 low, and after 5 minutes it had recovered within 1 in 5000; about 1½ hours were required for its complete recovery. The restoration of the E.M.F. of the third cell was much slower; 1 minute after the circuit was opened its E.M.F. was about 0·1 volt, which value it appeared to retain for 3 minutes. The E.M.F. then changed suddenly from 0·1 to 0·85 volt, and at the end of 4 minutes its voltage was 0·9. The recovery was then more gradual. Ten minutes after breaking the circuit the E.M.F. was 0·0061 volt below normal, 20 minutes afterwards 0·0028 volt low, and 5 hours afterwards it was low by 0·00040. It recovered within 1 in 10,000 in 24 hours, but 3 weeks were occupied in its complete recovery. The cell which was short-circuited for 5 days had an E.M.F. less than 0·05 volt 5 minutes after breaking the circuit, and its E.M.F. did not rise above 0·08 volt for

Fig. 13. Recovery curve of cell short-circuited for 1 minute.
more than 6 hours. Twenty-four hours afterwards, however, its E.M.F. was normal within 2 parts in 10,000, and it completely recovered within 6 weeks.

In 1884 Lord Rayleigh made some experiments on the polarisation of Clark cells and conclusively showed that the effect of short-circuiting for a few minutes rapidly passed away.

Recovery curves for the Clark cell have been published by Fisher,* for a large type of cadmium cell by Tinsley,* and for the Calomel or Hibbert cell by Hibbert.* An analysis of such curves leaves little doubt that short-circuiting is only temporarily injurious.

Charging the Cell.

In practice, a standard cell is usually placed in a circuit in which a very small current alternates in direction. These small charging and discharging currents can have no immediate serious effect on the cell, as is amply proved by many cadmium cells in use at the National Physical Laboratory which are frequently checked in the

Electrical Standards Department. That a small current may be taken from the cell without any permanent effect is proved from the observations when cells have been short-circuited, but the effect of a comparatively large charging current may be more serious. Lord Rayleigh attempted to manufacture a Clark cell by the formation of electrolytic mercurous sulphate inside an H vessel, the anode being mercury, the electrolyte zinc sulphate, and the cathode an amalgam of zinc. The cells so formed were not constant, and their E.M.F.'s were low. In 1904 we attempted in a similar way to produce cadmium cells, but it was evident that normal mercurous sulphate was not formed, as the resulting salt was highly coloured; it was sometimes yellow, but more often green. The fact that the depolariser in some of our anomalous cells has, after a long period, turned a yellowish-green suggested to us that its formation might be accelerated by small charging currents. The constancy of other cells subject to the same treatment is certainly against such a view, but a slight difference in the original composition of the depolarisers might account for the more rapid change. To test this point, we placed a normal cell in circuit with, but in opposition to, two Leclanché cells for 18 hours. At the end of that time a green compound had formed between the mercury electrode and the glass, but the depolariser appeared to be unchanged. There is little doubt, however, but that some of the green salt was present over the whole surface of the mercury. The E.M.F. of this cell was at first very high, but in 4 weeks it gradually fell to 1.01833 volts. The observations which we have so far made do not enable us to say whether any further fall is probable, but it is evident that the small charging currents to which a cell is subjected in a potentiometer circuit do not seriously affect its E.M.F.

**Portability of the Cell.**

Many of the cells made at the National Physical Laboratory are portable, and may be sent through the post. In these cells the two limbs of the H vessel are constricted at points about 1½ centims. from their lower ends, and when making up the cell, cadmium sulphate crystals are added until the upper surface of a crystalline layer is on a level with the narrowest part of the tube in which the crystals are placed. Cadmium sulphate solution is then added and the cells are exposed in a warm room for a week or more before sealing. Some of the liquid evaporates, and many of the fine crystals are loosely cemented together. This crystalline plug keeps the contents in their proper places and enables the cell to be inverted.

**Conclusions.**

(1) The electromotive force of the Weston cadmium cell is the same whether it contains electrolytic mercurous sulphate, chemically prepared sulphate, the salt as precipitated by the dilution of hot strong sulphuric acid in which mercurous sulphate is dissolved, or that resulting from the action of fuming sulphuric acid on mercury.
(2) The size of the crystals of mercurous sulphate prepared by the first two and the last of the above methods usually varies from 5 microns to 15 microns, and we have found no electromotive difference between a saturated solution of these crystals in a cadmium sulphate solution and a saturated solution of very large mercurous sulphate crystals in the same solvent.

(3) The simplest method of preparing mercurous sulphate is by chemical precipitation, and the product is more uniform than that of any other method so far examined.

(4) The electromotive force is the same whether the cadmium amalgam is prepared by the electro-deposition of cadmium in mercury, or by the fusion of cadmium and mercury. At normal working temperatures either a 10 or a 12½ per cent. amalgam may be used.

(5) The electromotive force is probably constant over long periods of time, but the cells should be compared with those of a standardising institution every 12 months; failing this, they should be compared with freshly set up cells.

(6) The change of E.M.F. with temperature may be calculated from JAEGER and KAHLE’s equation or from that obtained at the National Physical Laboratory. As the former has been used for so many years, we suggest its universal adoption.

(7) The small charging and discharging currents to which a cell is subjected in a potentiometer circuit do not seriously affect the value of the electromotive force.

We desire to express our thanks to the Committee of the British Association for grants of money for the purchase of materials; to Dr. GLAZE BROOK for much advice concerning the construction of the cells, and to Mr. J. A. SADD, of the Central Technical College, and Mr. TINSLEY, for constructing standard cells to compare with ours.

APPENDIX.

_Added December 4, 1907._

**On the Comparison of the Electromotive Forces of Weston Cadmium Cells Prepared at Washington, at Paris, at Berlin, and at Teddington.**

Dr. Burgess of the National Bureau of Standards, Washington, journeyed to Paris and Berlin after his visit to Teddington, and very kindly took with him a number of cadmium cells from the National Physical Laboratory in addition to others from Washington. Dr. F. A. WOLFF has forwarded us a report on the measurements of the cells in Paris, from which we make the following abstracts.
MR. F. E. SMITH ON THE NORMAL WESTON CADMIUM CELL. 417

Eight of the American cells and eight of the English cells were compared at the Laboratoire Central d'Électricité under conditions which allowed of an approximation to 1 part in 100,000. The maximum deviation of the eight American cells from their mean was found to be 0'00002 volt, and the difference between this mean and the mean of the Weston cadmium cells of the Laboratoire Central was of the order of 0'00001 volt. The maximum deviation of the eight English cells was about 0'00003 volt, and their mean E.M.F. differed from the E.M.F. of the French cells by about 0'00001 volt. A second set of comparisons, made at Paris in August, confirmed the first measurements on the American cells.

Dr. Burgess left four English cells at the Laboratoire Central, and M. Janet, the Director of the Laboratory, has compared these with the French cells, with the following results.

**Table VII.**

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Approximate difference from mean in microvolts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 52</td>
<td>+10</td>
</tr>
<tr>
<td>P 210</td>
<td>-10</td>
</tr>
<tr>
<td>H 28</td>
<td>0</td>
</tr>
<tr>
<td>C 17</td>
<td>-10</td>
</tr>
<tr>
<td>K 14</td>
<td></td>
</tr>
<tr>
<td>K 13</td>
<td></td>
</tr>
<tr>
<td>K 12</td>
<td></td>
</tr>
<tr>
<td>Mean E.M.F. of English cells</td>
<td>mean E.M.F. of French cells</td>
</tr>
</tbody>
</table>

The cells K 12, K 13, K 14, were set up at the National Physical Laboratory on October 2, 1907, and Mr. Agar Baugh kindly took them to M. Janet. The cells H 26, H 28, and H 29 (see p. 402) were set up with pastes which may be very slightly acid.

Eight of the American cells and eight of the English cells were compared at Berlin, June 20 and June 21, while two American cells and four English cells remain at the Reichsanstalt and have been intercompared from June 20 to September 30, 1907. The following statements are extracted from a formal report by Messrs. Jæger and Lindeick.

The results of the tests of the Weston cells brought over from America and England are given in Table VIII. Since only the cells 183 and 184 from America, and H 29, P 55, C 117, and C 12 from England, have been left in Charlottenburg,
the mean (indicated by A) of these six cells is taken as the basis of values given in Table VIII.

### Table VIII.

<table>
<thead>
<tr>
<th>Weston cells—America</th>
<th>Weston cells—England</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cell No.</strong></td>
<td><strong>Difference from A in microvolts.</strong></td>
</tr>
<tr>
<td></td>
<td><strong>June 20.</strong></td>
</tr>
<tr>
<td>19</td>
<td>-3</td>
</tr>
<tr>
<td>105</td>
<td>-13</td>
</tr>
<tr>
<td>P8</td>
<td>-8</td>
</tr>
<tr>
<td>P9</td>
<td>-8</td>
</tr>
<tr>
<td>P10</td>
<td>-8</td>
</tr>
<tr>
<td>183</td>
<td>+7</td>
</tr>
<tr>
<td>184</td>
<td>-3</td>
</tr>
<tr>
<td>187</td>
<td>-3</td>
</tr>
<tr>
<td><strong>Mean. . . .</strong></td>
<td><strong>-5</strong></td>
</tr>
</tbody>
</table>

It will be seen that the American and English cells agree very well among each other. In the first series of measurements: Mean E.M.F. of English cells—Mean E.M.F. of American cells = +0·000006 volt, and in the second series of measurements the difference is +0·000009 volt. Two cells which Mr. Rayner of the National Physical Laboratory kindly took from Teddington to the Reichsanstalt, in September, show equally good agreement.

The German cells mentioned in Table IX. (the series are designated by P, O, and M) were prepared in March, 1907, with three different samples of mercurous sulphate made by the von Steinwehr precipitation method. During the first few months after their preparation these cells showed on the average a decrease in E.M.F. of about 1 part in 10,000, and the E.M.F. had not attained a state of constancy at the commencement of the measurements in question. Drs. Jaeger and Lindeck suggest that the cause of this alteration lies in the fact that the three samples of mercurous sulphate were washed out with dilute sulphuric acid in course of preparation. The relative agreement in the individual groups is, however, very good. In the P group there are eight cells and the difference between any one cell and the mean has at no time exceeded 2 parts in 100,000; in the O group there are six cells, and in the M group six cells, and the corresponding differences for these groups are about 1 and 1·7 parts in 100,000, respectively. Intercomparisons were made with the older cells (1899) of the Reichsanstalt, which were taken as constant during the period June 20 to September 30, 1907.
Table IX.

Mean E.M.F. of the Single Groups — the mean E.M.F. of the American, German (September 9, 1907), and English Cells.

<table>
<thead>
<tr>
<th>Group</th>
<th>Differences in microvolts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>June 20, 1907</td>
</tr>
<tr>
<td>A. (2 American and 4 English)</td>
<td>-15</td>
</tr>
<tr>
<td>B. (8 German P cells)</td>
<td>+25</td>
</tr>
<tr>
<td>C. (6 O)</td>
<td>+54</td>
</tr>
<tr>
<td>D. (6 M)</td>
<td>+67</td>
</tr>
<tr>
<td>Mean German P, O, M cells</td>
<td>+49</td>
</tr>
</tbody>
</table>

As will be seen from the above table, the cells from America and England have remained constant during the period June 20 to September 30; the German cells of Groups P, O, M, have, however, decreased 4 parts in 100,000. Drs. Jaeger and Lindecker think that it is not improbable that the alteration will continue, but owing to the slightness of the change this can only be tested after long periods.

It would seem, as the result of the last measurements on September 30, that the differences between the various cells compared were, at that time, only a few parts in 100,000. By making use of the average value of the cells P, O, M, obtained at this time, and taking into consideration the data given in Dr. Wolff's report (and part of that given on p. 403 of this communication), Drs. Jaeger and Lindecker give the following differences for the cells of the different countries, the figures being rounded off to the hundred-thousandth part:

\[
\text{E.M.F. of English cells} \quad \left\{ \begin{array}{c}
\text{E.M.F. of American cells} \\
\text{Mean of more than 100 cells}
\end{array} \right\} - \left\{ \begin{array}{c}
\text{E.M.F. of American cells} \\
\text{Mean of 12 cells}
\end{array} \right\} = +1 \times 10^{-5} \text{ volt,}
\]

\[
\text{E.M.F. of German cells} \quad \left\{ \begin{array}{c}
\text{E.M.F. of English cells} \\
\text{Mean of P, O, M cells}
\end{array} \right\} = \pm 0 \times 10^{-5},
\]

\[
\text{E.M.F. of German cells} - \text{E.M.F. of American cells} = +1 \times 10^{-5}.
\]

As the French cells are also in good agreement with the American and English cells, considerable advance would appear to have been made with the standard cell question.

The English cells, H 26, C 19, P 53, and P 54, were received at Washington on August 22. On the same date C 19 was about 40 microvolts higher than its companion cells, but on August 27 a comparison led to the results given in 3 H 2.
Table X. Dr. Wolff has also forwarded the results of comparisons made by him on P 8, P 9, P 10, and 187 (American), of PCN 4 and PCN 6 (French), and O 1 and O 2 (German). Unfortunately, the depolariser in the German cells was disturbed in transit, and the results obtained are not, therefore, given in Table X.

Table X.

August 27, 1907. E.M.F. of Cell—Mean E.M.F. of the American, French, and English Cells.

<table>
<thead>
<tr>
<th></th>
<th>E.M.F. of the American, French, and English Cells.</th>
</tr>
</thead>
<tbody>
<tr>
<td>American</td>
<td>P 8 $= 2 \times 10^{-6}$ volt</td>
</tr>
<tr>
<td></td>
<td>P 9 $= 5 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>P 10 $= 5 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>187 $= 5 \times 10^{-6}$</td>
</tr>
<tr>
<td>French</td>
<td>PCN 4 $= +16 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>PCN 6 $= -18 \times 10^{-6}$</td>
</tr>
<tr>
<td>English</td>
<td>H 26 $= 5 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>C 19 $= 5 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>P 53 $= 4 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>P 54 $= 5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Mean</td>
<td>Mean $= -2 \times 10^{-6}$ volt</td>
</tr>
<tr>
<td></td>
<td>Mean $= -1 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Mean $= +2 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

We heartily thank the various gentlemen who have assisted in these comparisons.
XI. Electric Furnace Reactions under High Gaseous Pressures.

By R. S. Hutton and J. E. Petavel.

Communicated by Professor A. Schuster, F.R.S.

Received January 31,—Read March 7, 1907.

[PLATE 6.]

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INTRODUCTION.

Some ten years ago the classical work of Henri Moissan laid the foundations of the scientific study of high-temperature chemical reactions.

It is hardly necessary to recall the rapid and extensive development which the subject has since experienced; it must, however, be remembered that the progress has been almost exclusively along technical lines, and even at the present time very little detailed work on the chemical and physical sides of the question has been published.

Doubtless individual inventors have acquired extensive experience and knowledge each of his special branch of the subject, but they have seldom found it advisable to impart the results of their researches.

The field of investigation, even with regard to the purely chemical phenomena
occurring in quite ordinary cases, is far from exhausted, and practically nothing is known of the modifications introduced by abnormal conditions, such for instance as the combination of high pressure and high temperature.

The present research has been undertaken with a view to determine the correlation between the physical conditions and the chemical effects in the electric furnace, and more especially to ascertain the direct results produced by high gaseous pressures. In such work, if it is to be of real value, it is necessary to carry out the experiments on as large a scale as the limitations of cost and labour will permit; it is also particularly desirable to provide means for the modification of the various factors within the widest possible range. The chief factors being power, current, electro-motive force, and above all, pressure.

In work carried out during preceding years under atmospheric pressure the necessity for employing now one type, now another of electric furnace determined us to select an apparatus suitable for both open and smothered arc, as also for resistance heating.*

The above considerations accentuated the already somewhat difficult task of designing a furnace suitable for high gaseous pressures. For, as already suggested, it would have been of little use to provide for a slight increase of pressure over that of the atmosphere.

The apparatus constructed is capable of employment for electric heating according to the most varied type of furnace, and has frequently been used for pressures as high as 200 atmospheres. We were thus in a position to extend our direct experimental study up to the limits which engineering difficulties set to practical application.

With regard to the experimental work, the first step was to investigate the additional effect of high pressure upon the more characteristic electric furnace reactions, it being obviously advisable to start by repeating the better known preparations, retaining as far as possible all other conditions similar to those at present in use.

It is with a general investigation of this character that our communication has to deal.

To avoid burdening the description of the work with the many numerical results, we have collected these in tables in an appendix to the paper.

**Description of Apparatus.**

*Large High-Pressure Furnace.*

From what has been said above it will be clear that an apparatus was necessary capable of being adapted to very varied requirements.

This end was met by designing a large steel enclosure of about 20 litres capacity,

* We have frequently had occasion to divide the enclosure into a number of separate chambers, e.g., for absorbing gaseous products inside the furnace, as also for a condensing chamber in volatilisations and distillations.
provided with various fittings for the introduction or circulation of gas, gauges for measurement of pressure, windows for observation and, finally, with insulated carbon holders leading the current to the inside of the furnace. Within this shell many different forms of furnace, such as vertical or horizontal arc or resistance core, could be built up as illustrated in fig. 11 (p. 438).

The construction of the enclosure will be easily understood by reference to figs. 1 and 2, giving sectional drawings. The shape of the interior is cylindrical, 10 inches diameter by 17 inches long, with hemispherical ends, one of which forms the cover B and is held in place by ten 2¼-inch studs (F₁, F₂) which are fixed into a flange of the main forging. The cover is rendered gas-tight by a spigot joint S, packed with lead; it is surmounted by a cast-iron casing H, through which cooling water was circulated.

The main forging A is surrounded by the cast-iron water jacket C.

Both the hemispherical ends of the furnace have projections K₁, K₂ bored out to a distance of 3 inches.

The carbon holders which move in these recesses are thus protected from the direct heat or flame of the furnace. The length of the projections K₁, K₂ is sufficient to allow.

---

**Fig. 1. Sectional drawing of large pressure furnace.**

A. Main forging, 1½ inches ruling thickness increased to 2 inches over central belt, through which the various openings are bored.

C. Water jacket surrounding the body of the furnace.

H. Water jacket surmounting the cover.

B. Cover held down by ten 2¼-inch studs, the joint being made by a lead ring placed in the spigot groove S. The projection N protects the joint from contact with the hot gases when the furnace is in use and shields it from mechanical injury while the cover is being lifted or replaced.

L. Cast-iron lining.
a feed of 8 inches. To obviate any risk of damage to the main forging by contact with the hot furnace materials, a cast-iron lining L was always used.

When in a horizontal position the furnace rests on four cast-iron feet (not shown in the figure). When vertical it is supported by the cover of the water jacket, the lower carbon feeder passing through a hole cut in a massive wooden stand.

Fig. 2. Transverse section through the centre of the large furnace.

W. Water jacket.
F. Main forging.
L. Cast-iron lining.

The inlet valve is screwed into A, whereas the openings B and C receive the windows shown in fig. 4, outlet valves and gauge connections, or, when required, auxiliary insulated terminals.

The main forging is provided with three openings, as shown in fig. 2, which is a section through the centre of the furnace perpendicular to the axis of the carbons.

The aperture A served to receive the valve through which the enclosure was filled with compressed gas, whereas in most cases one of the windows shown in fig. 4 was screwed into B. The third opening was connected to a pressure gauge and served also, when desired, for the escape of the gaseous products of reaction.

**Carbon Feeding Mechanism.**

This is shown in detail in fig. 3. A ring B is fitted to each of the projections K of the furnace. To this ring the small cover A is bolted. The joint is made, as in the case of the main furnace cover, by means of the lead-packed spigot V. The cover
carries two columns $C_1$, $C_2$ surmounted by a yoke $Y$ which is insulated from them by micanite bushes and washers $R$. To this yoke the main terminals (not shown in the figure) are fixed. The nut $N$ is revolved by means of steel levers inserted in the holes $T$, and thus the feeding rod $S$ is moved forward. The feather $F$ fits in a groove cut in this rod and prevents it following the rotary motion of the nut.

Fig. 3. Carbon feeding mechanism of the large furnace.

The small cover $A$ is bolted down to the ring $B$, which is fitted on to the projection $K$, forming part of the main forging.

Two columns, $C_1$, $C_2$, support the insulated yoke $Y$, in which the nut $N$ is revolved by steel levers fitting into $T_1$ and $T_2$.

A stream of water flows through the hollow feeding rod $S$, the nipples $I$ and $O$ carrying the inlet and outlet pipes. A central pipe can be used to pass a flow of compressed gas through the axis of the electrode $M$.

The glands $Q$ of the stuffing box $P$ are electrically insulated from the cover $A$.

The electrode $M$ is soldered into the cup-shaped holder $H$ which screws on to the end of the feeding rod.

The feeding rod passes into the furnace through the insulated stuffing box $P$.

This stuffing box serves the double purpose of making a gas-tight joint and providing insulation sufficiently perfect for the relatively low electromotive force which is generally required with this furnace. As packing, a mixture of asbestos and tallow is used, which in itself assists the insulation.

The stuffing box is compressed by means of the ring $D$, which presses on the gland $Q$, but is electrically insulated from it by mica washers and bushes. The inner gland is insulated in a similar manner from the steel cover.

The feeding rod is hollow. The current of water passes into it at $I$, and flowing through an inner brass tube is delivered at the extremity of the rod and passes back to the outlet $O$. A gas connection $G$ is also provided by means of which compressed gas can, when necessary, be passed directly into the centre of the furnace through the axis of a hollow electrode ($M$).
**Carbon Holders.**

These are of two different patterns, according to the size of the electrode used. Carbons of 30 millims. diameter or less are held by clamps similar to those used with the smaller furnace, as shown at T in fig. 6 (p. 429).

For larger carbons the limited space available prohibits the use of such an arrangement, which in any case would hardly provide a sufficiently good contact for heavy currents (500 to 1000 amperes). The larger carbons are therefore electro-coppered at their ends, and soldered into cup-shaped holders, as shown at H (fig. 3). The lip of the cup is fitted with a ring of refractory insulating material, U, which nearly fits the bore of the tube K, and thus protects the stuffing box from flame and dust.

![Diagram of Windows](image)

**Fig. 4. Windows.**

A and B. Gun-metal fittings carrying the glass windows W.  
F. Steel wall of furnace enclosure.  
a. Gas-tight ring joint.  
R. Ring making water-tight joint between the fitting and the water jacket K.  
The design A is used when working with arcs of small intensity, and B for larger currents.

**Windows.**

Although unnecessary for the purely chemical work, it was of considerable importance to be able to observe, project, or photograph the arc itself or its spectrum under conditions of high pressure.* By providing two openings (B and C, fig. 2) diametrically opposite, absorption spectra could be observed during the operation of the arc.

The forms of construction are shown in fig. 4. The window itself consists of a glass or quartz cone (W) \( \frac{3}{4} \) inch thick and \( \frac{1}{2} \) inch diameter at its smaller end. This

transparent cone is forced into the gun-metal fitting after being surrounded with a thin film of cement, and is held in place by a metal ring, the shape of the glass tending to make the joint more perfect the higher the pressure.

The joint between the fitting and the aperture in the main forging is made by the ring \( a \) turned on the end of the fitting, which presses tightly against a steel ledge, no packing being required.

The joint between the fitting and the water jacket is made by means of a gun-metal ring \( R \), which screws on to the fitting itself.

The two types of window differ only in the relative position of the transparent plug. The design shown at \( A \) gives a clearer view of the arc, but for very large currents it is advisable to make use of the fitting \( B \), in which the glass plug is more carefully protected from the source of heat.

Valves and Gas Connections.

The types which have already been described* were employed for regulating the flow of the various gases used.

After the construction of the furnace was completed it was tested to 450 atmospheres, and has since been used frequently up to 200 atmospheres gaseous pressure.

At first it was anticipated that so large a joint as that of the main cover would show some leakage at the higher pressures, the total stress on the bolts retaining the cover amounting under ordinary working conditions to over 100 tons. These fears were, however, not realised, the only precautions necessary being to keep the joint perfectly clean and, of course, to tighten up the nuts evenly all round. Occasionally, as the pressure rose, a slight escape of gas was noticed, but this was stopped without any difficulty by tightening up the corresponding stuffing box or joint.

In fact, it may be said that throughout the work no difficulty has been experienced in keeping the apparatus gas-tight.

The furnace is, of course, equally suitable for work in vacuo, and has occasionally been used in this way—in connection, for instance, with spectroscopical investigations.

In the course of the present research the electrical conditions have varied widely, in some cases as much as 1000 amperes, in others 500 volts, having been employed without difficulty. The power used in most experiments was between 10 and 15 kilowatts. When it is desired to use high-tension currents (1000–25,000 volts) with this furnace the carbon feeding mechanism of the small apparatus can be used to replace that described above, with which it is interchangeable.

The weight of the enclosure was, of course, considerable, and to facilitate its manipulation a crane was fixed to the main laboratory wall. The crane is regularly employed for the removal of the cover, and serves also to lift the entire furnace and change its position from horizontal to vertical, or vice versa.

Small Furnace for High-Tension Currents.

Since there are a considerable number of electric furnace reactions, as, for instance, most gas reactions, for which very high-tension currents are necessary, it was decided to complete the equipment by providing a furnace specially for this class of work.

In this case a large capacity, instead of being an advantage, would constitute a serious drawback, owing to the difficulty of preparing and purifying such a quantity of gas. Moreover, in the case of a high-tension arc, the natural temperature gradient is so steep that the maximum temperature is easily and safely attained even in a small enclosure. The rapid rate of cooling which results from the proximity of the arc to the cold walls of the furnace is also of material advantage.

![Diagram of the furnace](image)

Fig. 5. Sectional view of small furnace.

The body of the furnace is suspended from a cast-iron plate A bolted to a wooden stand B. The two ends $K_1, K_2$ are closed by covers which carry the feeding mechanism (see fig. 6). The body of the furnace is surrounded by a water jacket W.

A little below the centre the walls are thickened up to 2 inches and are pierced by two openings. The inlet valve screws into H, and a window (see fig. 4) into G.

The smaller furnace is of one-tenth the capacity of the larger, and consists of a mild steel cylinder about 3 inches internal diameter, with walls $1\frac{1}{2}$ inches thick, surrounded on the outside with a water jacket (see fig. 5). The walls are thickened up a little below the centre, and two openings are bored in the ring thus formed. One of these
(H) serving for the inlet valve, the other (G) for receiving one of the windows we have already described, the size and form of the openings being such as to render all fittings interchangeable with those used in the larger furnace.

Fig. 6. Carbon feeding mechanism for the small electric furnace.

The ring B screws on to the end K of the furnace and supports the cover A. Into this are screwed the columns C which carry a thick plate of insulating material M.

The feeding screw Q is rotated by means of a cord passed over the pulley W; this screw works in the nut P which is fixed in the centre of the insulating plate (M).

The electrode X is held in a clamp T which is fixed to the feeding rod R.

This rod passes into the furnace through the stuffing box S, which forms the upper part of the central steel plug E. This plug is forced by the nut N against a cupped insulating piece D which fits a recess in the furnace cover.
The chief characteristic of this furnace lies in the means employed for insulating and moving the carbon holders. The mechanism is clearly shown in figs. 6 and 7. A conical hole tapering outwards is bored in the centre of the covers of the cylinder, and receives a cup-shaped insulating bush (D) of ebonite or red fibre. A central plug E is provided with a mushroom-shaped end which fits closely into this cup and is lightly drawn against it by means of the nut N placed on the outside, this nut in turn pressing on the insulating ebonite washer I.

The gas pressure itself forces down this plug firmly on its seat and secures a satisfactory joint. The upper end of the steel plug contains the necessary stuffing box (S) through which passes the feeding rod R.

From each cover of the furnace project three steel pillars, carrying at their extremities a thick triangular plate M of insulating material. To the centre of this
is fixed the nut (P) in which the screw-gear works. This screw-gear is rotated by means of a cord passing over the pulley W. Thus, when the furnace is being used for very high electric tensions, the feeding gear can be manipulated from a safe distance. This form of insulation has been found to work satisfactorily up to 3000 volts. For higher electromotive forces one of the steel feeding rods is removed and replaced by a thick-walled glass tube. The current, which under these conditions is of course very small, is led by a number of fine platinum wires fused through the glass to the electrode, which is supported on the end of this rod.

With this modification the furnace has been used up to 25,000 volts.

Gas Preparation and Compression.

In connection with this research it was necessary to manufacture and compress relatively large quantities of hydrogen, carbon monoxide, ethylene, and nitrogen.

The question has been dealt with fully in a recent publication to which we must refer those specially interested in this branch of the subject.*

GENERAL OBSERVATIONS ON THE ELECTRIC ARC UNDER HIGH GASEOUS PRESSURES.

At the time the present research was started very little information was available with regard to the electric arc burnt in a compressed atmosphere, the investigations having been limited to small arcs and pressures of about 15 atmospheres. The belief was then current that it would prove to be impossible to maintain an arc under gaseous pressures of 100 or 200 atmospheres.

This erroneous conclusion was due to a misconception of the nature of the difficulties which had been encountered by the various workers.†

For spectroscopical investigations it is necessary to obtain a relatively long arc giving a clear flame between the extremities of the electrodes. Such an arc, it is undoubtedly true, can only be maintained in a dense atmosphere by means of an exceptionally high electromotive force.

It should nevertheless be clearly understood that even low-tension arcs will burn without difficulty. At ordinary current densities the entire phenomenon is, however, confined to the crater itself, and a projected image of the arc shows merely the outline of the white-hot crater, and only occasionally is a flash of flame visible on the periphery.

Electrically the arc is still well characterised by its high electromotive force, which instantly disappears if the electrodes are brought into actual contact.

When the arc is started in a compressed oxidising atmosphere, the current is at first unsteady and the electrodes must be rapidly fed up. Soon, however, a steadier state is reached. If, after such a run, the furnace is opened and the carbons examined, it will be observed that, by the action of the current, the electrodes have been so shaped as to nest one into the other as shown by the dotted lines in fig. 8. In this way a considerable cross-sectional area is produced over which the discharge can occur.

The E.M.F. of the arc rises as the pressure of the surrounding atmosphere increases* and at the high pressures used in the course of this work it becomes more than double the normal value.

It is, however, the first few atmospheres which produce the greatest effect upon the voltage.

A detailed analytical investigation of the arc would in itself, as can be judged from the great amount of work carried out at ordinary pressures, require considerable expenditure of time and is outside the scope of the present research. We therefore limit ourselves here to the few observations recorded in Table I. (p. 451), in which the behaviour of the arc under certain definite conditions of pressure and current is recorded.

An interesting effect is throughout noticeable. Although the maximum length of arc is so much reduced, the voltage is in all cases abnormally high, and consequently a large amount of power is concentrated in a small space.

Two very distinct types of arc exist. The most usual in these enclosed furnaces is found with a non-oxidising atmosphere such as carbon monoxide or nitrogen.

In such arcs at ordinary current densities the electrical conditions are complicated by the rapid growth of a deposit of carbon, chiefly around the negative electrode and often completely enclosing the end of the positive electrode. The difference between a resistance and an arc is then less marked.

The arc flame is not visible, but is replaced by a zone of brightly incandescent carbon; electrically the conditions are ill-defined and difficult to reproduce. It is consequently only during the early part of the experiment that concordant measurements can be obtained. As time goes on the carbon deposit builds itself up, the voltage shows a tendency to rise, and the general appearance

* Duncan, Rowland, and Todd, 'Electrical World,' 1893, vol. 22, p. 101, for 6-ampere arcs up to 10 atmospheres pressure.
indicates that the electrical conditions more nearly approach those of a resistance than of a true arc.

It is, however, almost inconceivable that a power of 5 or 10 kilowatts (see fig. 10, B and C) can be expended in such a limited volume of solid material without volatilising it; and, as we shall see, the amount of disruption as evidenced by the feed required is under these conditions extremely small.

With an exceptionally high current density the arc in a non-oxidising gas at high pressure gives a well-defined flame.

In fig. 10, D, a comparison is given between arcs in carbon monoxide at 11 and 16 atmospheres and an experiment made by Mrs. AYKTON* with an enclosed arc at ordinary pressure, using carbons of similar size. It will be seen that the increase of voltage due to an increase of pressure of 15 atmospheres is very considerable. For

---

* Mrs. AYKTON, 'The Electric Arc,' p. 304.
these high current densities the apparent resistance of the arc under pressure remains positive just as at atmospheric pressure.

An entirely different type is obtained in an oxidising atmosphere, and in this case alone are the results comparable with the well-known conditions of the ordinary open arc.

In fig. 10, E, the E.M.F. of a 150-atmosphere arc of about 2 millims. length is given and compared with measurements made at atmospheric pressure, the positive carbon being 41 millims., the negative 27 millims. diameter.

![Diagram of electromotive force and current of the arc in various compressed gases.]

Fig. 10. Curves of the electromotive force and current of the arc in various compressed gases.

The data refer to the conditions existing while a fair proportion of the oxygen was still present; the arc then shows a bright flame which, if the electrodes are fed up rapidly and with regularity, can be easily maintained. Here again the increased voltage observed is due principally, as shown by other experiments, to the first 10 or 15 atmospheres.

For the purpose of general comparison, few data on large current arcs being available, a number of measurements were made with an open arc burning at atmospheric pressure between carbons (positive 41 millims., negative 27 millims.) and maintained at a constant length of 8 millims. The curve thus obtained is recorded in fig. 10, A.

Finally it should be mentioned that, in the course of the chemical work to be described, constant use has been made of “smothered” arcs, as, for instance, in the
production of calcium carbide. With arcs of as much as 500 ampères between the extreme limits of our experiments, i.e., from 0·5 atmosphere up to nearly 200 atmospheres, no consistent effect on the voltage which could be ascribed to the influence of gas pressure was apparent.

A noticeable feature in all the experiments carried out in air is the very rapid rate of burning of the electrodes.

To take one instance: with 27-millim. carbous and a 30-ampère arc under a pressure of 29 atmospheres the carbon was consumed at a rate of about 6 millims. per minute, which is nearly twenty times as fast as at ordinary pressures.*

This burning is principally limited to the positive electrode, which in the above experiment was consumed seven times as fast as the negative, the relative rates at ordinary pressures being about as 3 : 1. At a still lower current density the negative carbon shows practically no loss of weight.

Under the normal conditions of most of our experiments, that is with very high current densities, the combustion becomes very violent.

The oxygen thus becomes rapidly exhausted and the subsequent feeding required is relatively very small.

At first carbonic acid is formed which is in turn reduced to carbon monoxide. This reduction occurs also when the arc is run in an atmosphere of compressed carbonic acid. In the latter case an interesting observation was the separation of flocculent carbon which was seen to be moving rapidly in the convection currents. This phenomenon is observed from the commencement of the experiment.

The decomposition of the carbonic acid under these conditions is comparatively slow, in one experiment less than half being decomposed by the end of half an hour.

A somewhat similar* process goes on also in non-oxidising gases. Finely divided carbon is deposited in considerable quantities on the cool walls of the enclosure, the weight collected being in fair agreement with the loss from the electrodes. With such gases the atmosphere, however, remained perfectly clear.†

* R. Monasch, 'Der elektrische Lichtbogen;' p. 22.
† In cases in which a hydrocarbon gas atmosphere (e.g., coal gas) is employed, the deposition of carbon is augmented by the breaking up of the higher hydrocarbons.

The following analyses give the constitution of the coal gas before and after a run at about 60 atmospheres, which lasted 36 minutes with a power of about 10 kilowatts, a horizontal arc being employed. In this case both electrodes had increased in weight, the positive by 6, the negative by 15 grammes:

<table>
<thead>
<tr>
<th>Component</th>
<th>Before run.</th>
<th>After run.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon vapours</td>
<td>1·0</td>
<td>0·0</td>
</tr>
<tr>
<td>Heavy hydrocarbons</td>
<td>4·2</td>
<td>0·7</td>
</tr>
<tr>
<td>CO₂</td>
<td>2·0</td>
<td>0·6</td>
</tr>
<tr>
<td>CO</td>
<td>15·0</td>
<td>14·7</td>
</tr>
<tr>
<td>CH₄</td>
<td>18·0</td>
<td>24·9</td>
</tr>
<tr>
<td>H</td>
<td>42·0</td>
<td>41·8</td>
</tr>
<tr>
<td>O</td>
<td>1·7</td>
<td>0·0</td>
</tr>
<tr>
<td>N (by difference)</td>
<td>16·1</td>
<td>17·3</td>
</tr>
</tbody>
</table>

Total: 100·0             100·0
The interesting results thus obtained with regard to combustion led us to carry out some experiments on the oxidation of electrodes of other materials, the production of an atmosphere free from oxygen and the oxides of carbon being also of considerable practical importance for the further work we had in view. *A priori* one would be led to believe that copper, iron, or aluminium when heated and fused in highly compressed air (100 atmospheres) would not only rapidly fix the available oxygen, but would do so with sufficient intensity to make the combustion self-supporting.

Repeated attempts were made to produce this result, a summary of which will be found in Table II. (p. 452).

Briefly speaking, we may say that with an iron bar maintained for one hour at a bright red heat and then partially melted by means of a current rising to 1000 amperes, the percentage of oxygen fixed was hardly appreciable.

A similar result was obtained in the case of copper, whereas even aluminium melted in the arc at a pressure of 26 atmospheres only oxidised on the surface, the well-known tenacity of the oxide films being sufficient to prevent the rapid combustion of the metal.

The negative results thus obtained led to some experiments being carried out with oxygen.

An arc was struck between two iron bars of 1\(\frac{1}{10}\)-inch diameter, surrounded by oxygen at 15 atmospheres pressure; as soon as the temperature reached a bright red heat, a vivid combustion commenced on the positive electrode and continued quite steadily, although the current was then cut off.* After the combustion had proceeded a short time the pressure was gradually reduced, the combustion ceasing when the pressure had fallen to about 5 atmospheres. A length of some 5 inches of the bar had by this time been consumed, the loss of weight being 535 grammes, the loss on the negative electrode being only 15 grammes. The product of the reaction was collected in a crucible placed for this purpose under the arc, and on analysis proved to be magnetic oxide \((\text{Fe}_3\text{O}_4)\).

It is worthy of note that although the partial pressure of the oxygen in the experiments previously referred to was considerably above that required in the case of the pure gas, the combustion was not merely insufficient to maintain the temperature required for continued combustion, but even with the assistance of the arc the total iron burnt was almost negligible. The result is due probably to the high effective heat conductivity which is characteristic of compressed gases, the evolution of heat due to oxidation being, in the diluted gas, insufficient to overcome this cooling effect.†

It was thought also that oxygen might easily be removed from the atmosphere by the introduction of successive small quantities of hydrogen, care being taken to always

† J. E. Petavel, 'Phil. Trans.,' A, vol. 197, pp. 229-254, 1901.
keep below the explosive limit, a small arc being maintained to effect the combination. Under these conditions, however, the water vapour produced was rapidly converted into carbon monoxide and hydrogen under the action of the arc. The method had, therefore, no advantage over the direct combustion by carbon, and was abandoned.

In many of the cases in which a carbon arc was maintained after all the oxygen of the air had been fixed, small traces of hydrocyanic acid were detected. In the above experiment, in which hydrogen was present in considerable amount, the formation was much increased.*

**On the Formation of Calcium Carbide.**

The production of calcium carbide, constituting a simple and typical example of electric furnace reactions, was considered a suitable subject for the first series of experiments.

From previous experience we were impressed with the necessity of maintaining the greatest possible uniformity in the conditions under which the furnace was operated.

Above all it was desirable to avoid the variations introduced by the use of different forms of furnace construction, and therefore for all the experiments dealt with in this section we have employed the simple type represented in fig. 11, A, the dimensions of the furnace, the size of the electrodes, the weight and constitution of the reacting mixture being kept the same and, as far as possible, the factors under consideration varied only one at a time.

The building up of the furnace entailed the use of the enclosure in a vertical position as shown in Plate 6, fig. 1. The furnace cover having been removed, by means of a crane installed for the purpose, the cast-iron liner is raised and deposited on a separate stand where it is prepared for the experiment. To protect the bottom of this receptacle from the direct action of the arc, a layer of powdered retort carbon is first introduced, which thus constitutes the lower electrode. The mixture of lime and carbon (about 10 kilogs.) is then filled up around a paper tube which serves to keep a central passage free for the upper electrode.

If there is any doubt as to the perfect desiccation of the raw materials, the cast-iron pot with its contents must be maintained at a red heat for some hours before it is placed in the enclosure. This not only ensures more consistent results, but renders it possible to follow the progress of the reaction by a measurement and examination of the gases generated. The cover of the enclosure is lowered carefully into position, the carbon electrode sliding into the cylindrical space which has been reserved for it.

After the bolts have been tightened up and the desired quantity of gas introduced, the arc is started by lowering the upper electrode, which then comes in contact with the carbon bed beneath it.

During the experiment the voltage and current are read at frequent intervals; the watts, at these instants, plotted on a curve enable the total kilowatt hours supplied to the furnace to be obtained by integration.

Fig. 11. Sectional views of various types of electric furnace.

A. Smothered arc (before run).
   l is the cast-iron liner in which the charge was placed. h, cover of same. e, vertical carbon electrode (41 millims. diameter). d, granular carbon bed forming the lower electrode. c, charge.

   a, ingot of fused product. b, fused and fritted material forming walls of cavity. c, unacted-on material.

B. Resistance (before run).
   e, carbon electrode. f, graphite end-piece leading current to core. g, resistance core of granular material or carbon rod, or other solid "resistor." c, charge. d, granular carbon bed or other form of lower electrode.

B1. Resistance (after run).
   a, ingot of fused product. b, fused and fritted material forming walls of cavity. c, unacted-on material.

C. Horizontal arc: radiation heating.
   e1, e2, electrodes. f, walls or jacket of heat insulating material. c, charge in carbon or other crucible.

D. Smothered arc with two carbons embedded in the material (used horizontal or vertical position).
   e1, e2, electrodes. c, charge.
As the reaction proceeds, the pressure in the furnace, due to the evolution of carbon monoxide, rises rapidly and the fused carbide collects upon the bed of carbon and soon accumulates sufficiently to come in contact with the end of the electrode. The sharp drop of the electromotive force thus produced serves to indicate that the time has arrived to raise the carbon slightly.

There is no difficulty in maintaining these smothered arcs even at the highest pressures, and the regulation of the power is quite a simple matter. Currents of some 500 amperes have frequently been employed in the course of this work and maintained as long as desired.

It is very noticeable that, contrary to experience with such arcs when maintained at atmospheric pressure, the upward rush of the gases through the finely divided charge causes very little displacement of material. For a given rate of reaction the velocity of the gas currents is of course roughly in inverse proportion to the working pressure. At high pressures, therefore, the gaseous products of reaction rise at a relatively slow speed and percolate through the mixture without disturbing it. When, on the other hand, the enclosure is evacuated the projection of the material is very marked and causes considerable trouble.

An extremely low consumption of the carbon electrodes is characteristic of these enclosed furnaces, the deterioration of the electrodes being so slight that they can be repeatedly used. In general practice the loss in weight of the electrodes is an important question and in favourable cases is still between 1 and 3 per cent. of the output of carbide. The consumption in ordinary furnaces on a laboratory scale is still larger, whereas in the present experiments the loss has always been so small as to be hardly appreciable.

We may therefore conclude that the corrosion is not due to the dissociation of the lime as suggested by Gin,* but is to be ascribed to atmospheric oxidation.

A summary of the more important experiments will be found in Table III., whereas Table IV. gives the detailed observations referring to one typical case.

Before discussing these results it may be well to consider briefly the mechanism of the chemical reaction upon which the formation of the carbide depends.

It is generally stated that carbon first commences to react readily with lime when the latter reaches its melting point, the production of carbide below this temperature being limited and of little practical importance.†

In a careful investigation of Rothmund‡ it has however been shown that a definite equilibrium exists at about 1600° C., as represented by the equation

\[ \text{CaO} + 3\text{C} \rightleftharpoons \text{CaC}_2 + \text{CO}, \]

the reaction tending to go from right to left at higher, from left to right at lower

temperatures than this. The formation of carbon under these conditions has also been observed by A. Frank.*

From this it would at first sight appear that, if the carbon monoxide resulting from the formation of calcium carbide were retained in the furnace and the pressure allowed to accumulate, the reaction would soon come to a standstill.

Our experiments are, however, in direct opposition to this conclusion, proving that the temperature prevailing in the furnace is sufficiently far above the point of equilibrium to preclude the inverse reaction so long as the heating is continued.

On the other hand, the above considerations alone might lead one to suppose that, already at any temperature above 1600° C., the formation of carbide would progress rapidly to completion, provided only that free exit were allowed for the gaseous products of reaction. It must, however, be remembered that the process is endothermic, and can therefore only proceed at a pace measured in terms of the rate at which energy is being supplied to the furnace.

We have carried out a large number of experiments specially to study the effect of the presence of carbon monoxide upon the yield (see Table III.).

In these and in other cases the resulting product was submitted to a careful examination and analysis.

The sectional view shown in fig. 11, A, gives an idea of the general appearance of the furnace after the run.

The furnace contents consist of (a) ingot of fused calcium carbide, (b) fritted mass surrounding the central cavity, (c) residual unacted-on material. These were separately collected and weighed, then parted and sampled, and subsequently analysed in the manner described below.

Generally speaking, the central lump represented the entire yield of carbide, although small quantities of acetylene were sometimes obtained from the fritted mass.

The yields recorded are all calculated from the amount of acetylene produced. The gas evolved was always carefully analysed, as the possibility presented itself of the formation of other carbides or free calcium metal. The amount of impurity was, however, invariably found to be insignificant. The outside unfused material was examined, but gave no appreciable evolution of a combustible gas when acted upon by water, or even by dilute hydrochloric acid.

The ingots of carbide showed a good crystalline fracture. The purity of the lump was, as might be expected, below that of a good grade technical product, but increased as the rate of power expenditure rose, and, curiously enough, was entirely independent of the presence or absence of carbon monoxide.

When the carbon monoxide was retained in the furnace the ingot frequently showed on its upper surface a thin coating of bright graphite, giving it a metallic appearance, and in some few cases narrow strata of graphite plates occurred within the mass itself.

The experiment detailed in Table IV. was one of those in which all the gaseous products of reaction were retained in the furnace until long after the completion of the run.

Fig. 12, which refers to this experiment, is reproduced, since it is typical of many of those dealt with in the section.

![Energy, power, and pressure curves of a calcium carbide experiment.](image)

The curves refer to the experiment dealt with in Table IV., in which the furnace was started at atmospheric pressure and all the gas generated was retained.

Curve A represents the power in kilowatts at each instant.

Curve B is obtained by integration of A, and gives therefore the total energy expended up to any given time.

The readings of the pressure gauge on the furnace, taken at intervals, are marked on the diagram, and fall nearly upon the energy curve.

The power at each instant during the run is given in curve A, whilst the total energy expended up to any given moment, obtained by an integration of this, is given at B.

In all the experiments the pressure after the first few minutes rose at an almost constant rate. When the pressure observations are plotted to a suitable scale they coincide with the integrated power curve. In the figure their position is indicated, and the concordance can thus be clearly seen.

The interpretation is not so simple as it appears, for there are two disturbing...
factors which must be taken into account: firstly, the thermal loss, which increases as the hot zone widens out, and, secondly, the variation of the average temperature of the furnace, the effect of which will superpose itself upon the actual gas evolution and thus augment the pressure readings. Apparently these two factors counter-balance each other.

From the analysis of the furnace gas [see Table IV. (3)] a re-absorption of carbon monoxide is clearly indicated. The fall of pressure after the end of the run cannot of course form the criterion, as its amount will vary with the distribution of temperature in the furnace. The considerable decrease in the percentage of the carbon monoxide can, however, only be ascribed to re-absorption, and the results are thus so far in agreement with those of the observers mentioned above.

That this absorption is not due entirely to physical causes is shown clearly by comparison with a similar series of analyses carried out in the case of carborundum (Table VII.).

There is little doubt that the graphitised surface of the ingot, referred to in a preceding paragraph, is a result of the recombination of the carbon monoxide. The instant the power is cut off, the temperature of the molten mass begins to fall rapidly, and it is during this period that the back reaction chiefly occurs. As soon as the product has frozen, further attack is limited, for the ingot of carbide is of a very compact and impermeable texture, and is protected by the graphite film.

Such a "skin reaction" would doubtless become predominant were the experiments carried out on a few grammes of material, but when dealing, as we are here, with larger quantities, the total loss is too small to influence appreciably the result. This is shown by the fact that the yield is not increased when the carbon monoxide is let off immediately upon stopping (cf. Table III., C 26).

The further question, as to whether the presence of an atmosphere of carbon monoxide during the run has an unfavourable effect on the efficiency of the process, is also answered in the negative by a comparison with furnaces operated at atmospheric pressure, but otherwise under identical conditions.

These unexpected results called for more detailed study, and a number of experiments were undertaken in which provision was made for carrying away the carbon monoxide as soon as it was formed. The first method which suggested itself was to remove the gaseous products of reaction by dilution with some inert gas, which was alternately introduced and discharged, the pressure in the furnace being made to fluctuate between two fixed values. The record of such an experiment with coal gas will be found in Table III. (C 22), showing, if anything, a decreased yield.

A more efficient method of washing out the carbon monoxide was then devised. A hollow carbon electrode was brought into use, and during the entire run a constant stream of pure hydrogen was injected directly into the reaction zone of the furnace. The current of gas was also maintained during the cooling, the quantity of gas
employed in each experiment being some 2000 litres. The pressure in the furnace was regulated and kept constant by one of the valves placed on the side of the enclosure, through which the required amount of gas was allowed to escape.

In view of these experiments, arrangements had been made for communication between those engaged in operating the furnace and the worker in charge of the compressor. The gas connections were so disposed that the gas could be delivered either directly into the furnace or into a receiver communicating therewith. Gauges in the furnace room indicated the pressure on the pump, and also the working pressure of the enclosure.

Most gases had of course to be simultaneously manufactured and compressed, but coal gas, drawn directly from the mains, was occasionally used for simply washing out of the products of reaction.

The result of the circulation was not to increase, but considerably to decrease the efficiency of the carbide formation. It occurred to us, however, that the low yields might be ascribed to the thermal losses entailed by the specific heat and the relatively high conductivity of the hydrogen used for dilution.

In order to be quite free from such objections, it was decided to remove the carbon monoxide as fast as it was formed by means of a pump, and carry out the reaction under a partial vacuum.

To protect the pump from the large quantities of finely divided material, which are carried away with the stream of gas, a number of scrubbers and filters were used. When the furnace is operated at full power, the gas generated by the reaction amounts to some 30 litres per minute, and, although an exceptionally powerful vacuum pump was available, it was only possible to maintain the vacuum at about 30 to 40 centims. of mercury. The average yield obtained in the vacuum experiments does not materially differ from the results already given.

We are therefore justified in concluding that, however contradictory it may seem, even a concentrated and compressed atmosphere of carbon monoxide has no deleterious effect upon the formation of calcium carbide.

Having entered so fully into the important question of the influence of carbon monoxide, it is necessary to deal very briefly with other sides of the question.

Generally speaking, within wide limits (between 5 and 20 kilowatt hours) the total power consumption does not affect the efficiency of the process.

The influence of pressure per se has not resulted in any marked change in the chemical or physical nature of the products, neither can a considerable decrease in the yield be traced to this cause. Such variations in the purity or richness of the carbide as have been noticed are attributable only indirectly to pressure, being accounted for by the increased thermal losses in high pressure gases.

Finally, we hope that the general methods of following the course of the reaction by a measurement and analysis of the gaseous products will be as useful when applied to other problems as they have been in this special case.
ON THE FUSION OF SILICA.

When quartz is subjected to a high temperature it attains the vitreous condition and becomes sufficiently plastic to be moulded and shaped.

It was shown some years ago that silica can be heated in direct contact with carbon and brought to a plastic state without marked reduction occurring.

The heating was effected either by radiation from an electric arc or by placing the material around a carbon core* through which the current was passed.

At ordinary pressures it is, however, impossible to maintain any considerable quantity of silica in a really liquid state.

When the power expenditure in the core is increased a rapid volatilisation sets in which effectually puts a limit to the temperature.

It seemed probable that more satisfactory results could be attained by carrying out the fusion under a considerable pressure in the enclosure described above.

Details of the principal experiments will be found in Table V. A resistance furnace of construction similar to that shown in fig. 11, B, was first employed, the central core of granular carbon being replaced by a carbon tube held in two massive graphite terminal pieces to which the current was led. This core was arranged centrally and surrounded by pure quartz sand, the experiments being carried out in air at 50 and 100 atmospheres.

Thick-walled hollow cylinders, 25 centims. long and 15 or 20 centims. external diameter, were in this way easily obtained.

At first sight more complete liquefaction seemed to have occurred. Upon fracture, however, the material was found still to contain innumerable small gas bubbles, giving it a translucent appearance and tending to show that the fluidity had not been much increased.

Proof of the diminished volatilisation of the material was, however, given by the absence of a deposit of condensed silica vapour, as also by the very small formation upon the core of carborundum, both of which are evident at atmospheric pressure.

It was then decided to study two modifications of the régime, either of which seemed likely to give improved results.

The well-known ease with which hydrogen passes through heated silica led us to believe that if a compressed atmosphere of this gas were employed any bubbles imprisoned at the moment of fusion would disappear, leaving the glass clear. None of our experiments, however, verified this assumption. Not only is the occlusion of the gas apparently unaffected, but from the nearly explosive violence with which the

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material splits when subjected to shock there is little doubt that each minute cavity still retains gas under a considerable pressure.*

The small weight of vitrified product is ascribed to the high cooling effect of hydrogen, but the properties of the material were similar to those noted in the earlier work.

Finally, an attempt was made to attain the highest possible temperature by concentrating the heat of a powerful arc in the centre of a mass of sand, the equipment of the furnace being of the type shown in fig. 11, D.

No difficulty was experienced in maintaining an arc of some 10 kilowatts for an hour or more, the electromotive force rising to 120 volts under a pressure of 180 atmospheres.

A hollow sphere of 18 centims. external diameter and weighing about 5 kilogs. was obtained, which, however, was no more transparent than with the less intense heating.

ON THE FORMATION OF CARBORUNDUM.

In 1893 Acheson discovered that a mixture of carbon and silica heated around a resistance core readily produces a carbide of silicon to which the name of carborundum was given. Its preparation is now carried out on a large scale. It was therefore of some interest to study the reaction, first under the usual conditions, then under high pressure.

We have prepared some quantity of this material in the laboratory and found it to differ from the commercial product only in the smaller size of the crystals. The amorphous variety invariably occurs in considerable amount surrounding the crystalline layers.†

In carrying out the reaction in the pressure furnace the mixture of sand and carbon was disposed around a core of granular retort carbon as shown in fig. 11, B.

To insure a uniform cross-section this resistance core was tightly packed into a thin brass tube which was placed in the axis of the furnace and supported between the two graphite electrodes. As the mixture when heated becomes somewhat conducting, it is advisable to line the furnace with a thin insulating layer of sand or other material in order to avoid a short circuit through the iron.

In these experiments the gas generated by the reaction was retained in the furnace and the pressure allowed to accumulate up to some fixed limit (100 atmospheres).

A typical example of such a run is given in Table VI. As will be seen, the brass

* Relative to this subject an interesting investigation has been carried out by Arthur L. Day in America. Using lower pressures, which, however, were only applied after a high temperature had been attained, he has prepared a glass containing relatively few air bubbles. ‘Science,’ N.S., 1906, vol. 23, pp. 670–672.

tube fuses within the first few minutes; the power can then be rapidly increased, and the temperature of formation of carborundum is soon attained.

There is little doubt that the production of carborundum is the result of the interaction of the vapour of silica and the highly heated granular carbon. From the previous work on quartz we were therefore led to anticipate that under pressure the reaction would not occur very readily.

Several experiments confirmed this impression. An examination of the furnace after the run showed, in every case, that, though the mixture of sand and carbon had attained a sufficiently high temperature to effect the fusion of the quartz to a considerable depth, thus agglomerating the mixture, only a small quantity of carborundum was formed and that immediately around the central core.

Another distinctive feature of the pressure experiments is the almost entire absence of the amorphous variety of carborundum. The reaction progresses at a slow rate, but apparently uniformly, the resulting pressure being, as in the case of calcium carbide, a linear function of the time (see fig. 12).

In order to study more in detail the progress of the reaction, an experiment was planned in which the whole of the gas generated was retained in the furnace.

As is shown in Table VII., analyses were made at intervals both during the run and in the subsequent cooling period. From these it is clear that in this case there is no inverse reaction. The high absorbing power of carbon for carbon monoxide as compared with hydrogen fully accounts for the slight decrease in the percentage of the former.*

**On the Direct Reduction of Alumina by Carbon.**

The methods used in practice for obtaining aluminium from its ores are indirect and inefficient.

The preparation involves a lengthy and complicated purification of the oxide, followed by its electrolysis in a bath of cryolite. Early work showed that where aluminium alloys are required they could be obtained by a simple method involving the reduction of alumina by carbon, but the process has never been successful for the production of the pure metal. Up to the present time opinion seems to be divided as to the effect of heating alumina and carbon together in the electric furnace.

Several authorities definitely state that alumina is irreducible by carbon,† whilst others affirm that it is quite easily reduced.‡

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FURNACE REACTIONS UNDER HIGH GASEOUS PRESSURES.

Moissan,* taking an intermediate position, asserts that the two materials only react when in the form of vapour. The question, which for many reasons is of considerable importance, has never received the detailed investigation which it deserves.

Our experiments at atmospheric pressure, as we shall see, pointed to the fact that a well-marked thermal reaction does take place, but not until the fusing point of alumina is reached.

Héroult,† while admitting that reduction occurs, attributes it to electrolytic action. Having carried out some experiments in which the reacting substances were heated by radiation alone and in which good yields of aluminium bronze were obtained, we contend that the assumption of electrolysis is by no means necessary.

No information was available as to the temperature of vaporisation of metallic aluminium, but various observations led us to believe that a large proportion of the reduced metal was lost by volatilisation and subsequent combustion where the furnace gases come in contact with the air.

The high-pressure furnace seemed to us therefore particularly suitable for studying this question, the advantages to be gained consisting firstly in the complete protection of the products from oxidation, and secondly in the decreased volatilisation which might be expected under the high gaseous pressures.

Some of the experiments tried under pressure to study this problem are given in Table VIII., details of one experiment being reproduced in Table IX.

By a cursory inspection of Table VIII. the two following facts may at once be deduced:

(1) That in the resistance furnace neither aluminium nor its carbide is produced.

(2) That on the other hand all arc furnaces give a more or less marked reduction; although it will be noticed (in section B) that the product chiefly occurs as carbide of aluminium.

In several cases small malleable lumps of the metal were condensed in the powdered material surrounding the fused product.

From this it would appear that the required conditions for which we are searching had for some short period been accidentally fulfilled—these conditions being the rapid removal of the metal vapour from the reduction zone and its condensation under circumstances which precluded carburisation.

The idea that, by reducing the partial pressure of the carbon monoxide by a circulation of hydrogen or coal gas, more favourable results would be attained led to the experiments quoted in Table VIII., C and D. From these we infer that the reaction is considerably favoured by a dilution of the carbon monoxide. It is further noticeable that this precaution results in an increase in the relative quantity of

aluminium metal, although it is still accompanied by a considerable amount of the carbide.

It therefore became evident that further work at high pressures must be preceded by a more detailed study of the conditions of reduction. The several problems which arise may briefly be stated as follows:—

(1) At what temperature does alumina first show signs of reduction by carbon?
(2) In the production of aluminium alloys, what is the function of the auxiliary metal in facilitating the reduction of alumina?
(3) What precautions are necessary to limit the formation of carbide and increase the production of metal?

Since it is well known that alumina cannot be reduced under ordinary circumstances in the Moissan furnace, it was thought advisable to see whether, by carrying out the reaction in an atmosphere of hydrogen, a definite indication of reduction could be obtained. The Moissan furnace was, of course, modified to exclude the use of limestone and the accompanying production of carbon monoxide.

As will be seen from Table X., A, a negative result was obtained.

As a means of limiting the temperature of reaction, calcium fluoride was introduced, but no signs of reduction were apparent at the boiling-point of the bath. From these and similar negative results at lower temperatures, which it is unnecessary to record, we assumed as a working hypothesis that the temperature of reduction of alumina is above the boiling-point of aluminium metal under atmospheric pressure.

The hypothesis we confirmed by experiments (Table X., B) in which special precautions were taken to protect the material from access of air and to provide a condensing chamber in which the vapours were cooled down before their exit from the furnace. The deposit so obtained showed unmistakeable evidence of the presence of finely divided aluminium.*

It therefore became necessary to devise some better means for indicating the production of any metal vapour.

A method which suggested itself to us, and one which has proved of considerable usefulness, was the employment of a bath of molten copper, on the surface of which the reaction mixture was placed. The copper served as an absorbent for any aluminium vapour liberated.

To determine the lowest temperature at which reduction occurs, a series of experiments was carried out. Small carbon crucibles were used to contain the mixture. These were heated either in a carbon tube furnace, or, for higher temperatures, more conveniently by embedding them in a granular carbon resistance. From the summary of these experiments in Table X., C, it will be seen that the minimum temperature of reduction coincides fairly sharply with the melting-point of alumina, and is not appreciably lowered by the introduction of either fluor spar or lime as a flux.

* See also C. F. Maery, 'Amer. Chem. Journ.,' 1887, vol. 9, pp. 11-15.
By referring again to Table VIII, it will be found that this view is substantiated
by a comparison between the arc and resistance experiments.

In the latter the yield is always extremely low. This may be explained by the
fact that as the inner layer of mixture approaches its fusing point it flows away by
gravity, and, ceasing to transmit the current, is not maintained at the requisite
temperature for marked reduction to occur.

We come now to that curious apparent contradiction of facts which has for so long
puzzled investigators in this field; namely, that though aluminium bronze and ferro-
aluminium can be so readily produced, no process exists by which the metal itself can
be obtained from the oxide, except by indirect means. What is, then, the function of
the auxiliary metal? It has been suggested that a marked chemical affinity exists
between the aluminium and the metal with which it alloys, the evidence in support
of this being the high heat evolution which is noticeable when aluminium is added to
the metals in a molten state.

It must, however, be remembered that under ordinary conditions the fused metals
contain dissolved oxide, and it therefore seemed worth while to carry out a preliminary
investigation of this question.

Upon adding aluminium to molten copper in a thoroughly reduced condition, there
is no visible evidence of a reaction, and such pyrometric measurements as were made
sufficed to show that no considerable amount of heat could have been evolved.

Thus we feel justified in concluding that the copper or other metal serves chiefly
to condense and dissolve the aluminium, and does not itself take part in the primary
chemical reduction of the oxide.

A secondary function of the auxiliary metal is, however, possible. It occurred to
us that the absence of aluminium carbide, when reduction is effected in the presence
of other metals, might be explained by some chemical action of the aluminium carbide
upon the copper or iron or one of their oxides.

An investigation of this matter has been undertaken by J. N. Pring,* whose
results clearly show that at the temperatures we are considering, namely, at or above
the melting-point of alumina, aluminium carbide reacts with either the oxide or the
metal, forming an alloy.

The third problem, viz., the limitation of the formation of carbide, seems to be the
most difficult to solve.

As we have seen, the metal may be considered to exist in the form of vapour at the
moment of its reduction. Owing to the well-known affinity of aluminium for carbon
monoxide,† it is obviously important to remove this gas as completely and rapidly as
possible.

A method of reducing the partial pressure of the carbon monoxide has been dealt
with above, and we have found it important to lead the gas used for dilution directly

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to the seat of reaction by means of a hollow electrode, the stream of gas thus not only effectively diluting the carbon monoxide, but serving to carry forward the metallic vapour into a zone more favourable for its condensation.

Even in the absence of carbon monoxide, carburisation can occur by direct union of the metal with solid carbon.

Some unpublished work of W. H. Patterson carried out in this laboratory has, however, shown that in the absence of carbon monoxide this reaction only occurs above a bright red heat, thus explaining the results already quoted in which the metal was obtained, although doubtless it had not altogether escaped contact with carbon.

We are therefore in the following position: we have proved the facility with which the direct reduction of alumina by carbon can be effected, and have shown that the minimum temperature at which it can occur is already sufficiently high for the metal to be produced in the form of vapour.

Future work must be directed towards the application of high pressure for reducing the vaporisation of the metal at the temperature of reaction, the rapid removal or dilution of the carbon monoxide by a stream of inert or reducing gas, and a modification of the régime to facilitate the condensation and prevent the collected metal from flowing into a bed of highly heated carbon.

Thus the necessary conditions for the successful direct reduction of alumina by carbon seem to be fairly well defined, the outstanding problem being chiefly a matter of the arrangement and construction of the furnace.

The cost of most of the apparatus, which was specially constructed for the above research, was defrayed by funds awarded by the Government Grant Committee of the Royal Society. We have also been materially assisted, so far as the gas preparation plant is concerned, by Messrs. Brunner, Mond & Co., Ltd., and the Tudor Accumulator Co., Ltd.

With regard to running expenses, the work has been much facilitated by the kind way in which the ample resources of the Physical Laboratory of the Manchester University have been placed at our disposal.

In concluding, we desire to express our heart-felt gratitude to Professor Arthur Schuster for the never-falling interest and encouragement which he has given us during the several years over which the research has extended.
Table I.—E.M.F. and Current of Carbon Arc under Pressure (see fig. 10).

A.  
In air at atmospheric pressure.

<table>
<thead>
<tr>
<th>ampères</th>
<th>volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>80</td>
<td>56</td>
</tr>
<tr>
<td>118</td>
<td>46</td>
</tr>
<tr>
<td>180</td>
<td>63</td>
</tr>
<tr>
<td>250</td>
<td>66</td>
</tr>
</tbody>
</table>

Length of arc 8 millims.*

B.  
In carbon monoxide.

Both carbons 27 millims.

Length of arc 1 to 2 millims.

<table>
<thead>
<tr>
<th>Pressure, atmospheric.</th>
<th>(2) At 150 atmospheres.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ampères</td>
<td>volts</td>
</tr>
<tr>
<td>10</td>
<td>57</td>
</tr>
<tr>
<td>30</td>
<td>43</td>
</tr>
<tr>
<td>50</td>
<td>37</td>
</tr>
<tr>
<td>80</td>
<td>40</td>
</tr>
</tbody>
</table>

(3) At 190 atmospheres.

<table>
<thead>
<tr>
<th>ampères</th>
<th>volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>95</td>
<td>120</td>
</tr>
<tr>
<td>100</td>
<td>108</td>
</tr>
</tbody>
</table>

* In A only the length of the arc is the distance between the point of the negative of the edge of the crater of the positive. In all other experiments it is the distance of feed required to produce actual contact between the two electrodes. Solid carbons were used throughout.
### Table II.—Oxidation of Metals in Air under High Pressures.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 1, 3, and 4</td>
<td>Crucible filled with copper, iron, or aluminium, heated for half-an-hour in furnace of type fig. 11, C, under carbon arc. Pressures, about 30 atmospheres. Power, 5 to 10 kilowatts. Metals fused, but the oxidation as shown by the gas analysis was practically limited to the carbon.</td>
</tr>
<tr>
<td>A 5</td>
<td>Arc between iron electrodes. Pressures, 27 to 75 atmospheres. Metal at end of electrode apparently violently boiling, but after more than an hour still over 20 per cent. oxygen. Subsequently iron bar maintained at bright red heat by current of 1000 ampères for about 2 hours without entering into combustion. Oxygen at end of run over 20 per cent.</td>
</tr>
<tr>
<td>A 6</td>
<td>Iron electrodes, $1\frac{1}{4}$ inches diameter, in oxygen at 15 atmospheres. Points of electrodes heated by 300-ampère arc. Vivid combustion started. Current at once cut off. Positive electrode continued burning until pressure was reduced to 5 atmospheres. Total iron burnt, 550 grammes.</td>
</tr>
<tr>
<td>A 7</td>
<td>Rod of iron, $\frac{5}{8}$ inch diameter, $1\frac{1}{4}$ inches long, between iron electrodes in air at 100 atmospheres, maintained at bright red heat by powerful current and then fused without starting combustion. Over 20 per cent. oxygen after run.</td>
</tr>
<tr>
<td>A 13</td>
<td>High-tension arc (1000 volts) between thin iron rods. Pressure, 110 atmospheres. Combustion not started.</td>
</tr>
<tr>
<td>A 12</td>
<td>Arc between copper electrodes at 92 atmospheres. After run, 20.5 per cent. oxygen.</td>
</tr>
</tbody>
</table>
FURNACE REACTIONS UNDER HIGH GASEOUS PRESSURES.

**Table III.**—Summary of the Principal Experiments on the Production of Calcium Carbide.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Total energy, kilowatt hours</th>
<th>Average power, kilowatts</th>
<th>Initial pressure, atmospheres</th>
<th>Maximum pressure, atmospheres</th>
<th>Product, grammes, CaC$_2$ from analysis</th>
<th>Yield, grammes per kilowatt hour</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 29</td>
<td>3.84</td>
<td>11.5</td>
<td>Atmospheric</td>
<td>30</td>
<td>283</td>
<td>73.7</td>
<td>CO from reaction retained in furnace.</td>
</tr>
<tr>
<td>C 27</td>
<td>6.2</td>
<td>12.0</td>
<td>Idem</td>
<td>50</td>
<td>504</td>
<td>81.4</td>
<td>Idem.</td>
</tr>
<tr>
<td>C 58</td>
<td>9.26</td>
<td>13.2</td>
<td>Idem</td>
<td>42</td>
<td>703</td>
<td>75.9</td>
<td>Idem.</td>
</tr>
<tr>
<td>C 61</td>
<td>12.6</td>
<td>14.5</td>
<td>Idem</td>
<td>120</td>
<td>1088</td>
<td>86.7</td>
<td>Idem.</td>
</tr>
<tr>
<td>C 23</td>
<td>15.0</td>
<td>15.8</td>
<td>Idem</td>
<td>15</td>
<td>1258</td>
<td>84</td>
<td>Pressure kept at 15 atmospheres, excess of CO being let off.</td>
</tr>
<tr>
<td>C 26</td>
<td>6.5</td>
<td>13.9</td>
<td>Idem</td>
<td>48</td>
<td>391</td>
<td>60.2</td>
<td>CO retained during run, but let off at once on stopping.</td>
</tr>
<tr>
<td>C 22</td>
<td>14.9</td>
<td>14.2</td>
<td>10 coal gas</td>
<td>25</td>
<td>1017</td>
<td>68.3</td>
<td>Circulation of coal gas by alternately admitting and blowing off gas from furnace enclosure. Total coal gas, 1420 litres.</td>
</tr>
<tr>
<td>C 65</td>
<td>9.75</td>
<td>12.7</td>
<td>50 hydrogen</td>
<td>50</td>
<td>405</td>
<td>41.5</td>
<td>Circulation of hydrogen through hollow carbon electrode. Total hydrogen, 1705 litres.</td>
</tr>
<tr>
<td>C 66</td>
<td>6.48</td>
<td>11.7</td>
<td>Atmospheric</td>
<td>Minimum 30 centims. Hg absolute</td>
<td>455</td>
<td>70.3</td>
<td>Vacuum. Maintained below $\frac{1}{2}$ atmosphere during entire run.</td>
</tr>
<tr>
<td>C 67</td>
<td>15.8</td>
<td>17.2</td>
<td>Idem</td>
<td>Minimum 35 centims. Hg absolute</td>
<td>1385</td>
<td>87.7</td>
<td>Vacuum. Idem.</td>
</tr>
<tr>
<td>C 73</td>
<td>13.5</td>
<td>13.5</td>
<td>Idem</td>
<td>Atmospheric</td>
<td>1437</td>
<td>106.4</td>
<td>Atmospheric pressure.</td>
</tr>
</tbody>
</table>
MESSRS. R. S. HUTTON AND J. E. PETAVEL ON ELECTRIC

Table IV. (1).—Details of one Typical Calcium Carbide Experiment (C. 61).

The large furnace enclosure was used in the vertical position (see Plate 6, fig. 1).
Iron liner filled as shown in fig. 11, A.
Lower electrode (−ve), bed of 2 kilogs. retort carbon.
Upper electrode (+ve), a 41-millim. carbon rod, 32 centims. long.
Weight with holder, 1657 grammes. Loss of weight during run, less than 5 grammes.
Charge: about 8600 grammes of a mixture of selected Buxton lime and petroleum coke (100 CaO : 65 C).
Lime all passed through a 20-mesh sieve, petroleum coke 60-mesh. The vessel with its contents was heated for some hours to a red heat before the experiment to ensure complete drying of material.
Initial pressure, atmospheric.
The gas capacity of the furnace when charged was found to be 11.6 litres per atmosphere.
All the gaseous products of reaction were retained during the experiment and for 42 hours after completion of same, with the exception of the small quantities required for gas analysis at intervals as recorded below.
The E.M.F. at the terminals of the generators was varied as required and was usually 5 to 10 volts above that on the furnace.

Table IV. (2).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>minutes</td>
<td>ampères</td>
<td>volts</td>
<td>kilowatts</td>
<td>atmospheres</td>
<td></td>
</tr>
<tr>
<td>start</td>
<td>70</td>
<td>27</td>
<td>1.89</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>21</td>
<td>4.20</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>30</td>
<td>9.00</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>360</td>
<td>48</td>
<td>17.2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>380</td>
<td>42</td>
<td>16.0</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>400</td>
<td>41</td>
<td>16.4</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>350</td>
<td>48</td>
<td>16.8</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>140</td>
<td>70</td>
<td>9.8</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>240</td>
<td>63</td>
<td>15.1</td>
<td>46</td>
<td>1st sample of gas taken for analysis.</td>
</tr>
<tr>
<td>23</td>
<td>300</td>
<td>50</td>
<td>15.0</td>
<td>48</td>
<td>2nd sample of gas taken for analysis.</td>
</tr>
<tr>
<td>25</td>
<td>360</td>
<td>40</td>
<td>14.4</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>340</td>
<td>47</td>
<td>16.0</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>300</td>
<td>54</td>
<td>16.2</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>280</td>
<td>58</td>
<td>16.2</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>300</td>
<td>58</td>
<td>17.4</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>280</td>
<td>58</td>
<td>16.2</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>240</td>
<td>67</td>
<td>16.1</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>220</td>
<td>69</td>
<td>15.2</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>200</td>
<td>58</td>
<td>11.6</td>
<td>120</td>
<td>5th sample of gas taken for analysis.</td>
</tr>
<tr>
<td>stop</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Temperature of outside of the main enclosure at stop, 40° C.*</td>
</tr>
</tbody>
</table>

* At 30 minutes after stop the cover attained a maximum temperature of 65° C., falling in 2½ hours to 30°.
FURNACE REACTIONS UNDER HIGH GASEOUS PRESSURES.

Table IV. (3).—Record of Analyses of Furnace Gas.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time after stop</th>
<th>Furnace pressure</th>
<th>CO₂</th>
<th>CO</th>
<th>H</th>
<th>CH₄</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>During run, see previous table</td>
<td>48</td>
<td>1.2</td>
<td>85.3</td>
<td>13.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>0.5</td>
<td>86.5</td>
<td>13.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>103</td>
<td>0.3</td>
<td>89.0</td>
<td>10.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>120</td>
<td>1.1</td>
<td>89.6</td>
<td>7.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>h. m.</td>
<td>92</td>
<td>3.4</td>
<td>85.3</td>
<td>11.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0 8</td>
<td>55</td>
<td>1.7</td>
<td>80.1</td>
<td>18.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0 25</td>
<td>43</td>
<td>2.7</td>
<td>77.9</td>
<td>19.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0 39</td>
<td>34</td>
<td>1.3</td>
<td>76.1</td>
<td>14.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0 58</td>
<td>30.5</td>
<td>2.0</td>
<td>74.0</td>
<td>4.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1 13</td>
<td>21.5</td>
<td>1.5</td>
<td>71.1</td>
<td>24.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2 43</td>
<td>18.5</td>
<td>1.8</td>
<td>69.1</td>
<td>16.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>3 40</td>
<td>15</td>
<td>1.4</td>
<td>66.9</td>
<td>19.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>22 0</td>
<td>12</td>
<td>1.4</td>
<td>65.6</td>
<td>20.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>42 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In this, as in most other cases, the furnace gas was found to contain a small percentage of iron carbonyl.

Table IV. (4).

The appearance of the furnace after run was similar to that shown in fig. 11, A₁.

The products from the different zones of the furnace were collected separately and submitted to analysis with the following results:

<table>
<thead>
<tr>
<th>Gross weight.</th>
<th>Weight of CaC₂ from analysis.</th>
</tr>
</thead>
<tbody>
<tr>
<td>grammes</td>
<td>grammes</td>
</tr>
<tr>
<td>Fused lump.</td>
<td>2090</td>
</tr>
<tr>
<td>Fritted mass round lump</td>
<td>1030</td>
</tr>
<tr>
<td>Fritted mass from base</td>
<td>770</td>
</tr>
<tr>
<td>Unacted-on mixture</td>
<td>6570</td>
</tr>
<tr>
<td>negligible</td>
<td>1088</td>
</tr>
</tbody>
</table>

"                                   |
"                                   |
Table V.—Summary of the Principal Experiments on the Fusion of Quartz.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>D 62</td>
<td>Resistance. Carbon tube, 4 centims. external diameter, length, 22 centims., between graphite terminals</td>
<td>8·34</td>
<td>10·0</td>
<td>Air</td>
<td>100</td>
<td>Product, a tube 23 centims. long, 4·5 centims. internal diameter, quite detached from core. External diameter about 8 centims. Weight of vitrified product, 2000 grammes.</td>
</tr>
<tr>
<td>D 68</td>
<td>Resistance. Carbon tube, 3 centims. external diameter, length, 21·7 centims., between graphite terminals</td>
<td>12·9</td>
<td>9·94</td>
<td>Air</td>
<td>100</td>
<td>Weight of vitrified product, 4100 grammes, for greater part of its length adhering to carbon core. At top blown out, forming a cup about 10 centims. internal diameter.</td>
</tr>
<tr>
<td>D 72</td>
<td>Resistance, as in D 68</td>
<td>11·3</td>
<td>9·14</td>
<td>Hydrogen</td>
<td>50</td>
<td>Weight of vitrified product, 2100 grammes, moulded around core.</td>
</tr>
<tr>
<td>D 74</td>
<td>Arc. 100 amperes at 120 volts, between carbon electrodes (fig. 11, d)</td>
<td>9·52</td>
<td>8·94</td>
<td>Hydrogen</td>
<td>180</td>
<td>Hollow sphere of vitrified material, 18 centims. external diameter, weighing 4800 grammes.</td>
</tr>
</tbody>
</table>
TABLE VI.—Details of One Typical Carborundum Experiment.

Large furnace enclosure used in vertical position (Plate 6, fig. 1).
Iron liner filled as shown in fig. 11, B.
Central resistance core of granular retort carbon packed in thin-walled brass tube 30 centims. long, 2·6 centims. diameter.
Electrical connection at top and bottom of core made by graphite discs 5 centims. thick and 8 centims. diameter.
Charge: mixture of 7½ kilogs. white Calais sand and 4½ kilogs. finely ground retort carbon; calcined shortly before experiment.
Iron pot lined with thin sheet of asbestos.
Initial pressure atmospheric; gaseous products of reaction retained up to about 100 atmospheres, then let off and pressure maintained constant.
E.M.F. at the terminals of the generator varied as required, and usually 2 to 3 volts above that in the furnace.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>amperes</td>
<td>volts</td>
<td>kilowatts</td>
<td>atmospheres</td>
<td></td>
</tr>
<tr>
<td>minutes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>start</td>
<td>220</td>
<td>4·0</td>
<td>0·88</td>
<td>Atmospheric</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>480</td>
<td>7·0</td>
<td>3·36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>7·0</td>
<td>4·20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>600</td>
<td>6·0</td>
<td>3·60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>840</td>
<td>8·0</td>
<td>6·72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1000</td>
<td>8·5</td>
<td>8·50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>500</td>
<td>12·0</td>
<td>6·00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>550</td>
<td>22·0</td>
<td>12·1</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>18</td>
<td>530</td>
<td>29·0</td>
<td>15·4</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>19</td>
<td>410</td>
<td>38·0</td>
<td>15·6</td>
<td></td>
<td>13</td>
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<tr>
<td>21</td>
<td>520</td>
<td>31·0</td>
<td>16·1</td>
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<td>520</td>
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<td>15·3</td>
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<td>26</td>
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<td>23</td>
<td>520</td>
<td>29·5</td>
<td>15·3</td>
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<td>25</td>
<td>500</td>
<td>30·5</td>
<td>15·2</td>
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<td>43</td>
</tr>
<tr>
<td>27</td>
<td>470</td>
<td>32·5</td>
<td>15·3</td>
<td></td>
<td>52</td>
</tr>
<tr>
<td>30</td>
<td>370</td>
<td>40·5</td>
<td>15·0</td>
<td></td>
<td>71</td>
</tr>
<tr>
<td>34</td>
<td>300</td>
<td>45·0</td>
<td>13·5</td>
<td></td>
<td>93</td>
</tr>
<tr>
<td>37</td>
<td>340</td>
<td>41·0</td>
<td>13·9</td>
<td></td>
<td>108</td>
</tr>
<tr>
<td>38</td>
<td>360</td>
<td>41·0</td>
<td>14·8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>380</td>
<td>40·0</td>
<td>15·2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>410</td>
<td>38·0</td>
<td>15·6</td>
<td></td>
<td>107</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>56 litres had been collected in gasometer.</td>
</tr>
<tr>
<td>44</td>
<td>440</td>
<td>36·0</td>
<td>15·8</td>
<td></td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>269 litres had been collected in gasometer.</td>
</tr>
<tr>
<td>46</td>
<td>470</td>
<td>35·0</td>
<td>16·4</td>
<td></td>
<td>101</td>
</tr>
<tr>
<td>49</td>
<td>470</td>
<td>33·0</td>
<td>15·5</td>
<td></td>
<td>108</td>
</tr>
<tr>
<td>52</td>
<td>470</td>
<td>33·0</td>
<td>15·5</td>
<td></td>
<td>107</td>
</tr>
<tr>
<td>55</td>
<td>470</td>
<td>33·0</td>
<td>15·5</td>
<td></td>
<td>102</td>
</tr>
</tbody>
</table>
TABLE VI.—Details of One Typical Carborundum Experiment (continued).

<table>
<thead>
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<th></th>
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<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>minutes</td>
<td>ampères</td>
<td>volts</td>
<td>kilowatts</td>
<td>atmospheres</td>
</tr>
<tr>
<td>58</td>
<td></td>
<td>490</td>
<td>32·0</td>
<td>15·7</td>
<td>106</td>
</tr>
<tr>
<td>62</td>
<td></td>
<td>490</td>
<td>32·0</td>
<td>15·7</td>
<td>100</td>
</tr>
<tr>
<td>65</td>
<td></td>
<td>490</td>
<td>32·0</td>
<td>15·7</td>
<td>—</td>
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<td></td>
<td>480</td>
<td>32·0</td>
<td>15·4</td>
<td>104</td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>480</td>
<td>32·5</td>
<td>15·6</td>
<td>—</td>
</tr>
<tr>
<td>73</td>
<td></td>
<td>480</td>
<td>32·5</td>
<td>15·6</td>
<td>103</td>
</tr>
<tr>
<td>76</td>
<td></td>
<td>480</td>
<td>32·5</td>
<td>15·6</td>
<td>103 Stop</td>
</tr>
</tbody>
</table>

Total gas production during the run calculated to be 840 litres at 0° C. and 760 millims.

Product closely adhering to central core formed a fritted mass cylindrical in shape, about 15 centims. diameter and 27 centims. long.

Total weight, 3600 grammes. Inner layer about 2 centims. thick, consisting of crystalline carborundum surrounded by thin sheath of the amorphous variety. The outer layers on analysis found to consist of agglomerated carbon and sand, containing only small percentage of carborundum.

Granular carbon core had been graphitized, but contained no carborundum.

TABLE VII.—Record of Furnace Gas Analyses in a Carborundum Experiment.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time.</th>
<th>Furnace pressure.</th>
<th>CO₂</th>
<th>CO</th>
<th>H</th>
<th>CH₄</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>minutes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>From start, 21</td>
<td>26</td>
<td>5·2</td>
<td>70·0</td>
<td>86·2</td>
<td>3·9</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>34</td>
<td>55</td>
<td>3·7</td>
<td>83·3</td>
<td>85·6</td>
<td>9·9</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>62 (stop)</td>
<td>122</td>
<td>2·9</td>
<td>89·0</td>
<td>83·8</td>
<td>10·5</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>After stop, 5</td>
<td>120</td>
<td>4·9</td>
<td>86·2</td>
<td>82·7</td>
<td>10·9</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>20</td>
<td>94</td>
<td>4·5</td>
<td>85·6</td>
<td>85·6</td>
<td>10·5</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>36</td>
<td>80</td>
<td>5·7</td>
<td>83·8</td>
<td>83·8</td>
<td>10·5</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>61</td>
<td>67</td>
<td>6·4</td>
<td>82·7</td>
<td>82·7</td>
<td>10·9</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>154</td>
<td>46</td>
<td>5·4</td>
<td>83·5</td>
<td>83·5</td>
<td>3·6</td>
</tr>
</tbody>
</table>
TABLE VIII.—Summary of Principal Experiments on the Reduction of Alumina by Carbon under High Pressure.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kilowatt hours</td>
<td>kilowatts</td>
<td>atmospheres</td>
<td>atmospheres</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G 19</td>
<td>16·0</td>
<td>9·6</td>
<td>63 air</td>
<td>157</td>
<td>Insignificant</td>
<td>Insignificant</td>
<td>Granular carbon core graphitized and containing much alumina fused around its particles.</td>
</tr>
<tr>
<td>G 41</td>
<td>2·5</td>
<td>9·0</td>
<td>6 nitrogen</td>
<td>25</td>
<td>Insignificant</td>
<td>Insignificant</td>
<td>Core of soot and alumina surrounded by pure alumina; to ascertain effect of fine division and intimate mixing. Tubing of fused alumina around core, but no evidence of reduction.</td>
</tr>
<tr>
<td>G 44</td>
<td>3·2</td>
<td>6·5</td>
<td>Atmospheric</td>
<td>17</td>
<td>Insignificant</td>
<td>Insignificant</td>
<td>Experiment similar and confirmatory to G 41.</td>
</tr>
<tr>
<td>G 17</td>
<td>9·4</td>
<td>7·8</td>
<td>Atmospheric</td>
<td>44</td>
<td>5·0</td>
<td>47·7</td>
<td>Central cavity formed (see fig. 11, A₄) having, at bottom disc of fused reduction product resting on graphitized pillar of carbon.</td>
</tr>
<tr>
<td>G 32</td>
<td>4·6</td>
<td>8·2</td>
<td>Atmospheric</td>
<td>35</td>
<td>13·0</td>
<td>102</td>
<td>Similar to G 17.</td>
</tr>
<tr>
<td>G 18</td>
<td>16·0</td>
<td>16·0</td>
<td>26 hydrogen</td>
<td>110</td>
<td>3·3</td>
<td>20·9</td>
<td>No diluting gas added during run. Furnace type, fig. 11, B. Resistance core granular carbon, after run no core remaining, appearance being similar to fig. 11, B₂.</td>
</tr>
<tr>
<td>G 77</td>
<td>11·4</td>
<td>11·7</td>
<td>55 hydrogen</td>
<td>100</td>
<td>3·2</td>
<td>60·1</td>
<td>Current of hydrogen through hollow electrode. During run, 900 litres; during cooling, 420 litres. Furnace type, fig. 11, D, with core of alumina and carbon between the two carbons.</td>
</tr>
<tr>
<td>G 20</td>
<td>7·2</td>
<td>17·2</td>
<td>39 coal gas</td>
<td>133</td>
<td>46</td>
<td>262</td>
<td>No diluting gas added during run. Some lime added to mixture. Fused product contained large amount of graphite flakes. Furnace type, fig. 11, A.</td>
</tr>
<tr>
<td>G 21</td>
<td>8·0</td>
<td>16·0</td>
<td>15 coal gas</td>
<td>25</td>
<td>49</td>
<td>106</td>
<td>The furnace was alternatively filled with coal gas to 25 atmospheres and gas blown down to 15 atmospheres; 600 litres coal gas during run, 1200 litres during cooling period. Some lime added to mixture. Little graphite formation. Furnace type, fig. 11, A.</td>
</tr>
<tr>
<td>G 24</td>
<td>14·6</td>
<td>13·4</td>
<td>60 coal gas</td>
<td>90</td>
<td>31·8</td>
<td>198</td>
<td>Current of coal gas continuously passed through furnace at a rate of about 0·5 litre per second, pressure being maintained approximately constant at its maximum value. Furnace type, fig. 11, A.</td>
</tr>
<tr>
<td>G 33</td>
<td>9·1</td>
<td>9·8</td>
<td>15 coal gas</td>
<td>30</td>
<td>46</td>
<td>228</td>
<td>Regime of gas circulation similar to G 21. During run, 800 litres; during cooling about 800 litres also. Furnace type, fig. 11, A.</td>
</tr>
<tr>
<td>G 36</td>
<td>2·0</td>
<td>8·0</td>
<td>3 hydrogen</td>
<td>5</td>
<td>6·5</td>
<td>45</td>
<td>Reduction of alumina by calcium carbide. No diluting gas added during run. Furnace type, fig. 11, A.</td>
</tr>
<tr>
<td>G 75</td>
<td>15·3</td>
<td>9·8</td>
<td>50 hydrogen</td>
<td>70</td>
<td>17·7</td>
<td>130</td>
<td>Current of hydrogen through hollow carbon electrodes. During run, 900 litres; during cooling, 600 litres. Furnace type, fig. 11, D.</td>
</tr>
<tr>
<td>G 76</td>
<td>6·3</td>
<td>7·9</td>
<td>40 hydrogen</td>
<td>80</td>
<td>23·5</td>
<td>76·2</td>
<td>Regime of gas circulation similar to G 75. 510 litres during run, 110 litres during cooling.</td>
</tr>
</tbody>
</table>
TABLE IX. (1).—Typical Experiment on the Reduction of Alumina by Carbon (G 33).

The large furnace enclosure was used in the vertical position.
Iron liner filled as shown in fig. 11, A.
Lower electrode, bed of 2 kilogs. retort carbon.
Upper electrode, a 41-millim. carbon rod 32 centims. long; weight with holder, 1650 grammes.
Charge: about 5500 grammes calcined alumina (Brit. Al. Co.), mixed with 1130 grammes petroleum coke (60-mesh).
Initial pressure, 20 atmospheres coal gas.
Gaseous products of reaction washed out with coal gas (see p. 442), the gas being let off about every 10 minutes until the pressure had fallen to 15 atmospheres, a fresh supply of coal gas being at once forced in, raising the pressure to 25 or 30 atmospheres.

TABLE IX. (2).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>volts</td>
<td>volts</td>
<td>ampères</td>
<td>kilowatts</td>
<td></td>
</tr>
<tr>
<td>minutes start</td>
<td>60</td>
<td>42</td>
<td>200</td>
<td>8·4</td>
<td>Initial pressure, 20 atmospheres coal gas.</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>30</td>
<td>300</td>
<td>9·0</td>
<td>Gas blown off down to 15 atmospheres, coal gas admitted to 25 atmospheres.</td>
</tr>
<tr>
<td>5</td>
<td>47</td>
<td>30</td>
<td>340</td>
<td>10·2</td>
<td>2nd lot of gas let off as before.</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>70</td>
<td>150</td>
<td>10·5</td>
<td>3rd lot of gas let off as before.</td>
</tr>
<tr>
<td>14</td>
<td>80</td>
<td>70</td>
<td>150</td>
<td>10·5</td>
<td>4th lot of gas let off.</td>
</tr>
<tr>
<td>16</td>
<td>65</td>
<td>57</td>
<td>200</td>
<td>11·4</td>
<td>5th lot of gas let off.</td>
</tr>
<tr>
<td>20</td>
<td>62</td>
<td>45</td>
<td>250</td>
<td>11·3</td>
<td>6th lot of gas let off.</td>
</tr>
<tr>
<td>23</td>
<td>56</td>
<td>42</td>
<td>250</td>
<td>10·5</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>55</td>
<td>42</td>
<td>250</td>
<td>10·5</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>60</td>
<td>48</td>
<td>220</td>
<td>10·6</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>60</td>
<td>50</td>
<td>180</td>
<td>9·0</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>60</td>
<td>50</td>
<td>180</td>
<td>9·0</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>60</td>
<td>50</td>
<td>180</td>
<td>9·0</td>
<td></td>
</tr>
<tr>
<td>stop</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE IX. (3).

The total volume of coal gas used during the experiment was 800 litres, and about the same volume during the subsequent cooling period.
Product: central fused lump surrounding the vertical electrode, to which it adhered; had a weight of about 1560 grammes, and had the appearance of fused alumina containing some aluminium carbide.
The fused lump contained 228 grammes of aluminium carbide and 36 grammes of aluminium, some of which was found in the form of plates after crushing.
The outside fritted material, about 1125 grammes in weight, contained a further 9 grammes of aluminium in large pieces. No reduced material was found in the outer layers of the charge.
Total yield was therefore 228 grammes aluminium carbide 45·7 grammes aluminium.
TABLE X.—Experiments on the Reduction of Alumina by Carbon at Atmospheric Pressure.

A. Radiation Heating from Arc.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>G 45</td>
<td>40 volts</td>
<td>140 ampères</td>
<td>5 minutes</td>
<td>Fused (\text{Al}_2\text{O}_3), No Al metal or carbide</td>
<td>Mixture corresponding to (\text{Al}_2\text{O}_3 + 2\text{C}) placed under arc on alumina bed. Furnace enclosed. Hydrogen circulation.</td>
</tr>
<tr>
<td>G 46</td>
<td>25</td>
<td>240</td>
<td>14</td>
<td>Fused lump of (\text{Al}_2\text{O}_3), No Al metal or carbide</td>
<td>Similar experiment to G 45.</td>
</tr>
<tr>
<td>G 47</td>
<td>40</td>
<td>300</td>
<td>10</td>
<td>No aluminium or carbide</td>
<td>(\text{CaF}_2) used as flux (28 per cent.) with same mixture as above. Heated until very rapid vaporisation of fluor spar. Furnace, ordinary Moissan type. Material in carbon crucible.</td>
</tr>
<tr>
<td>G 48</td>
<td>42</td>
<td>300</td>
<td>10</td>
<td>No aluminium or carbide</td>
<td>Larger percentage of fluoride (61 per cent.), otherwise similar experiment to G 47.</td>
</tr>
</tbody>
</table>

B. Resistance Core of Mixture.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Product.</th>
<th>Observations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>G 61</td>
<td>Total energy, about 1 kilowatt hour Power, 4 kilowatts</td>
<td>Fused lump of alumina. No Al or carbide</td>
</tr>
<tr>
<td>G 62</td>
<td>Total energy, 5.8 kilowatt hours Power, 7 kilowatts</td>
<td>Condensate, but negligible Al in fused lump</td>
</tr>
</tbody>
</table>
Table X.—Experiments on the Reduction of Alumina by Carbon at Atmospheric Pressure (continued).

C. Approximate Estimation of Temperature of Reduction.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>G 55</td>
<td>A. 10 grammes (Al₂O₃ + 2C) + 40 grammes Cu</td>
<td>M.P. Ni. . .</td>
<td>No appreciable reduction</td>
<td>Experiment in carbon tube furnace with careful adjustment of temperature.</td>
</tr>
<tr>
<td></td>
<td>B. 10 grammes (Al₂O₃ + 2C) + 40 grammes Cu</td>
<td>M.P. Pt. . .</td>
<td>No appreciable reduction</td>
<td>Experiment in carbon tube furnace with careful adjustment of temperature.</td>
</tr>
<tr>
<td></td>
<td>C. 10 grammes (Al₂O₃ + 2C) + 40 grammes Cu</td>
<td>Above M.P. Pt, but below M.P. Al₂O₃</td>
<td>No appreciable reduction</td>
<td>Experiment in carbon tube furnace with careful adjustment of temperature.</td>
</tr>
<tr>
<td>G 57</td>
<td>A. 8 grammes (Al₂O₃ + 2C) + 25 grammes Cu + 10 grammes CaF₂</td>
<td>Above M.P. Pt, but below M.P. Al₂O₃</td>
<td>No appreciable reduction</td>
<td>Experiment in carbon tube furnace with careful adjustment of temperature (mixture well fused).</td>
</tr>
<tr>
<td></td>
<td>B. 72 grammes (Al₂O₃ + 2C) + 25 grammes Cu + 8·5 grammes CaO</td>
<td>Above M.P. Pt, but below M.P. Al₂O₃</td>
<td>No appreciable reduction</td>
<td>Experiment in carbon tube furnace with careful adjustment of temperature (mixture well fused).</td>
</tr>
<tr>
<td>G 58</td>
<td>A. 10 grammes (Al₂O₃ + 2C) + 50 grammes Cu</td>
<td>Just above M.P. of alumina</td>
<td>46 grammes alumina-bronze (6·6 per cent. Al)</td>
<td>Crucible containing mixture embedded in granular carbon, covered with a second crucible containing alumina. Latter showed no sign of fusion.</td>
</tr>
<tr>
<td></td>
<td>B. 10 grammes (Al₂O₃ + 2C) + 50 grammes Cu</td>
<td>Considerably higher temperature</td>
<td>49 grammes alumina-bronze (7·8 per cent. Al)</td>
<td>Similar construction alumina in upper crucible also fused. All the mixture either combined or volatilised.</td>
</tr>
</tbody>
</table>
XII. A New Current Weigher and a Determination of the Electromotive Force of the Normal Weston Cadmium Cell.


Received June 5,—Read June 27, 1907.

[PLATES 7-8.]

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VOL. CCVII.—A 424.
HISTORICAL NOTES ON THE ABSOLUTE MEASUREMENT OF CURRENT.

A CURRENT can be measured absolutely in the electro-magnetic system of units either by means of the action of the current on a magnet, or of the current on a current. The former method has the disadvantage that at least two independent measurements are necessary. For example, in using an electro-magnetic balance, the strength of the magnet acted on by the electric circuit has to be determined, as well as the force exerted on the magnet by the circuit. In galvanometers, either of the sine or tangent type, the magnetic field produced by the electric circuit is compared with the earth's horizontal field, the strength of which is determined independently. Further, as the strength of artificial magnets cannot be regarded as truly constant, and the earth's field is subject to diurnal and secular variations, this class of measurement is not ideal.

In the electrodynamical class of measurement the mutual action between two or more coils carrying current takes the form of a torque, as in electrodynamometers, or a direct force, as in current weighers. In electrodynamometers the torque may be measured with a bifilar suspension, the torsion of a wire or spring, or by means of a gravity balance. Current weigher measurements are almost always made by direct comparison with gravity, which is believed to be constant, and is known to a higher degree of accuracy than the strengths of any magnet or magnetic field that has yet been measured.

Shortly after the absolute system of units was devised by GAUSS and WEBER in 1832, A. BECQUEREL* weighed the attraction between a coil and a magnet; and two years later LENZ and JACOB† used and modified BECQUEREL's balance by arranging a coil and magnet at each end of the beam. In 1840 W. WEBER determined the electrochemical equivalent of water, using the tangent galvanometer as his instrument for measuring current; and in 1843 similar measurements were made by BUNSEN and by CASSEL-MANN, followed in 1851 by JOULE.

Meanwhile W. WEBER‡ had, in 1846, invented his two forms of electrodynamometer, one with the suspended coil inside, and the other with this coil outside the fixed coil, and he measured the torque with bifilar and unifilar suspensions.

The first current weigher appears to have been constructed by CAZIN§ in 1863. This consisted of two rectangular coils with their planes horizontal, one hanging from the beam of a balance directly above the other, which was supported on an adjustable table. The instrument was used for determining the electrochemical equivalent of water.

In 1864 JOULE|| made a current weigher having three circular flat coils wound with copper strip, one being suspended from a balance, so that its mean plane, which was horizontal, was midway between those of the other two fixed coils. This instrument had the correction to its principal constant determined by comparison with a standard tangent galvanometer, and was employed in JOULE's electrical determination of the mechanical equivalent of heat. Its object was to enable a constant current to be maintained through the calorimeter, independent of variations in the earth's magnetic field.

LATIMER CLARK,* in determining the E.M.F. of his standard cell in 1872, used a bifilar electrodynamometer with circular fixed and moving coils, each arranged in the Helmholtz fashion. The fixed coils were of large size relative to the suspended ones, a fact which considerably simplified the calculation of the torque per unit current. The instrument had been constructed for the Electrical Standards

* 'Comp. Rend.,' vol. V., p. 35, 1837.
† 'Pogg. Ann.,' XLVII., p. 227, 1839.
|| 'B.A. Report,' 1864.
* 'Roy. Soc. Proc.,' May 30, 1872; also 'Phil. Trans.,' 1874, Part I.
A NEW CURRENT WEIGHER, ETC.

Committee of the British Association, and was wound by CLERK MAXWELL. LATIMER CLARK also used a sine galvanometer for his E.M.F. measurements, and arrived at the values $1.4573$ and $1.4562$ B.A. volts at $15.5^\circ$ C. with the two methods respectively.

In 1873 F. KOHLRAUSCH* employed the tangent galvanometer and magnetometer in determining the electrochemical equivalent of silver, which he found to be $1.1363$ milligrammes per coulomb.

MASCART,† in 1882, constructed his current weigher formed of a long solenoid hung from a balance arm, with its lower end in the mean plane of a large circular coil, and published the number $1.124$ milligrammes as the mass of silver deposited by one coulomb. This was corrected in 1884 to $1.1156$.‡

At the British Association Meeting in 1882§ Lord RAYLEIGH discussed the several methods of measuring current absolutely which had been employed by previous experimenters, more especially those used by KOHLRAUSCH and by MASCART. He pointed out that a large part of MASCART's long solenoid was comparatively ineffective, and considered that the moving coil should be compact and situated near the position of maximum effect. A further advantage would, he pointed out, be gained by duplicating the fixed coil, thus making the arrangement symmetrical and doubling the force. The dimensions of (current)$\|$ in the electromagnetic system being the same as those of force, Lord RAYLEIGH showed that the constant of a current weigher arranged as described above, must be a numeric, depending on the mean radii of the coils as a ratio, which could be determined electrically with high precision without any linear measurements whatever having to be made.

In 1883 Lord RAYLEIGH published the result that he had obtained with a current weigher thus constructed, viz., $1.119$ milligrammes of silver per coulomb. Meanwhile F. and W. KOHLRAUSCH had carried out measurements of high precision with the tangent-galvanometer and suspended-coil method, obtaining the values $1.11833$ and $1.11822$ respectively in 1881 and 1883, although these results were not published until later.¶

In a classical memoir** Lord RAYLEIGH and Mrs. SIDGWICK showed that the number given by Lord RAYLEIGH in 1883, viz., $1.119$, was too high by nearly 1 in 1000, owing to inclusion of mother liquor with the silver. This was due chiefly to the solution being filtered through silver acetate to secure firmer deposits. With pure silver nitrate they found the equivalent to be $1.11794$, the greatest difference from the mean of thirteen experiments being less than 1 part in 2500. The paper contains a full description of the current weigher, the method of using it, the calculation of the force between the coils, and a table of numbers for facilitating the making of these calculations by elliptic integrals. Also a very careful determination of the E.M.F. of a number of CLARK cells is given. It is important to notice that no measurements of length, moment of inertia, or time are necessary in determining current with a current weigher made on Lord RAYLEIGH's plan, and this constitutes one of its great advantages.

THOMAS GRAY, in 1886,†† determined the electrochemical equivalent of silver by means of a sine galvanometer of his own design, and in 1887 KOEPSEL,‡‡ used an electromagnetic balance of most ingenious construction, made according to VON HELMHOLTZ's instructions, for the same purpose. The results obtained, although approximating closely to those of F. and W. KOHLRAUSCH, and of Lord RAYLEIGH and Mrs. SIDGWICK respectively, are not so trustworthy.

* 'Pogg. Ann.,' 149, S. 170, 1873.
† 'Jour. de Phys.,' [2], t. i., p. 109, 1882.
‡ 'Jour. de Phys.,' t. III., p. 283, 1884.
** 'Phil. Trans.,' 175, p. 411, 1884.
†† 'Phil. Mag.,' 22, p. 339, 1886.
In 1890 Pellat and Potier* employed an electrodynamometer balance in silver deposit work, which had a short cylindrical coil secured with its axis vertical to one arm of a balance; this arm projected along the axis of a long horizontal solenoid fixed symmetrically with respect to the moving coil. The torque between the coils was balanced by weights, the magnitude of which gave 1·1192 as the mass of silver deposited per coulomb.

With a view to simplifying the use of Rayleigh's current weigher, Heydweiller† in 1891 modified the arrangement by placing the coils with their common axis horizontal, the moving coil being carried directly below the centre of the balance beam. Nearly the whole of the force was balanced by weights on the horizontal arm, and the rest determined from the slight displacement of the coil from the vertical position.

To determine the E.M.F. of Clark cells in 1896 Kahle‡ used a Helmholtz electrodynamometer balance of novel construction, in which the moving coil and balance beam were supported by, and so that they rolled on, thin metal strips which served also as leads. Rectangular coils of many turns embraced the balance case in planes perpendicular to the length of the beam. The constants of these coils, as well as of the suspended one, were determined by comparison of their magnetic effect with that of a large rectangle of copper band stretched round a strong metal frame, the dimensions of which could be accurately measured. The experiments gave the result 1·4322 at 15° C.

In 1897 the late Professor J. Viriamu Jones, in collaboration with one of the authors (W. E. A.), devised a current weigher in which the forces could be calculated with great exactness by a formula developed by the former;§ and a preliminary instrument was constructed with single layers of wire in screw grooves, and described at the British Association Meeting in 1898.||

Messrs. Patterson and Guthè,¶ working under Professor Carhart, employed a torsion electrodynamometer with fixed coils on wood and suspended coil on vulcanite, and made determinations of silver deposit (1·1192 milligrammes per coulomb) which they believed accurate to 1 part in 5000. In the following year (1889) Carhart and Guthè** measured the E.M.F. of Clark cells with the same instrument, obtaining the value 1·4333 at 15° C., and in 1902 Callendar†† published the result (1·4334 at 15° C.) got by R. O. King with an electrodynamometer of the British Association pattern employed in his (Callendar's) researches on “Continuous Electric Calorimetry.”

Further determinations of the electrochemical equivalent of silver with Pellat's electrodynamometer balance were made in 1903 by Pellat and Leduc,‡‡ who obtained 1·1195 milligrammes per coulomb. In the same year Van Dijk and Kunst §§ carried out a very careful research in a new laboratory free from iron and vibration, using two tangent galvanometers, magnetometer and variometer, and from the mean of twenty-four closely accordant determinations of the electrochemical equivalent of silver deduced the value 1·11818. This they believed to be accurate to 1 part in 10,000.

Professors Carhart and Patterson|| described, at the meeting of the Electrical Congress at St. Louis

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* 'Jour. de Phys.,' t. VI., p. 175, and t. IX., p. 381, 1890.
† 'Wied. Ann.,' 44, p. 533, 1891.
†† 'Phil. Trans.,' A., 199, p. 81, 1902.
‡‡ 'Comp. Rend.,' 136, p. 1649, 1903.
§§ 'Versl. van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling,' Dec., 1903.
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in 1904, a new torsion electrodynamometer of the Gray* pattern, having single-layer coils on cylinders of Paris plaster. Experiments on Clark and cadmium cells were then in progress.

Last year (1906) Guthrie published the results of a lengthy research on Clark and cadmium cells in which another Gray electrodynamometer was employed. He arrived at the values 1·43296 at 15° C. and 1·01853 at 20° C. for the respective cells, and deduced from this and previous work 1·11773 milligrammes per coulomb as the electrochemical equivalent of silver. The instrument employed by Guthrie suffers from non-uniformity of winding, but this was allowed for approximately. Its influence on the accuracy of the electrodynamometer is discussed by Rosa in the same number of the 'Bulletin' (p. 71).

SECTION 1.—INTRODUCTORY.

The instrument herein described is the outcome of conversations between the late Professor J. Viriamu Jones and one of the authors (W. E. A.) on their return from the British Association meeting, held in Toronto in 1897.

Absolute determinations of resistance had been made on many occasions, and with considerable precision, whilst those of current were comparatively few; the want of agreement between the results obtained by different observers was by no means satisfactory. It was therefore decided to make a new determination of the ampere by means of a current weigher formed of coils with single layers of wire, such as had been so successfully employed by Professor Jones in his determination of the "Specific Resistance of Mercury in Absolute Measure" ('Phil. Trans.', A, 1891), and by Professors Ayrton and Jones in their determination of the ohm at the Central Technical College, London, in 1897.†

By using coaxial coils, with single layers of wire wound in screw-thread grooves, advantage could be taken of the convenient formula developed by Professor Jones for calculating the electro-magnetic force between a helix and a circular current sheet,§ viz.,

\[ F = \gamma_h \gamma (M_2 - M_1), \]

where \( \gamma_h \) is the current in the helix, \( \gamma \) the current per unit length of the current sheet, and \( M_1, M_2 \) the coefficients of mutual induction of the helix and the two circular ends of the current sheet.

To test the stability of the proposed current weigher, or "ampere balance" as it is frequently called, as well as to get experience regarding the conditions necessary for successful operation, a preliminary apparatus was constructed at the Central Technical College in 1898, and there used to make an approximate

* 'Gray's Absolute Measurements, &c.,' vol. 2, part 1, p. 274.
‡ 'B.A. Report,' Toronto, p. 212, 1897.
determination of the electro-chemical equivalent of silver.* In this instrument
the coils were formed by winding insulated wire in the grooves of screw threads
cut in metal cylinders, but the springiness of the covering prevented very exact
measurements of the dimensions being made. To obtain greater precision, it was
decided to use, in the proposed balance, bare wire wound on insulating material,
as originally employed in the Lorenz apparatus designed by Professor J. V. Jones
for the McGill University, Montreal, and to avoid the uncertainty as to leakage
between adjacent turns of such a spiral† the arrangement devised by one of the
authors (W. E. A.) of having double-threaded screw grooves wound with separate
bare wires, subsequently connected in series after the insulation resistance between
them had been made satisfactory, was adopted.

Experience with the preliminary apparatus showed that air convection currents
should be minimised, and that easy access to, and independent adjustments of, both
fixed and suspended coils were very desirable. In designing the new current weigher,
in collaboration with the late Professor Jones, these points were kept in view, and
the arrangements chosen were such as would take full advantage of the mechanical
precision attainable with modern machine tools, a subject which Professor Jones had
very much at heart. In fact, he had long advocated that the instruments employed
in realising the concrete values of the electrical units from their absolute definitions
should be engineering tools rather than ordinary physical laboratory apparatus.

Complete working drawings and specifications of the proposed instrument, and its
adjustable support, were prepared at the Central Technical College during the Session
1898–99, the drawings being made by Mr. J. P. Gregory, then a student of the
College, and now of the British Thomson Houston Co., Rugby. Tenders were
obtained for the construction of the instrument, to defray the cost of which the
British Association for the Advancement of Science made a grant of £300.§

As the amounts of the tenders for the balance, and the adjustable phosphor-bronze
stand for supporting it, much exceeded the above-named sum, Sir Andrew Noble,
F.R.S., was approached, and took so much interest in the apparatus and the important
work that was to be carried out with it, that he generously presented the carefully
made adjustable support, constructed by Messrs. Sir W. Armstrong, Whitworth
and Co., Limited, free of cost.

The physical balance was built by Mr. L. Oertling, of London, and the electrical
portions were made at the National Physical Laboratory, under the supervision of the
Director, Dr. R. T. Glazebrook, F.R.S.

We may here remark that the current weigher has proved to be the most perfect
absolute electrical instrument hitherto constructed, and has enabled us to determine

† This uncertainty necessitated the removal of the original winding of the Lorenz apparatus, and
‡ 'B.A. Report,' 1898, p. 147.
the ampere to a very high degree of accuracy. In fact, this unit is now known with a precision considerably greater than any other electrical quantity of which absolute measurements have been made.

Section 2.—General Description.

The instrument consists of a very sensitive physical balance supporting a coil with vertical axis from each end of the beam, these coils hanging coaxially within fixed coils carried from the base of the balance. A diagrammatic sketch of the arrangement is shown in fig. 1, and a view of the complete instrument in fig. 2, Plate 7.

From the former it will be seen that the current flows in opposite directions in the upper and lower parts of the outer coils. On the left-hand side of fig. 1 the current in the upper half of the outer coil flows clockwise (looking from above) and in the lower half counter-clockwise, whilst in the left-hand suspended coil the circulation is shown clockwise. The tendency is, therefore, to lift the suspended coil SL. It will also be seen that the outer coils on the right will tend to depress the suspended coil SR, so that the two sets of coils exert a clockwise torque on the beam. This torque is balanced by weights added to or taken from scale pans supported independently on the knife edges which carry the suspended coils, an arrangement which avoids displacement of the suspended coils when the weights are placed or removed.

All the coils are wound with bare wire on hollow marble cylinders, having double-threaded screw grooves cut on the surfaces, into which separate wires are laid as shown in fig. 3. In this figure one wire is indicated by two thin lines, and the other is shown thick. The two wires, hereafter distinguished as No. 1 and No. 2, form two adjacent helices, which, in the use of the instrument, are connected in series and act as one coil. They can, however, be readily disconnected from each other and an
insulation test made between them. This applies to each of the six coils forming the current weigher, arrangements being made whereby the six No. 1 wires may be connected together, the six No. 2 wires similarly grouped, and the insulation between adjacent wires of the whole instrument tested simultaneously. Any leakage between the two adjacent helices can thus be readily detected and localised and remedied.

Each of the fixed cylinders carries four helices, two upper and two lower, and each suspended cylinder two. There are therefore twelve helices in all, and these are connected in series in the normal use of the current weigher by means of small concentric cables running to a plug board and commutators outside the balance case. Flexible connections are used as leads and returns to and from the suspended coils. The commutators enable the direction of the current in any coil to be changed at will. By reversing the current in the coils on the fixed cylinders the forces between the fixed and suspended coils are reversed, and the apparent change of weight thus produced is a measure of the square of the current used.

Fig. 4. General view of instrument, showing outer coils lowered.
The position of the balance beam is observed by viewing a finely divided scale carried by the pointer through a microscope seen in fig. 2, Plate 7, and in fig. 4.

A double glazed case or cover, with ¾-inch air space between the sheets, resting on a phosphor-bronze plate, serves to exclude dust and draughts, and to minimise convection currents which may be caused by unequal radiation or conduction from surrounding objects.

The whole instrument is supported on an adjustable phosphor-bronze stand or pedestal at a convenient height (see fig. 4), levelling screws being placed at the corners of the base.

Section 3.—Adjustable Support for Balance.

On opposite sides of the central pillar of the pedestal (see fig. 4) are sliding brackets BB, like the tables of small milling machines, which can be lowered through distances of about 14 inches (35 centims.) by means of vertical screws SS. Each bracket supports a slide rest having a circular top-plate which can be moved half-an-inch horizontally in two directions at right angles by means of screws with graduated heads. The nuts on the vertical screws are of large diameter, and they

![Diagram](Fig. 5. Section through top-plate of slide rest for supporting fixed cylinders.)

and the heads of the horizontal screws are divided to read thousandths of an inch. As each division can be subdivided by eye to tenths, it is possible to read the position of either fixed cylinder to a ten-thousandth of an inch.

The weights of the fixed cylinders and brackets are sufficient to overcome the friction in the vertical slides and thus avoid backlash in these motions. In the horizontal movements backlash is avoided by using strong phosphor-bronze springs shown at α, fig. 5, capable of moving the corresponding slide when tightened up
to prevent shake and loaded with a fixed cylinder. These springs keep the horizontal screws always in tension.

When the brackets B, figs. 4 and 5, are near their highest positions, the circular top-plates P’P’ of the slide rests project through holes in the phosphor-bronze plate, PP, fig. 5, which forms the base of the balance. Copper spinnings $s$ of section 7 fit closely round the top-plates, and can slide between the plate P and ring r, thus forming a draught-tight joint, and at the same time permitting horizontal motion of about half-an-inch in any direction.

For supporting the marble cylinders M, fig. 5, annular phosphor-bronze castings C, of inverted channel section, rest on fine-threaded levelling screws $l$, projecting through the top-plates of the slide rests, the heads being below the plates, so that levelling can be done from beneath the balance case. This arrangement is on the "hole, slot and plane principle," to avoid constraint and yet ensure precision in position.

**Section 4.—The Physical Balance.**

A photograph of the instrument, without coils, is shown in fig. 6, Plate 8. It has a beam 20 inches (50.8 centims.) long, capable of supporting 5 kilogrammes at each end, and turning with about one-tenth of a milligramme, a rider beam, divided into 100 parts on each side, and two rider carriers are fitted. All the knife edges and planes are of agate, and as fine as possible consistent with the loads they have to carry.

From each of the outer knife edges $K$ there depends a three-armed spider $S$, with heavy nuts $N$ at the end of each arm, and adjustable hooks $a$, $a$, from which the corresponding suspended cylinder hangs on three phosphor-bronze wires $w$, $w$, $w$. The object of the nuts is to enable the suspended cylinder to be levelled, two very sensitive levels being fixed to the cylinder for this purpose.

Below the suspended cylinder, and quite clear of it, is a copper disc $d$, fig. 6, carried by three wires $w'$, $w'$, $w'$ attached to the clamping beam $F$ of the balance, for supporting the cylinder should one of the wires $w$, $w$, $w$ become unhooked.

The scale pans for carrying the weights used to balance the forces exerted by the coils, hang from separate planes on the same knife edges as support the suspended cylinders. These may be seen in fig. 7, where $K$ is the knife edge, $H$ is the hook carrying the spider $S$, and $h$ the hook supporting the scale pan $p$. This arrangement is novel, and of considerable utility, for it permits of removal or replacement of the weights without affecting the levelling of the suspended cylinder. Its adoption, however, necessitates the perfect straightness of the knife edges. This condition has been satisfied to a very high degree of accuracy by Mr. Oertling, for shifting a weight of 16 grammes from the scale pan to the cylinder produced no appreciable difference in the rest-point of the balance, when the sensitiveness was such that one-tenth of a milligramme could be detected. As will be seen from figs. 2, 6, and 7, the scale pans are of unusual shape. Rods
Fig. 7. End and side elevations to show mode of supporting scale pan and spider from same knife edge.

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Fig. 8. Arrangement of leads to coils on fixed cylinders.
R, R, R, fig. 7, project upwards from the plate $p'$, and from the middle and upper ends of these rods sector-shaped pieces $q$ project inwards and form tripods on which the weights may rest. Claw-shaped lifters on the arms $A$, $A$, figs. 6 and 7, are operated by cams $C$ fixed in the corners of the balance case, and serve to remove or replace the weights. The arrangement is very convenient, and works with perfect smoothness, the result of the excellent workmanship of Mr. Oertling. Two weights and two lifters are provided at each end of the balance. These may be seen in the end view of the instrument shown in fig. 7a, Plate 8, and also in fig. 6.

Another novel feature of the balance is the arrangement employed for taking the beam off the centre agate plane and fixing it in the zero position without appreciably raising or lowering the suspended cylinders. This is of considerable importance, as it allows of the coils being levelled and adjusted vertically to the sighted position, without continually clamping and freeing of the beam for making and testing the adjustment. The specification for the balance stated that “the displacement of the suspended coils caused by fixing the beam must not exceed 4 mils (one-tenth of a millimetre).” Mr. Oertling has, however, used a construction which reduces the displacement to a far lower figure, as the fixing is effected without raising the beam more than 0.004 millim. (4 microns), and the planes carrying the suspended coils are clamped with a movement less than 0.08 millim.

The handle seen at the front of the case in figs. 2 and 6 actuates the clamping arrangements. Turning it clockwise through 180° from the position shown lowers the whole clamping beam $F$, fig. 6, thus bringing the centre knife edge against its plane, and allowing the planes supporting the scale pans and cylinders to rest on the end knife edges. By sliding inwards a tube surrounding the horizontal clamping axle, and turning the handle through another 90°, two agate hemispheres $m, m$ are brought into contact with agate planes on the beam immediately above them and fix the beam in the zero position whilst the scale pans and cylinders still hang on the beam. This device is made use of when changing the weights, and on reversal of current in making measurements.

For observing the rest-point of the balance a microscope, seen at $M_a$, fig. 6, is used to view a finely divided ivory scale carried by the pointer at a distance of $14\frac{2}{3}$ inches (37.2 centims.) from the knife edge. The magnifying power of the microscope is about 48, and the scale is $\frac{3}{4}$ of an inch long, divided into 200 parts; each division is therefore $\frac{3}{500}$” (0.0095 millim.). The cross wires and the lines on the scale are sufficiently fine to permit of one-twentieth of a division to be estimated quite easily, and with care and practice it is possible to read to fiftieths of a division, and in some cases to hundredths.* In all observations the method of vibrations was employed in determining the rest-point, the amplitude being limited to a few divisions on either side of the middle.

* For illuminating the scale, a lens and a Nernst lamp placed some 6 feet away were used, and proved most satisfactory.
To allow of free access to the balance there are two sliding sashies, S', S', fig. 6, both at the front and back of the case, and the ends have hinged doors, D, opening outwards. The middle portion of the case carrying the microscope and the corresponding piece at the back can also be removed. It is thus possible to make any adjustment required with comparative ease. Fig. 2, Plate 7, shows a view of the balance with sides of the case taken away.

Although it is not essential that the arms of the balance should be of equal length in a current weigher used in the manner described on p. 526, it was thought desirable to determine the ratio of their lengths. Employing weights of 50 grammes, it was found that

\[
\text{length of left arm} \div \text{length of right arm} = 1.00001,
\]

so a very close approximation to equality exists.

Section 5.—Magnetic Tests.

As it is of considerable importance that the permeability of all parts of the current weigher be practically unity, magnetic tests were made on the materials employed.

Before the phosphor-bronze support for the balance was cast, Sir Andrew Noble forwarded to the Central Technical College in September, 1899, a bar of the alloy it was intended to use, and careful experiments were made on the material. Tested by a very sensitive magnetometer the bar showed no magnetic property. An induction balance having two primary coils in series, and two secondaries in series opposing, with a sensitive moving-coil galvanometer in the same circuit, was therefore set up. One of the induction coils was in the form of a solenoid 2·4 centims. diameter and 36 centims. long, wound with 457 turns of No. 18 S.W.G. wire as primary and 1600 turns of No. 34 S.W.G. as secondary. The other half of the balance was formed of two separate coils whose relative position could be varied continuously until their mutual induction exactly balanced that of the solenoid windings when the core was of air. By shunting a known fraction (\(1/1000\)) of the current from the primary of the second pair the swing obtained on the scale of the galvanometer gave a measure of the sensitiveness of the arrangement; this was sufficient to show a change of 1 part in 30,000.

On removing the above-mentioned shunt and inserting the phosphor-bronze rod (2 centims. diameter and 30 centims. long) into the solenoid, a quick jerk of the galvanometer spot was observed on starting and stopping the primary current, and a rapid return to zero. The direction of the kick was such as would be produced by a permeability less than unity; the effect, however, was traced to be mainly due to eddy currents in the rod, and was nearly neutralized by putting a tertiary coil, with a resistance box in series with it, in proximity to the second pair of coils. The resistance in the tertiary circuit could be so adjusted that the movement of the spot
on starting or stopping the current was barely perceptible when the bronze rod was inside the solenoid, and on removing the rod and opening the tertiary circuit, without making any other change whatever, the balance was to all appearances perfect. We were therefore certain that the permeability of the alloy differed very little, if at all, from unity, so the casting of the stand was proceeded with.

Similar tests were made on the completed stand when received at the Central Technical College in 1900. The shape and size of the stand, however, made it difficult to place within coils of manageable dimensions, so a modified method of testing was used. The College possessed a standard of mutual induction (called S in this section), of 0.01 henry, made in 1892, consisting of coils wound in grooves on a wooden disc 9 1/4 inches diameter and 2 3/4 inches thick, so it was decided to test the stand by observing whether the mutual induction of these coils was altered by placing them on the circular top-plates of the slide rests which were to support the coils. To do this, an induction balance formed of the mutual induction standard S and another pair of coils was arranged as described above. The system was carefully balanced when S was supported on one end of a pine* board, 1 inch by 11 inches by 12 feet long, the other end of which rested on one of the top-plates. On moving S to the middle of the board the balance was not disturbed, but on placing it over the stand a quick jerk of 85 divisions and rapid return to zero was noticed. This kick, the effect of eddy currents in the metal of the support, was neutralised as far as possible by a tertiary circuit. It could not, however, be entirely eliminated by the tertiary coils available, a phenomenon attributed to want of equality in the time-constants of the tertiary circuit and of the eddy-current circuits in the continuous metal. The procedure adopted was to observe the swing produced by shunting 1/100 of the current from the primary of the balancing pair of coils, when the test pair were supported above air, and on the top-plate of the stand respectively, the tertiary circuit being open in the former case and closed in the latter. In each of the two positions the swing produced was 33 divisions. The sensitiveness of the arrangement was thus 1 in 33,000 per division, and under these conditions no difference would be detected. Four sets of tests were made giving precisely equal swings.

The experiments were repeated on the top-plate of the second slide rest of the stand with the same result. The eddy-current effect was somewhat different in the two cases, for in one the resistance in the tertiary circuit necessary to give minimum kick was 134 ohms and in the other 124 ohms.

To test whether the two ends of the pine board differed magnetically, it was turned end for end, and the whole cycle of operations repeated. No difference could be detected. In all cases great care was taken to twist the leads together in pairs, so as to avoid mutual induction in parts of the circuit other than that under test. The test coils S and the balancing coils were kept far apart and with their planes at right

* Pine was used because previous work in connection with very sensitive moving-coil galvanometers had shown this material to be non-magnetic.
angles, so that there was no mutual induction between the members of one pair and those of the other pair.

After the complete ampere balance was set up at the National Physical Laboratory, further magnetic tests were made on the stand and surrounding parts by sending a current of 1 ampere (approximately) round one of the suspended coils only, and observing whether the rest-point of the balance was affected thereby. The same test was made with the current reversed, and the whole repeated on the other suspended coil. In neither case could any change in the rest-point be detected. Experiments were also made by bringing masses of iron in proximity to the balance when the suspended coils were carrying their normal current. The effects of these masses were much smaller than expected; in fact, the iron had to be placed very near a current-carrying coil to produce any observable change on the rest-point. It may, therefore, be concluded that there can be no appreciable error in the balance due to magnetism or diamagnetism of the phosphor-bronze support.

Magnetic tests on marble were made at the Central Technical College in 1897, using the large marble cylinder employed in the Lorenz apparatus constructed by Messrs. NALDER Bros. & Co. for the McGill University, Montreal.* Its permeability differed from that of air by an amount too small to be detected.† This fact, together with the high specific resistance of marble, decided the material to be used for the cylinders of the proposed current weigher.

All the marble used in the fixed and suspended cylinders of the ampere balance was tested at the National Physical Laboratory, when received from the merchants, by observing the swing (if any) of a galvanometer in the secondary circuit of a pair of coils when the marble was quickly inserted as a core, the current in the primary circuit being kept quite constant. The primary coil had 1000 turns of No. 32 S.W.G. copper wire, and the secondary 10,000 turns of No. 42 S.W.G. With a current of 0.5 ampere in the primary the arrangement was extremely sensitive, as a change in the primary current of 1 part in 10,000 produced a swing of 5.4 millims. The scale could be read to 0.2 millim., so that a change of flux of 1 part in 270,000 could be detected. The tests showed that the permeability of the marble did not differ from that of air by 1 part in 100,000, a result which is in agreement with the American measurements mentioned above.

By means of the same coils the susceptibility of solid ferrous sulphate was measured as $73 \times 10^{-8}$, crystallised salt being used, and the air space determined by the aid of alcohol. KöNIGSBERGER‡ gives $37 \times 10^{-8}$ as the susceptibility of powdered ferrous sulphate.

* 'B.A. Report,' 1897, p. 218.
† More recently tests made in America by Wills, Guthe, and Stebbins, show the magnetic susceptibility of several kinds of marble to be extremely small, probably less than $1 \times 10^{-6}$. See 'Bulletin of Bureau of Standards,' vol. 2, pp. 52, 89.
‡ 'Wied. Ann.,' 66, 698, 1898.
The castings, drawn tubes, screws, &c., intended for making the beams, pillars, and other parts of the physical balance, were forwarded by Mr. Oertling to the National Physical Laboratory for magnetic test to determine their suitability, or otherwise, for the purpose. With the exception of the castings, all the first samples showed distinct paramagnetic properties, and were rejected, as also were several specimens submitted subsequently. It was found necessary to obtain the tubes and rods from special sources before satisfactory ones were secured. Many samples of brass screws were purchased and tested, but none were sufficiently free from magnetism, so Mr. Oertling was obliged to cut all used in the instrument in his own shops. The locks and keys for the balance case had also to be specially made, phosphor bronze being the chief material used. No trouble was experienced with the paraffin wax used to coat the windings.

In the magnetic tests on the metallic parts of the physical balance the eddy-current effects were small. When a brass rod was quickly inserted as a core to the primary, a swing of 4 millims. resulted, the direction being the reverse of that corresponding to increased permeability. To overcome this effect a thick brass rod was cut in two and the metallic substance placed between and in contact with the two portions, the whole being connected together by means of a metal tube so as to realise as nearly as possible a continuous metallic conductor. The brass rod was so long that when introduced into the primary it projected about 40 centims. from the far end when the metal under test was about to enter the coil. An axial motion of the metallic rod did not give rise to eddy currents capable of producing a swing of 0.2 millim.

Further tests on the suspended system were made after the erection of the balance by sending a current through one of the fixed coils when lowered so that the corresponding suspended cylinder was without it. The rest-point of the balance was unaffected thereby, and remained unchanged when the current was reversed. Similar observations were made when the current was sent through the other fixed coil, but no change was detected.

SECTION 6.—Construction, Measurement, and Insulation of Coils.

Preliminary tests at the Central Technical College and subsequent ones at the National Physical Laboratory led to the choice of "First Statuary" Carrara marble for the material of the cylinders. The tests showed this to be an excellent electrical insulator and of negligible magnetic susceptibility. The preliminary insulation tests were made on a small cylinder 4 inches in diameter and 2 inches in axial length. A double screw thread (36 turns to the inch) was cut on this, and helices of No. 24 bare copper wire wound thereon. The insulation resistance between adjacent strands was low at first, but rose to 4000 megohms when the cylinder was immersed in hot liquid paraffin wax, removed, and allowed to cool. The magnetic tests have already been described.
The cylinders were prepared in the rough by Messrs. Goody and Cripps, the large ones being 13 inches in diameter, 11 inches in axial length, and 2 inches thick. The corresponding dimensions of the small cylinders are 8, 6, and 0.5 inches. A few veins run through the large cylinders, but the dark material, of which these consist, is of negligible magnetic susceptibility. An appreciable quantity of the substance was collected from a number of rough pieces of marble sent by the marble merchants, and this was subjected to the magnetic tests already dealt with; there was no indication that the permeability differed from unity.

The cylinders are of an inconvenient shape and size for a direct determination of their coefficient of expansion; moreover, it was inadvisable to immerse them in water, and this latter operation was desirable if satisfactory observations were to be made. A bar of marble, $45 \times 5 \times 2.3$ centims., was therefore procured from the same source; this was baked in an oven at $140^\circ$ C. and soaked in hot paraffin wax previous to any linear observations being made. The mean coefficient of expansion between $1^\circ$ C. and $25^\circ$ C. was determined by Mr. Attwell to be $24 \times 10^{-7}$ per $1^\circ$ C.

The marble cylinders were examined for flaws and freedom from cavities; they were then turned until their dimensions were approximately correct, and afterwards baked in an oven at a temperature of $140^\circ$ C. for 30 hours. On the completion of the baking, and whilst in a hot condition, they were immersed in hot paraffin wax at $110^\circ$ C. No bubbles of gas were evolved from either of the four cylinders used in the ampere balance, but from one part of another cylinder, which was rejected for reasons mentioned hereafter, a tiny stream of bubbles escaped for a minute or two after immersion in the wax. Each cylinder remained immersed for at least 36 hours; on removal it was again examined for flaws, but none were detected. Previous to the turning of the marble cylinders, a long steel rod was turned on the lathe set apart for this work, and its ellipticity and conicality were determined by measurement. The ellipticity was very small and the lathe was adjusted until the conicality was too small to be measured with certainty; notwithstanding, the marble cylinders turned subsequently are distinctly conical, and, in the case of the large cylinders, those ends are the larger which were nearer to the face plate when the spiral grooves were cut. We conclude, therefore, that the weight of a cylinder produced a tilt, and that better results might have been obtained by turning between dead centres. The two small cylinders were turned in this way.

A cylinder was secured to the face plate of the lathe by four external dogs, the space between the face plate and the end of the cylinder nearest to it being about $1\frac{1}{2}$ inches. This mode of support enabled the two ends to be turned truly parallel, and the interior surface to be turned normal to them. To turn the outer surface, four large metal studs were turned in position on the face plate, and one end of the cylinder fitted over them; this end was pressed into contact with the face plate by two long bolts passing through the cylinder to a rectangular bar of steel pressed against the other plane end; the outer surface was then turned. The inner and
outer surfaces were thus practically concentric, and the ends at right angles to the axis. The turning was necessarily slow, more than five weeks being occupied on each of the large cylinders; the winding of the coils was, however, completed in a few hours. Alternate cuttings were made of the spirals, of which the grooves were V-shaped, with an angle of 95°, and of $\frac{1}{16}$ inch pitch. It was very important that each groove should be midway between its neighbours, and the lathe was operated to effect this; subsequent microscopic examination proved the equality of distance. While in the lathe, the diametral uniformity of the grooves was tested by winding in different parts of the cylinder a couple of turns of No. 24 copper wire, and estimating the difference in the diameters of the various turns by the touch of callipers. The cutting tool used was hardened in mercury and was not tempered.

On each large cylinder there are two pairs of coils, the central portion being left unwound for an axial distance of $\frac{9}{16}$ of an inch. The leads of all the coils must lie in a plane containing the axis of the cylinder, or otherwise the current through them will exert a force on the current in the suspended coils of the balance. To ensure the absence of such a force, the following scheme was adopted for the winding of each coil (see fig. 8, p. 473). From the outside of the cylinder and near one end, two radial cylindrical holes, a and b, were drilled; these are $\frac{9}{16}$ inch in diameter, $\frac{3}{16}$ inch from centre to centre, and 1$\frac{1}{2}$ inches in depth; they lie in a plane containing the axis of the coil. From the inside surface two other $\frac{9}{16}$-inch holes, c and d, were drilled to a depth of 1$\frac{1}{2}$ inches in the same axial plane as the others; one of these, d, is near the centre of the cylinder, and the other, c, is $\frac{3}{16}$ inch from b, the innermost of the previous ones. The holes a and b have slotted brass nipples, shown in section, screwed into them, and c and d are bushed on the inside of the cylinder with ivory pieces. After these bush pieces were screwed into position, the fine radial holes passing through the nipples, the ivory, and the marble, were drilled; the diameter of these holes is 0.024 inch, and they admit of the free motion of a straight piece of No. 24 wire. The radial holes were drilled in the following manner:—A bar of steel, 2 inches square and 30 inches long, with two opposite planed surfaces, was bolted to the slide rest so that it projected towards and was perpendicular to the axis of the lathe; a $\frac{1}{4}$-inch hole was then drilled through the far end of it. Into this hole a spindle was fitted, and on the spindle a small pulley was fixed, so that the whole could be driven by a motor. The bar was then turned into an axial position, the spindle set parallel to the face plate, and the radial holes drilled by a fine drill fitted in the spindle head; the feed was governed by the pressure of the hand. A check on the accuracy with which the holes were drilled was obtained in the following manner:—Adjacent helices are supposed to start in the same diametral plane and at an angular distance of 180° apart; the prolongations of the holes a, b, c, d should therefore be in line with those drilled for the leads of the adjacent coil. To test this, a straight piece of No. 24 wire was passed through corresponding holes, and pulled taut; there was no undue friction, and a centre finder indicated that the wire cut the axis of the cylinder. As
each coil consists of a whole number of turns, there was no necessity to rotate the
cylinder from the time the drilling of the first radial hole was commenced to the
completion of the last.

An estimate was made of the accuracy with which the number of turns is known.
On the fixed cylinders there are 90 turns to each coil and the diameter is about
33·0 centins. From observations on the radial holes, the number of turns is con-
sidered to be correct within 2 parts in 1,000,000.

Between the inner orifices of the passages b and c, fig. 8, a short \textbf{V}-groove \(e, \frac{1}{2} \) inch
deep, was cut, and between the corresponding apertures of \(a\) and \(d\) a groove \(f\),
\(\frac{1}{16}\) inch deep, was made; in these grooves portions of the leads of the coils were laid.

The copper wire with which the four coils were wound was supplied by the
London Electric Wire Company, Limited, on bobbins of the same diameter as the
cylinders. It is hard-drawn bare No. 24 S.W.G., and has a conductivity such that
1 metre weighing 1 gramme has a resistance of 0·149 ohm at 15°·5 C. The mean
diameter of the wire is 0·559 millim.; this is the average of several hundreds of
measurements, the maximum variation being 1 per cent.

As a guide in winding, an arm was fixed to the saddle and tool carriage of the
lathe which supported the bobbin and a small grooved brass pulley over which the
wire passed on its way to the cylinder. At the commencement the pulley was set in
position for a straight feed and the tool carriage was placed in gear with the leading
screw. On the axle carrying the bobbin a grooved pulley was fixed, and around this
a rope passed; one end of the rope was attached to a spring balance fixed to the
lathe saddle, and the other end was tied to a heavy weight which just swung clear of
the floor. The effective load on the wire during the winding of the coils was 10 lbs.,
which resulted in an extension of 0·16 per cent., the limit of elasticity not being
exceeded. \textsc{Young}'s modulus for the material of the wire was experimentally deter-
mined as \(1·14 \times 10^{12}\) (C.G.S. units). The coefficient of linear expansion of copper is
\(1·7 \times 10^{-6}\); hence for an increase in temperature of 80° C, the expansion is 0·14 per
cent. When the coils were immersed in paraffin wax the temperature of the copper
was very nearly 100° C, but the wire appeared to be quite taut on the cylinders.
The reason for this is apparent.

In the case of the fixed cylinders the winding was commenced by threading a free end
of the wire from the outside through the hole \(c\) and back through \(b\), fig. 8. When a
few centimetres had been pulled through the nipple, it was passed through the slit
therein and pressed back towards the surface of the marble; it was then given a
couple of turns about the nipple and soldered to it. The wire was afterwards pulled
taut and the necessary bends made to commence the winding. The position of these
bends was estimated beforehand and the wire in the vicinity softened over the flame
of a spirit lamp. During the winding the cylinder was rotated very slowly and
stopped after each revolution for a couple of measurements to be made of the diameter
of the wire. On its way from the bobbin to the marble the wire passed between two

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pads of silk moistened with alcohol and afterwards between two pads of dry silk. From time to time the strands were examined with a lens, but nothing unsatisfactory was observed. When the winding was complete except for about 10 centims. of the last turn, the lathe was stopped, and a long U-shaped clamp slipped over that end of the cylinder farthest from the face plate; a grooved piece of ebonite was placed over the last strand and the latter clamped between the ebonite and the marble; this enabled the tension on the wire of the bobbin to be relaxed. A length of wire sufficient to complete the connections was then measured off, the free end passed through the radial hole d, fig. 8, along the \( V \)-groove \( ff \), through \( a \), and finally secured to the nipple by soldering. Throughout these operations the wire was kept as taut as possible. On the completion of the helix the clamp was removed, the \( V \)-grooves filled in with paraffin wax, and the cylinder wrapped round with silk. It was then removed for diametral and axial measurements.

The turning of two small cylinders for the suspended coils was completed in a manner very similar to that described for the large cylinders, but as the ellipticity of these was comparatively great, they were rejected. Two other cylinders were chosen and their inner and end surfaces turned as in the previous cases, but their outer surfaces were turned between dead centres. The arrangement is shown in fig. 9. A, B, and C are tight-fitting collars on the mandril M; the outer collars have shoulders, and these and the collar B are turned so as to be a good fit in the cylinders, which are clamped between A and C by means of three bolts. The outer surfaces of the cylinders were finished in this way, and afterwards the double spiral grooves were cut; the result is very satisfactory.

The connections to the suspended coils (fig. 10) are much simpler than those for the fixed coils. The terminating nipples are placed inside the cylinder and one-half of each is cut away where it projects from the marble; the
portions which project are thus half-cylinders: they have axial grooves into which the leads are soldered.

After winding the coils the traces of fourteen axial planes at equal angular distances apart were marked on the end faces of each fixed and of each suspended cylinder and on the ungrooved portions of the outer cylindrical surfaces. A number of holes for the fixing of spirit levels and sighting pieces were also drilled.

Table I.—Observations for Axial Length of Coils on Suspended Cylinder No. 1.
Temperature = 15°.5 C.

<table>
<thead>
<tr>
<th>Number of turns. N.</th>
<th>Axial length of N turns.</th>
<th>Mean of values in Column 2.</th>
<th>Calculated axial length of 184 turns.</th>
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</thead>
<tbody>
<tr>
<td>184</td>
<td>12.9838</td>
<td>12.9833,</td>
<td>12.9833,</td>
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<td></td>
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</tr>
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<tr>
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<td></td>
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<tr>
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<td>02</td>
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</tr>
<tr>
<td></td>
<td>08</td>
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<td></td>
</tr>
<tr>
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<td>10.5134,</td>
<td>12.9829,</td>
</tr>
<tr>
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<td>29</td>
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<td>39</td>
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<tr>
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<td>8.5376,</td>
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<tr>
<td></td>
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</tbody>
</table>

The turning of the marble cylinders was very ably done by Mr. Taylerson, of the Engineering Department of the National Physical Laboratory.

Axial Length of the Coils.—The axial length of each helix was computed from a large number of measurements; some of these were made on the complete helix and others on portions of it. In addition, the mean value was checked by observations on a steel cylinder, on which a fine spiral groove was cut of the same pitch as the coil.
The steel and marble cylinders were turned at or about the same temperature, and the same portion of the leading screw of the lathe was used. For the axial measurements of the coils a cathetometer was employed, but the observations are subject to a greater probable error than the generality of high-precision cathetometer measurements owing to the boundaries of the wires being somewhat ill-defined. The axial length of the helices traced on the steel cylinder was determined by a simple comparator, and the value thus obtained is associated with a very small probable error. Table I. contains the results of the measurements on the coils of suspended cylinder No. 1. The first set of measurements was made on the whole number of turns, viz., 184; the next observations on 163 turns chosen in various parts of the coil, and the third, fourth, and fifth measurements were on 149, 135, and 121 turns similarly chosen. Each of the values recorded in column 2 is the mean of at least four readings; in all, about 100 observations were made.

If equal weights are given to each set of observations, the mean of the values recorded in the last column is 12.9829 centims. The observations on the outer end wires are not quite so reliable as those on intermediate ones, for a little irregularity is always possible when starting and finishing a winding; eight observations (each being the mean of four) are therefore included in the first set. The mean of eight measurements on the steel cylinder is 12.9830 centims., a much closer agreement than was anticipated. Taking the value 12.9829 centims. and the values recorded in Column 4 of Table I., the differences (observed – mean) are +4, −4, +1, −1, and −1\(\mu\),* from which a probable error of 0.001 per cent. is deduced if we exclude the error of the gauges employed. The observations on the helices of the other three cylinders are equally satisfactory, and the means of the readings obtained with them are given in Table II.

As the tool carriage travelled over different portions of the leading screw of the lathe when cutting the spiral grooves in the suspended cylinders 1 and 2, the uniformity of the screw was tested and an estimate of 2\(\mu\) was made as the probable difference in length of the coils on the two cylinders, that of the coils on No. 1 being the greater. The recorded measurements show that No. 2 is probably the longer by this amount, the values being 12.9829 centims. for No. 1 and 12.9831 centims. for No. 2. On the whole, the observation error of the axial lengths may be taken as of the order 1\(\frac{1}{2}\) parts in 100,000.

For the diametral measurements a machine, shown in fig. 11, was obtained from Messrs. STANLEY. This consists of a double-webbed rectangular steel girder, two micrometer heads, and various supports for gauges, &c. To each of the micrometer heads an optical lever of the form shown in fig. 12 was attached. A well-fitting hardened steel piston P is tapered and ground at one end so as to form a plane edge \(\frac{1}{4}\) inch wide and \(\frac{1}{16}\) inch deep; the other end tapers more slowly and terminates in a rounded end \(\frac{3}{16}\) inch in diameter. This end of the piston fits into a rectangular

* \(\mu = 1\) micron, or \(\frac{1}{1000}\) of a millimetre.
### Table II.—Observations for Axial Length of Coils. Temperature 15° C.

<table>
<thead>
<tr>
<th>Cylinder under observation</th>
<th>N = Number of strands observed</th>
<th>Axial length of N strands</th>
<th>Total number of observations</th>
<th>Total turns</th>
<th>Calculated axial length of coil</th>
<th>Difference from mean.</th>
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<td>Suspended cylinder No. 2</td>
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<td>32</td>
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<tr>
<td></td>
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<td>10.51335</td>
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</tr>
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</tbody>
</table>

* These values were determined by measuring the complete axial length of the upper and lower coils plus the central gap.

Observations on 163, 149 and 135 strands indicate practical equality of the axial lengths of the upper and lower helices and also enable the length of the central gap to be calculated. This latter length was subtracted from the total and the result divided by two. In taking a mean of the values given in Column 6, only half the weight has been attached to the "**" observations.
groove cut in a brass bar carrying a plane mirror M; the bar is free to rotate about a steel axle, its movement being in a vertical plane. A comparatively strong brass spring on each side of the bar causes it to continually press against the piston if the rounded end of the latter projects beyond the stop S. The vertical distance between

![Diagram of machine for measuring diameters of cylinders.](image1)

the axis of the mirror and the contact point of piston and brass bar is about 1.5 millims., and the height of the micrometer head above the upper surface of the girder is 30 centims. When the barrel B of the micrometer advances, the piston, mirror, bearings, &c., advance with it until the plane end of the piston comes in contact with a rigid body; an advance of the micrometer barrel then results in a tilt of the mirror

![Diagram of optical lever for measuring diameters of cylinders.](image2)

and the consequent deflection of a spot of light. All the parts are well made and the bearings lubricated with clock oil. A Nernst filament was used as a source of light, and a lens produced a sharp linear image on a white surface 150 centims. distant from the mirror. A forward motion of the micrometer barrel of 1μ resulted in a deflection
of 2 millims. on the scale; a difference of 1\(\mu\) was thus read with ease. As there was no silk on the wire to interfere with precise measurement, this high sensitiveness was well worth attaining. The contact planes of the pistons were tested for parallelism with satisfactory results; tests were also made which indicated that these planes were normal to the axes of the pistons.

To facilitate the diametral measurements, the marble cylinder under observation was supported on a turn-table provided with ball bearings and levelling screws (fig. 11). The original intention was to support this table on a separate platform and so avoid the bending of the girder which results when it supports the load; this, however, proved to be unsatisfactory, and ultimately a small wooden platform was bolted to the girder, and on this the turn-table and cylinder rested. The traces of the axial planes on the ends and ungrooved portions of the cylinder, and the knowledge that the ends were at right angles to the axis, enabled the coils to be rapidly set in position so that their axes were vertical; at the same time the adjustment ensured that the plane edges of the touch-pieces would come into contact with the copper wires at opposite ends of a diameter. Two spirit levels at right angles were used for the levelling of a cylinder, and it was usually found necessary to make a slight adjustment for every measurement made in a different axial plane. In general, observations were made in eight approximately equidistant diametral planes, and in each of these, 14 measurements were taken in equidistant axial planes; at the conclusion of the 14 observations the first was repeated as a check on the constancy of the apparatus. The method used was not a "null" one; the zero reading, i.e., that when a mirror was against a stop, was observed from time to time, and a constant deflection of 10 millims. from this was adhered to throughout the measurements. The apparatus worked very smoothly, the readings being easily reproduced to 1\(\mu\), and only in a few cases of uncertainty was more than one observation made of any one diameter. The temperature of the room was very nearly constant and equal to 15°5 C.; a Richard's thermograph recorded the variations.

At the commencement of a series of measurements, the Whitworth steel gauge (square section, flat ends) was placed in position, and the uprights carrying the micrometer heads were bolted to the girder. A mass equal to that of the turn-table and cylinder was next placed on the small platform between the micrometer heads, and the observations on the gauge were then made, the latter being displaced and reset between every two measurements. The cylinder was then placed in position and measured, and afterwards the gauge was again set up. With respect to the latter measurements, the difference in the readings of the micrometer heads never varied by more than 2\(\mu\) from the commencement to the completion of a series of observations. When measuring a diameter, the touch-pieces made contact with one wire of each helix and the mean of the observations gave, therefore, the mean outside diameter of the two coils. To determine the difference of the mean diameters of the coils, one of the micrometer heads was raised \(\frac{1}{36}\) inch and a few observations of
difference made; the value of this difference varies from 2μ to 3μ for the different pairs of coils. A confirmation of this difference appears on p. 516.

In Tables III. to VI. there are given the diametral measurements of the coils in various planes, the mean diameter of the wire with which the coils are wound, and the mean diameter of the coils to the central filament of the wire. In the

**Table III.**—Results of Measurements of the Diameters of the Coils, to Centres of Wires, on Suspended Cylinder No. 1. Temperature, 15°·5 C.

<table>
<thead>
<tr>
<th>Diametral plane number</th>
<th>Containing strand number—</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>79μ</td>
</tr>
<tr>
<td>2</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>74</td>
</tr>
<tr>
<td>7</td>
<td>76</td>
</tr>
<tr>
<td>8</td>
<td>77</td>
</tr>
<tr>
<td>9</td>
<td>76</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>11</td>
<td>80</td>
</tr>
<tr>
<td>12</td>
<td>78</td>
</tr>
<tr>
<td>13</td>
<td>80</td>
</tr>
<tr>
<td>14</td>
<td>78</td>
</tr>
</tbody>
</table>

Mean . . . 77₃ 78₅ 81₃ 81₁ 81₀ 83₈ 85₆ 89₁ 92₂

Number of observations made to determine the mean diameter of the wire, 46. Greatest difference between any two observations, 0·8 per cent. Mean diameter of wire, 0·559 millim. Approximate mean diameter of coils = mean of the values in table = 20·35831 centims. Mean diameter of coils, computed from calibration curve = 20·3583 centims. Difference of diameters of neighbouring convolutions = 0·0003 centim. (approx.).

conversion of inches to centimetres the ratio 2·539998 has been taken. For the data relating to the steel gauges employed we are indebted to Mr. Attwell, of the Metrological Department. A good conception of the ellipticity and conicality of the coils is afforded by the calibration curves which follow (figs. 13, 14, 15, 16). The suspended coils are very slightly elliptical, and the conicality is also very small and uniform. The difference in the extreme mean diameters of suspended cylinder No. 1 is 17μ, equivalent to an average slope of 1 in 8000; the corresponding value for
suspended cylinder No. 2 is about 1 in 10,000; the larger ends of these cylinders are the ends which were in contact during the turning. The ellipticity of the coils on the fixed cylinders is greater than that of the suspended coils, but it is much too small to influence the calculation of the mutual induction, for the variation of mutual

induction with small changes in radius is approximately linear. For the same reason the conicality of the coils may be neglected. The larger end of each fixed cylinder is that which was secured to the face plate of the lathe during the final turning and screw cutting.
TABLE IV.—Results of Measurements of the Diameters of the Coils, to Centres of Wires, on Suspended Cylinder No. 2. Temperature 15°.5 C.

<table>
<thead>
<tr>
<th>Diametral plane number.</th>
<th>Containing strand number—</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>84μ</td>
</tr>
<tr>
<td>2</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>84</td>
</tr>
<tr>
<td>6</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>85</td>
</tr>
<tr>
<td>8</td>
<td>85</td>
</tr>
<tr>
<td>9</td>
<td>84</td>
</tr>
<tr>
<td>10</td>
<td>84</td>
</tr>
<tr>
<td>11</td>
<td>84</td>
</tr>
<tr>
<td>12</td>
<td>83</td>
</tr>
<tr>
<td>13</td>
<td>83</td>
</tr>
<tr>
<td>14</td>
<td>85</td>
</tr>
</tbody>
</table>

Mean... . 84μ | 86μ | 87μ | 87μ | 87μ | 88μ | 88μ | 88μ | 89μ |

Number of observations made to determine the mean diameter of the wire, 46.
Greatest difference between any two observations, 0.8 per cent.
Mean diameter of wire, 0.559 millims.
Approximate mean diameter of coils = 20.3589, centims.
Mean diameter of coils, computed from calibration curve = 20.3589, centims.
Difference of diameters of neighbouring convolutions = 0.0002 centim. (approx.).

The following convention is adopted in numbering the 14 axial planes. The upper plane end of a cylinder is viewed and one of the two marked diameters nearest in line with the connectors of the coils is called No. 1. The direction of ascending numbers is clockwise, diameters 1 and 14 being on opposite sides of the plane containing the leads.

An idea of the probable error of the mean diameter of any one coil may readily be obtained. The values of the standards of lengths employed are known in terms of the National Physical Laboratory 12-inch end gauge of similar type standardised by the Board of Trade. The absolute values are not of importance, however, for if the dimensions of the fixed and suspended systems change in the same proportion and in the same direction, the force due to the current is unchanged. For the smaller coils, an 8-inch steel gauge was used; for the larger ones, this was combined with a 5-inch gauge. The ratio of the lengths of these gauges was known with an error certainly less than 5 in 1,000,000. The probable error due to the setting of the gauges in the
measuring machine bed was much greater than this, but an analysis of the readings leaves little doubt that the probable error is not more than $1\mu$. On each pair of coils not less than 112 observations were made, and the curves show that the error of a single observation must be small; hence the error of the mean diameter deduced from the 112 observations is not appreciably greater than the error of the gauge. We conclude, therefore, that the relative diametral dimensions of the coils are correct to 5 in 1,000,000. The probable error of the axial lengths given in Tables I. and II. is of the order 15 in 1,000,000, and the calculated value of the mutual induction should

Fig. 14. Suspended cylinder No. 2.
<table>
<thead>
<tr>
<th>Diameter plane number.</th>
<th>Upper coils.</th>
<th>Lower coils.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number of strand (from upper end)</td>
<td>Number of strand (from lower end)</td>
</tr>
<tr>
<td></td>
<td>7 28 30 59 86 120 135 152 175</td>
<td>175 152 135 120 86 59 28 7</td>
</tr>
<tr>
<td></td>
<td>= 33·0000 centims.</td>
<td>= 33·0000 centims.</td>
</tr>
<tr>
<td>1</td>
<td>-15µ -14µ -12µ -5µ -1µ +9µ +7µ +8µ +10µ</td>
<td>+8µ +8µ +9µ +13µ +11µ +8µ +8µ +12µ</td>
</tr>
<tr>
<td>2</td>
<td>-14 -11 -7 -2 +4 9 10 9 13</td>
<td>13 10 12 16 13 10 9 14</td>
</tr>
<tr>
<td>3</td>
<td>-6 -5 -2 +5 4 10 16 12 16</td>
<td>17 15 15 17 15 14 13 18</td>
</tr>
<tr>
<td>4</td>
<td>-4 +3 +3 +8 10 15 18 17 19</td>
<td>21 20 20 19 22 21 20 22</td>
</tr>
<tr>
<td>5</td>
<td>-1 +2 +5 +11 16 19 24 20 20</td>
<td>17 20 24 23 26 26 23 24</td>
</tr>
<tr>
<td>6</td>
<td>-1 +5 +7 +14 17 21 23 21 22</td>
<td>20 22 26 24 26 22 23 24</td>
</tr>
<tr>
<td>7</td>
<td>-7 -1 +5 +14 16 20 22 22 22</td>
<td>24 26 21 25 24 22 24 24</td>
</tr>
<tr>
<td>8</td>
<td>-13 +3 -1 +6 17 19 22 25 26</td>
<td>24 24 20 24 19 21 24 25</td>
</tr>
<tr>
<td>9</td>
<td>-15 -3 -2 +6 17 16 16 23 17</td>
<td>21 24 20 20 15 20 23 24</td>
</tr>
<tr>
<td>10</td>
<td>-15 -4 -4 +2 10 18 16 20 20</td>
<td>13 17 15 20 14 17 21 24</td>
</tr>
<tr>
<td>11</td>
<td>-13 -8 -7 -4 5 14 14 16 12</td>
<td>11 11 11 15 18 14 17 19</td>
</tr>
<tr>
<td>12</td>
<td>-14 -10 -1 -5 18 11 13 10</td>
<td>9 11 11 14 11 12 12 16</td>
</tr>
<tr>
<td>13</td>
<td>-14 -12 -10 -4 1 9 8 12 13</td>
<td>7 9 9 14 13 9 10 11</td>
</tr>
<tr>
<td>14</td>
<td>-13 -11 -10 -6 0 6 9 11 10</td>
<td>9 11 11 13 13 7 9 12</td>
</tr>
<tr>
<td>Mean.</td>
<td>-10µ -4µ -3µ +3µ +8µ +14µ +15µ +16µ +16µ +15µ +16µ +16µ +19µ</td>
<td>+15µ +16µ +16µ +18µ +17µ +15µ +16µ +19µ</td>
</tr>
</tbody>
</table>

Number of observations made to determine the mean diameter of the wire: 90 (upper), 90 (lower).
Greatest difference between any two observations: 0·7 per cent. (upper), 0·7 per cent. (lower).
Mean diameter of wire = 0·559 millim. (upper), 0·559 millim. (lower).

Approximate mean diameter of coils = 33·0006 centims. (upper), = 33·0016 centims. (lower).
Mean diameter of coils, computed from calibration curve, = 33·0005 centims. (upper), and = 33·0017 centims. (lower).

Difference of diameters of neighbouring convolutions = 0·0003 centim. (approx.).
Fig. 15. Fixed cylinder No. 1.
TABLE VI.—Results of Measurements of the Diameters of the Coils, to Centres of Wires, on Fixed Cylinder No. 2.
Temperature, 15°5 C.

<table>
<thead>
<tr>
<th>Diametral plane number</th>
<th>Upper coils. Number of strand (from upper end)</th>
<th>Lower coils. Number of strand (from lower end)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10µµ</td>
<td>14µµ</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td>Mean</td>
<td>16µµ</td>
<td>20µµ</td>
</tr>
</tbody>
</table>

Number of observations made to determine the mean diameter of the wire: 44 (upper), 44 (lower).
Greatest difference between any two observations: 1·0 per cent. (upper), 0·7 per cent. (lower).
Mean diameter of wire = 0·559 millim. (upper), 0·559 millim. (lower).
Approximate mean diameter of coils = 33·00273 centims. (upper), 33·0039 centims. (lower).
Mean diameter of coils, computed from calibration curve = 33·00282 centims. (upper), 33·00395 centims. (lower).
Difference of diameters of neighbouring convolutions = 0·0002 centim. (approx.).
Fig. 16. Fixed cylinder No. 2.
be correct within about 5 in 1,000,000. This conclusion assumes absolute constancy of the dimensions of the coils in the interval between measurement and erection, or the same relative change in dimensions. The values of the mutual induction of the coils on fixed cylinder No. 1 and on suspended cylinder No. 1, and of the coils on the No. 2 cylinders were independently calculated by two of us (T. M. and F. E. S.) in July, 1905 (see Section 10), the difference in mutual induction of the two systems, as calculated, being 0·0062 per cent., that of the first system being the greater. When the ampere balance was completed and the equipment and settings made satisfactory (September, 1905), the difference in mutual induction as found experimentally was, and still is (April, 1907), 0·0054 ± 0·0004 per cent., that of the first system being the greater. Particulars of this experimental determination will be found on p. 515. An experimental estimate of the difference in mean diameters of two coils on a suspended cylinder is $3·5\mu \pm 1\mu$ (p. 516), a value in satisfactory agreement with the difference found by direct measurement.

**Insulation of Coils.**—The insulation of the helices was next proceeded with. For this purpose an X-shaped framework of wood was mounted on a metal axle and fitted inside the marble cylinder under observation; the axle was supported on bearings, so that the whole could rotate freely. The marble is semi-transparent, and when an electric lamp is placed inside a cylinder the air gaps between the strands are easily inspected. Under these conditions the appearance of the coils was very beautiful, and close inspection with a lens failed to reveal any defects in the winding. The first measurement of the insulation resistance between adjacent helices indicated it to be of the order of 50 ohms, and the filament of an electric lamp glowed brightly when placed in a circuit containing the two helices and the gaps of what appeared to be marble and air. That the marble was not at fault was shown by tests on the unwound portion of the cylinder, and examination of the gaps with a powerful lens failed to reveal any metallic bridging pieces. In their shortest parts the gaps are 0·15 millim. long, and on the fixed cylinders there are four gaps, each nearly 93 metres wide; several days were spent in their examination, and on one occasion a silk thread was passed between neighbouring strands; the insulation resistance still remained less than 100 ohms. It is unnecessary to describe in detail all the subsequent attempts to locate the leaks. The cylinder and coils were washed with a thin shellac varnish, made by dissolving shellac in ether, but there was no improvement; afterwards they were washed in ether and then absolute alcohol, but without noticeable effect. The cause of the low insulation resistance was apparent, however, for at the bottom of a porcelain dish containing the used alcohol a fine sediment settled which consisted of minute particles of copper. Apparently the copper strands had a very loose, scaly skin, and thousands of these tiny particles of copper were bridging the air gaps and so diminishing the insulation resistance. The washing with alcohol was continued and the strands lightly brushed with a camel-hair brush, a 32-c.p. lamp being lit through the circuit containing the gaps. Eventually two 32-c.p. lamps were placed
in parallel, so that the current was about 2 amperes. After the washing with alcohol had been continued for 20 minutes or half-an-hour there was a crackling noise, and hundreds of tiny sparks appeared over the surface of the cylinder; simultaneously the lamps ceased to glow. A measurement of the insulation resistance between the coils showed it to be of the order of 300 megohms; the shorting pieces had been burnt out with a most satisfactory result. To prevent the recurrence of the low insulation resistance the washing was continued; occasionally the lamps glowed, but with continued washing the shorts were burnt out as before. When the insulation resistance was of the order of 1000 megohms, with an applied pressure of 20 volts, the cylinder was lifted from its bearings and placed in others secured to a framework resting on the top of a bath of melted paraffin wax. About one-third of the circumference of the cylinder dipped into the hot liquid. The cylinder was rotated until the marble was sufficiently warm to keep the wax on its surface in a liquid condition; it was then removed for the wax to solidify, and afterwards dipped once more, in order to obtain a thicker coat. The insulation resistance was measured while the cylinder was hot, and also when the wax had solidified; the latter value was always the greater. After the lapse of a week or ten days, the ends and interior of the cylinder were cleaned and preparations made for further measurements of diameters. The wax was carefully removed from several parts of the cylinder and the strands cleaned by rubbing with a small pad of silk; the measurement of six or eight diameters was then carefully made, the steel gauges being set up as before. A summary of these measurements follows (see Table VII.), from which it is inferred that there was no appreciable change in the diametral dimensions.

In one of the large cylinders the insulation resistance between the two upper and the two lower helices was at first comparatively low, viz., 2000 megohms. The cause of this was found to lie in the internal ivory plugs through which the copper leads passed. As it was impossible to remove these without stripping the cylinder, they were slotted in such a way as to reduce the section of the conducting material; the insulation resistance was thus increased to 10,000 megohms. Insulation tests on fresh ivory pieces were invariably satisfactory, but two such pieces inserted in the ampere balance appeared to deteriorate with time, and eventually had to be replaced by ebonite.

To prevent damage to the surface of the wax with which the coils were coated, it was thought desirable to cover it with a harder insulating material. Shellac varnish was tried and used for the larger coils, but the suspended ones were untouched owing to the results of experiments on equal surfaces of paraffin wax and shellac varnish. The latter was found to be much more hygroscopic than the former. From the measurements made it is estimated that each suspended cylinder coated with paraffin wax would change in mass by 6.8 milligrammes if removed from a dry atmosphere to one saturated with moisture; had the outer coating been shellac varnish the corresponding change would be 146 milligrammes.

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Table VII.—In which the Diametral Measurements on all the Coils, before and after Insulating with Paraffin Wax, are Compared.

<table>
<thead>
<tr>
<th>Coil</th>
<th>Diametral plane number</th>
<th>Strand number</th>
<th>Diameter before insulating.</th>
<th>Diameter after insulating.</th>
<th>Difference.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended No. 1</td>
<td></td>
<td></td>
<td>Centims.</td>
<td>Centims.</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>38</td>
<td>1</td>
<td>20·3579</td>
<td>20·3576</td>
<td>−3μ</td>
</tr>
<tr>
<td>1</td>
<td>38</td>
<td>2</td>
<td>81</td>
<td>80</td>
<td>−1</td>
</tr>
<tr>
<td>9</td>
<td>92</td>
<td>3</td>
<td>38</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>4</td>
<td>82</td>
<td>80</td>
<td>−2</td>
</tr>
<tr>
<td>Mean difference =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−14</td>
</tr>
</tbody>
</table>

| Suspended No. 2 |                        |               | Centims.                    | Centims.                    |             |
| 1               | 4                      | 1             | 20·3584                     | 20·3586                     | +2μ         |
| 1               | 80                     | 1             | 88                          | 86                          | −2          |
| 9               | 104                    | 4             | 85                          | 84                          | −1          |
| 9               | 4                      | 84            | 84                          | 83                          | 0           |
| 9               | 80                     | 84            |                             |                             | −1          |
| 9               | 104                    | 88            | 88                          | 89                          | +1          |
| Mean difference = |                        |               |                             |                             | −0.5        |

| Fixed No. 1, upper part |                        |               | Centims.                    | Centims.                    |             |
| 1               | 175                    | 1             | 33·0010                     | 33·0006                     | −4μ         |
| 3               | 175                    | 16            | 15                          |                             | −1          |
| 9               | 175                    | 17            | 18                          |                             | +1          |
| 12              | 175                    | 10            | 07                          |                             | −3          |
| 1               | 59                     | 1             | 32·9995                     | 32·9994                     | −1          |
| 8               | 59                     | 17            | 18                          |                             | +1          |
| 12              | 59                     | 10            | 07                          |                             | −2          |
| 10              | 59                     | 07            |                             |                             | −3          |
| Mean difference = |                        |               |                             |                             | −0.6        |

| Fixed No. 1, lower part |                        |               | Centims.                    | Centims.                    |             |
| 1               | 175                    | 1             | 33·0008                     | 33·0008                     | 0μ          |
| 10              | 175                    | 17            | 17                          |                             | 0           |
| 12              | 175                    | 13            | 10                          |                             | −3          |
| 1               | 59                     | 9             | 09                          |                             | −2          |
| 8               | 59                     | 08            | 07                          |                             | −1          |
| 11              | 59                     | 21            | 22                          |                             | +1          |
| 12              | 59                     | 14            | 18                          |                             | +4          |
| 12              |                        | 12            | 09                          |                             | −3          |
| Mean difference = |                        |               |                             |                             | −0.6        |

| Fixed No. 2, upper part |                        |               | Centims.                    | Centims.                    |             |
| 1               | 170                    | 1             | 33·0029                     | 33·0028                     | −1μ         |
| 5               | 170                    | 27            | 26                          |                             | −1          |
| 8               | 170                    | 37            | 34                          |                             | −3          |
| 2               | 125                    | 25            | 25                          |                             | 0           |
| 5               | 125                    | 34            | 33                          |                             | −1          |
| 10              | 125                    | 37            | 37                          |                             | 0           |
| Mean difference = |                        |               |                             |                             | −1.0        |

| Fixed No. 2, lower part |                        |               | Centims.                    | Centims.                    |             |
| 4               | 170                    |               | 33·0025                     | 33·0024                     | −1μ         |
| 6               | 170                    | 38            | 41                          |                             | +3          |
| 14              | 170                    | 34            | 33                          |                             | −1          |
| 1               | 125                    | 36            | 37                          |                             | +1          |
| 6               | 125                    | 45            | 45                          |                             | 0           |
| 10              | 125                    | 49            | 50                          |                             | +1          |
| Mean difference = |                        |               |                             |                             | +0.5        |
SECTION 7.—ERECTING AND ADJUSTING THE INSTRUMENT.

To facilitate the setting of the fixed cylinders on the balance table, two spirit levels and four sets of cross-wires are mounted on the upper plane end of each. The sensitiveness of the levels is such that a tilt of 20 seconds of arc displaces the air bubbles 1 millim from their central position. A Whitworth surface plate was levelled and on this the spirit levels were set; afterwards a marble cylinder was rested on the plate, which was then relevelled, and two other levels placed at right angles on the upper end of the cylinder; the displacement of a bubble from its mid-position was practically unreadable, the parallelism of the plane ends of the cylinder being thus confirmed. The levels were screwed to the cylinder and re-set to read correctly.

At opposite ends of two diameters at right angles, four slides with upright pieces carrying cross-wires are screwed to the upper plane end of each cylinder (see fig. 2, Plate 7). These are adjustable in azimuth and the final setting is such that the line joining the points of intersection of opposite cross-wires lies in a plane containing the axis of the coils. The setting was made by suspending a weighted thread inside the cylinder so as to coincide with the axis, the indicator of this adjustment being a centre finder. A cathetometer telescope was next focussed on the thread and on one of the cross-wires, and was altered in position until the plane of the vertical wire of the telescope lay in the same plane as the thread and the vertical cross-wire. The cross-wires opposite to this latter were then adjusted in azimuth until they also lay in this plane.

Each suspended cylinder carries a brass T-piece supporting two spirit-levels at right angles; in addition a tripod is supported which in turn carries a pointed rod to be seen projecting above the fixed cylinder in fig. 2 (Plate 7). The ends of the tripod legs enter into the cylinder and are turned to be an exact fit. The rod is for the adjustment to coincidence of the axes of the fixed and suspended coils; it is adjustable in vertical height and its pointed extremity lies in the axis of the coils; it is set so that when its extremity is in the plane of the cross-wire intersections the suspended and fixed coils are symmetrical as regards vertical height. The coils are concentric when the lines joining opposite cross-wires intersect in the axis of the rod.

Concentric cable is used for the leads to and from the various coils. The junctions of the cable with the fixed coils are shown in fig. 8, and those with the suspended coils in fig. 10. In the case of the fixed coils the ends of the wire leading to any one of the coils were first soldered to small brass blocks supported by a strip of ebonite which in turn was screwed to the cylinder; the ends of the leads of the concentric cable were similarly soldered to two small brass pieces which were screwed in contact with those leading to a coil. The cable could thus be easily removed without in any way damaging the connecting pieces. In the case of the suspended coils, the wires
PROFESSOR W. E. AYRTON, MR. T. MATHER AND MR. F. E. SMITH:

leading from them terminate at the brass connectors inside the cylinder. These connectors are grooved, and into the grooves stout pieces of copper wire are soldered and lead directly to the concentric cable. The junctions are shown in fig. 10, p. 482. To take part of the weight of the cable attached to the small cylinders and thus prevent the connections from being strained, two small curved arms project from each suspended cylinder, and to these the cables are clamped. They may be seen just above the fixed cylinders in fig. 2, Plate 7. Each small cylinder is suspended by three phosphor-bronze wires w, w, w, fig. 6, Plate 8, attached to a three-limbed spider S; to these wires the cylinders are hooked by brass strips screwed to the interior of the cylinder and bent at right angles at their lower ends; the feet thus formed fit into recesses cut in the marble. The effective length of the phosphor-bronze wires is adjustable, and by such adjustment, together with an alteration in position of the heavy nuts on the limbs of the spider, the cylinders are levelled. On the completion of the suspended coils and their fittings, the mass of one suspended system was different to that of the other by 2 grammes in a total of 5500 grammes; equality was obtained by loading one of the T-pieces.

Above each suspended cylinder a commutator C (fig. 17) is supported by one arm of the three-limbed spider. The concentric cables from the coils pass to this commutator, and from the latter two bare copper wires, shown black, are taken to an ebonite block B. A second ebonite piece B' is screwed to the main pillar of the balance, and between B and B' 160 silver wires are suspended; the diameter of a single wire is 1 mil (25μ). A long length of concentric cable completes the circuit to a multiple commutator and plug board. By appropriately setting the commutator C, the current can be made to circulate in the same or in opposite directions in the two helices, fig. 3, and by suitable connections to the multiple commutator and to the commutator C the insulation resistance between the helices can be measured. Wherever possible, the non-concentric leads to and from the coils are kept very short and placed radially or parallel to the axes of the cylinders; also, the feed and return leads are placed as close together as practicable; the design thus ensures the minimum of force between the current in the fixed coils and that in the commutator and leads to the suspended coils. The commutator C is a simple one of four copper quadrants with a turning head of ebonite, carrying two contact pieces; these latter are insulated from each other and are attached to the ebonite head by hard springy copper; they are split midway to ensure uniform pressure on all the quadrants when the turning head is correctly set. The commutator can reverse the current in one of the helices only, but the concentric leads from both coils pass to the commutator block; this is for convenience in making the connections, and to obtain symmetry of distribution of the current leads. By making one of the contact pieces (say Q, fig. 17, c) slightly longer than the other, the commutator may be set in position suitable for making the insulation test between the two helices.

The 160 silver wires are divided into two portions, which are insulated from each
other; in any one division the 80 strands lie in two parallel layers, the system being formed by winding a continuous length of silver wire over two brass rods cut with a screw thread of \( \frac{3}{8} \) inch pitch; no two strands are in contact. After the completion of the winding the silver wires were soldered to the rods by running a very soft fusible metal into the V-grooves. The length of a strand is 10.5 centims., but the distance between the rods is a little less than this. Fig. 17 illustrates the manner in which a set of silver wires is placed in position. Before their insertion the sensitiveness of the balance was such that an added load of 1 milligramme produced a deflection of 0.9 scale division; afterwards the corresponding deflection was 0.85 scale division, a diminution in sensitiveness of 6 per cent. only. The concentric cable attached to B' is clamped to the main pillar of the balance, and passes through a hole drilled in the base of the balance table to the multiple commutator and plug board described on p. 521.

The first setting of the coils on the tables of the balance involved the following operations:

(a) Levelling of one suspended cylinder by adjustment of the lengths of the suspension wires and of the masses on the limbs of the spider.

(b) Levelling of the concentric fixed cylinder.

(c) Approximate setting of the fixed cylinder, so that the mean diametral plane of all the coils on it coincided with the mean diametral plane of the suspended coils.

(d) Levelling and vertical adjustment of the other fixed cylinder until its mean diametral plane coincided with the corresponding plane of the first fixed cylinder.

(e) Levelling and adjustment in vertical height of suspended cylinder No. 2 in order that conditions (a) and (c) should hold with it.

(f) Setting of each pair of cylinders to be concentric.
This mechanical method of setting the coils is subject to errors which may be serious in an instrument intended for observations of high precision. So far as we know, no attempt has hitherto been made to set two coaxial coils in a position of maximum force by an electrical method. The ampere balance lends itself to such a setting, and the accuracy thereby attained is considerable.

**Electrical Method of Setting the Coils.**

(1) Setting to Coincidence of the Mean Diametral Plane of the Suspended Coils with the Corresponding Plane of all the Coils on the Concentric Fixed Cylinder.—If \( M_\alpha \) is the difference of the mutual induction of the upper fixed coils and the circular ends of the suspended coils, and \( M_\beta \), that of the lower fixed coils and the same, and if the currents flow in opposite directions in the upper and lower fixed coils, the force between them and the suspended system is \( \gamma \alpha \gamma (M_\alpha + M_\beta) \), where \( \gamma \) is the current through the fixed coils and \( \gamma \) is the current per unit axial length in the current sheet equivalent to the current in the suspended coils. This is the maximum force possible for the coaxial system, and variations in the force for small axial displacements are also small. The rate of change was determined by passing a current of 1·02 amperes through all the balance coils, the direction of the current in the various helices being such that the two suspended systems were subject to the maximum axial forces, but opposed to each other so that the total turning moment on the beam was small and almost nil. One set of fixed coils was now displaced through known axial distances and the change in the resting point of the balance observed; that position of these fixed coils when the force due to them is a maximum is the correct axial position for minimum mutual induction. The results obtained with one of the systems are plotted in fig. 18; for such displacements as those made the force is approximately given by the expression:—maximum force multiplied by \( (1-11 \times 10^{-8}d^2) \), where \( d \) is the displacement in mils and is measured from the plane of minimum mutual induction. The force may also be written:—maximum force multiplied by \( (1-0·017x^2) \), where \( x \) is the displacement in centimetres. For a displacement of 10 mils (254\( \mu \)) the change in force is 11 in 1,000,000, which for a current of 1 ampere is equal to 0·04 dyne approximately.

There is, however, another method of setting the cylinders which is even more sensitive. If, instead of the currents flowing in opposite directions in the upper and lower fixed coils, they flow in the same direction, the force between them and the suspended system is \( \gamma \alpha \gamma (M_\alpha - M_\beta) \). When the coils are set in their correct position, this is nearly the minimum force possible for the arrangement, and the rate of change of force with axial displacement is large. Observations were made with the current circulating in this manner in one set of fixed coils, the current in the system on the opposite side of the balance being so directed that no measurable force was produced by it. The correct position of the fixed coils in one of the systems is when the
force is equal to 0.14 dyne when the current is 1 ampere and circulates in the same direction through all the coils of the system. The corresponding force for the other system is 0.34 dyne. The value of the force for a displacement $d$ mils from the correct axial position when 1.02 amperes is passing is given by the expression $4.8 \times 10^{-4}dg$ dynes,

\[ \text{MILS} \]
\[ +307 \]
\[ +207 \]
\[ +107 \]
\[ +7 \]
\[ -43 \]
\[ -93 \]
\[ -193 \]
\[ -293 \]
\[ -393 \]

change of force in dynes (cur = 1.02 amp.)

Fig. 18. Change of force due to axial displacement of coils.

where $g = 981$ centims./sec². The force is also given by $0.19xg$, where $x$ is in centimetres. Thus, for an axial displacement of 1 mil of the fixed or suspended coils, a change in balancing mass of 0.48 milligramme results; the axial position may therefore be fixed to less than 1 mil.

(2) Setting of the Fixed and Suspended Coils to be Concentric.—When the coils are coaxial the mutual induction is a minimum with respect to radial position, and when the current flows in opposite directions in the upper and lower fixed coils the force changes with displacement from the coaxial position. The change in force with radial displacement was measured for both fixed cylinders, the displacements being made in two directions at right angles; the results were plotted in four curves, of which two (those for the left fixed cylinder) are given in fig. 19. Inspection shows that the rate of variation of mutual induction with radial displacement increases with
the value of the latter, and that the position for minimum rate of change of mutual
induction may be deduced with considerable accuracy. The force in every case is
approximately given by the expression:—maximum force multiplied by \(1 + 5.8 \times 10^{-8} d^2\),
where \(d\) is the radial displacement in mils from the coaxial position; the corresponding
expression when the displacement is in centimetres is:—maximum force multiplied by
\((1 + 0.009x^2)\). Thus a displacement of 10 mils from the coaxial position produces a
change in force of 5.8 parts in 1,000,000. By the aid of the curves the radial setting
can be made within 2 mils, so that the error introduced by faulty radial setting is not
greater than 1 part in 5,000,000.

Effect of the Leads.—It was possible that the current in the leads to and from
the fixed coils might exercise an appreciable force on the suspended system, and that
the movable leads connected to the latter might be affected by the current in the
fixed system. This was tested by completing the circuit through the leads only of
the fixed coils and through the suspended system, and noting the effect; afterwards
the current was passed through the leads only of the suspended coils and through
the fixed coils, and the result again noted. Absolutely no force was detectable, and
on a subsequent repetition of the experiment the same result was obtained.

Insulation Tests.—When making a determination of current, the greatest difference
of potential between any portion of the balance and the earth was about 74 volts, and
the greatest difference of potential between neighbouring strands on the same cylinder
was less than 7 volts. It is desirable, therefore, that the insulation resistance between
the balance circuit and earth should not be less than 100 megohms, and that between
neighbouring strands should not be less than 10 megohms. The insulation resistance

![Graph showing variation of force caused by radial displacement of coils.](image)
of the various parts has been measured on several occasions, and the lowest measured resistance between any two adjacent coils is 2000 megohms, and between the balance circuit and earth it is 1000 megohms. The applied pressure in the former measurements was, in general, 40 volts, and for the latter 200 volts. When the coils are arranged in two groups, so that each group consists of one coil of each pair, the insulation resistance is 1500 megohms. The first measurement was made in March, 1905, and the last in April, 1907.

SECTION 8.—ADVANTAGES OF DUPLICATING THE COILS.

As previously mentioned, there is a set of coils at each end of the balance. Several advantages are gained by this arrangement. In the first place, the force to be measured is doubled by using the two sets of coils, and the accuracy of the measurement is therefore increased. A much greater advantage, however, arises from the symmetry thus obtained, for mechanical disturbing causes will, on the whole, tend to be neutralised.

One of the principal disturbances arises from convection currents produced by the heat generated in the coils, and in the flexible connections to and from the suspended systems. Another is the change of buoyancy due to change of temperature of the air in which the suspended coils hang. Both these produce a fairly rapid drift of the rest-point of the balance when a single set of coils is used, but when both sets are employed the steadiness of the balance is greatly improved. The extent of this improvement will be seen on reference to fig. 20, which shows four pairs of curves taken to test this matter. During all these tests the adjacent helices on each cylinder were connected up, so that the current (if any) flowed in opposite directions in adjoining wires, thereby making the windings inoperative, and obviating the necessity of keeping the current very constant.

Several sets of about 12 readings of the swings of the balance were taken under each of the following conditions respectively:—

(a) No current through either set of coils.
(b) Normal current through both sets of coils.
(c) " " " left-hand set of coils.
(d) " " " right-hand set of coils.

The rest-points were calculated from each group of three successive readings throughout a set, and the values tabulated, thus giving the rest-points for each half period. From the several sets of observations taken under each of the conditions (a), (b), (c), (d) respectively, those showing the least and greatest drifts were plotted, the former being shown in full lines and the latter dotted in fig. 20. The points thus obtained were joined by straight lines, and no attempt made to smooth out irregularities. In this figure the middle of the balance scale is denoted by 100; one division of the scale is about $\frac{1}{100}$th of a millimetre (actually 0.095 millim.), and as this
is represented on the curve by a length of 100 millims., the magnification is over 1000.* In spite of this large magnification the resulting lines are fairly regular, a fact which bears eloquent testimony to the excellence of workmanship and definiteness of

![Steadiness of Balance under Various Conditions](image)

Fig. 20.

behaviour of the instrument. The perfection of the arrangements for reading the scale are also of a high order, seeing that 1 millim. on the ordinates of the curves corresponds to a length of less than 1 micron (\(\frac{1}{1000}\) millim.) on the scale, and the regularity of the curves shows that the scale can be read to an accuracy of this order under favourable conditions.

* In fig. 20 the scale is about \(\frac{1}{10}\) of the original.
From the curves it will be seen that with no current through the coils, or with normal current through both sets, the drift was comparatively small, amounting in the worst case to only 0·15 division (0·014 millim.) in five complete periods. With current through one set only, however, the drift was much greater, amounting to 0·76 division in five periods in the lowest curve, the direction being such as to indicate increase in weight of the suspended coil through which the current was flowing. As the sensitiveness of the balance during the above tests was 0·82 division for the reversal of 1 milligramme, the apparent rate of change of mass amounted to 0·38 milligramme per period (or 0·65 milligramme per minute), when current passed through one set of coils only, whilst with current through both sets the greatest change was about a fifth as great. There is, therefore, a considerable increase in steadiness of the rest-point when both sets of coils are used.

Other advantages of two sets of coils are (a) that two independent determinations of the ampere can be made by using the sets separately; (b) the two sets being very nearly alike, one serves as a check on the constancy of the other set by arranging them in opposition and weighing the difference between their effects, which difference should, of course, be constant for a given current; (c) the difference in the force, if any, produced by changing the relative positions in azimuth of the fixed and suspended helices as suggested by Lord Rayleigh* can be readily found by making the differential test above mentioned with one set of coils in a certain relative position, whilst that of the other set is varied. The result of such a test is given on p. 517, Section 11.

A lengthy experience with the current weigher proves that the self-checking facilities provided in the instrument are of very great utility and form one of the most valuable features of the balance.

**SECTION 9.—FORCE BETWEEN HELICAL CURRENT AND COAXIAL CIRCULAR CURRENT SHEET.**

As mentioned in the introductory section (p. 467) of this paper, the formula used for calculating the force between the fixed and suspended coils is due to the late Professor J. V. Jones, viz.:

\[ F = \gamma h \gamma (M_2 - M_1) \]  

(1),

the meanings of the quantities being as there defined. This formula is rigorously exact for a helix and current sheet, and a very close approximation for two helices of fine pitch. The order of the error is considered in Appendix B, p. 541.

The arrangement of the coils in the actual instrument may be represented diagrammatically in section by fig. 21, which is meant to indicate a vertical section through the vertical axes of the windings, the vertical dotted lines being the axes of the coils.

Here $a_1$ and $a'_1$ represent the lower and upper ends respectively of the left-hand suspended coil, whilst CBD and GJH indicate the lower and upper helices on the left-hand fixed cylinder. B and J are supposed to be on the mid-planes of the respective helices. The right-hand suspended and fixed coils are similarly represented by $a_2$ and $a'_2$ and $C'B'D'$, $G'J'H'$.

![Diagram](image)

Fig. 21. Vertical section through coils of current weigher.

If only one pair of coils be used for making a determination, the change of apparent mass due to a reversal of current in the fixed coils enables the current strength to be calculated directly. Using both pairs, however, introduces cross actions between them, and the forces due to these must be calculated or eliminated.

To distinguish the forces between the coils on one pair of cylinders from those between the suspended coil of one pair and the fixed coils of the other pair, we have called them “direct” and “secondary” forces respectively. For example, the forces between $a_1$, $a'_1$ and CD, GH are called “direct forces,” whilst the vertical component of the force exerted on $a_1$, $a'_1$ by $C'D'$ and $G'H'$ is called a “secondary” force. For shortness, these are designated by D and S.

A little consideration will show that when the current in $a_1$, $a'_1$ is in the same sense as that in $a_2$, $a'_2$, and both sets of coils are in use, assisting, the electromagnetic force operative is the sum of the direct and secondary forces $(D+S)$, whilst if the currents in the suspended coils are opposite in sense, the resultant force is $(D-S)$. Two sets of observations are therefore necessary to eliminate the secondary forces.†

Horizontal components of the cross forces will exist, as well as forces due to the action of the suspended coils on each other tending to push them apart or pull them together. These forces, however, are so small compared with the mass of the suspended cylinders that no appreciable displacement is produced. Careful observation by a telescope, made with a view to detecting side displacement, led to a negative result.

Considering one set of coils, say the left-hand ones in fig. 21, the value of $(M_2-M_1)$

* In each case the directions of the currents in the two pairs of coils (left and right hand) are made such as will produce torques on the beam in the same sense.

† Mr. Searle has developed an expression by which these secondary forces may be calculated.
in formula (1), p. 507, was determined as follows:—The mutual induction of one of the two helices on CD, the lower half of the fixed cylinder, and the circle \( \alpha_i \) was calculated by finding \( M \) for the circle \( \alpha_i \) and helix BC (half of CD) and doubling it. To find \( M_i \) two mutual inductions were calculated, viz., that between \( \alpha_i' \) and a helix of length JD, and that between \( \alpha_i' \) and a helix of length JC, and taking the difference. It was therefore necessary to calculate three coefficients of mutual induction; these, for convenience of reference, are designated by \( M_{\alpha}, M_{\alpha'}, \) and \( M_{\alpha} \), respectively. The value of \( (M_{\alpha} - M) \) for both helices* on CD is given by

\[
M_{\alpha} - M_1 = 2 \{2M_{\alpha} - (M_{\alpha} - M)\} 
\]

For the current sheet \( \alpha_i, \alpha_i' \) and the helices on GH the value of \( (M_{\alpha} - M) \) was determined from \( M_{\alpha}, M_{\alpha'}, \) and \( M_{\alpha} \) by the increment formula

\[
\frac{dM_{\alpha}}{M_{\alpha}} = q \frac{dA}{A} + r \frac{da}{\alpha} + s \frac{dx}{x} \dagger. 
\]

which gives the change in \( M_{\alpha} \) due to small changes in dimensions, \( A \) being the radius of the helix, \( \alpha \) that of the circle, \( x \) the length of the helix, and \( q, r, \) and \( s \) coefficients determined as shown on pp. 200, 201 (Ibid.).

The sum of the two values of \( (M_{\alpha} - M) \) thus obtained gives the total for the left-hand set of coils, and is designated by \( M_L \).

As the dimensions of the right-hand set of coils are very nearly equal to those of the left-hand set, the increment formula was employed for finding the two values of \( (M_{\alpha} - M) \) for this side of the current weigher and their sum called \( M_R \). The "direct" force between the fixed and suspended systems when arranged to assist each other may therefore be written

\[
F = \gamma_h \gamma (M_L + M_R). 
\]

and the mass required to balance this force is given by

\[
m = \gamma_h \gamma \frac{M_L + M_R}{g}. 
\]

Taking the values of \( M_L \) and \( M_R \) determined on p. 514, and assuming \( g \) to be 981·20, we get for both sets of coils (neglecting secondary forces)

\[
m \text{(for 1 ampere)} = 0.1 \times 0.1 \times 184 \times \frac{51922.47}{129830} \times \frac{981.20}{291.20} = 7.49964 \text{ grammes};
\]

or change of mass on reversal of 1 ampere = 14.99928 grammes.

* As previously mentioned, each cylinder has double-threaded screw grooves.


‡ There are 184 turns on each suspended cylinder, the axial length of which is 12·9830 centims.
Similarly for reversal of 1 ampere in left-hand set we get
\[ m_l = 7.49987 \text{ grammes} \quad \ldots \quad (7), \]
and for right-hand set
\[ m_r = 7.49942 \text{ grammes} \quad \ldots \quad (8). \]

Further, we may express the current in amperes in terms of the mass to balance change of force on reversal as
\[ \text{Amperes} = \sqrt{m/14.99928} \quad \ldots \quad (9), \]
when both sets of coils are used (secondary effects eliminated), or
\[ \text{Amperes} = \sqrt{m/7.49987} \quad \text{for left-hand set} \quad \ldots \quad (10) \]
and
\[ \text{Amperes} = \sqrt{m/7.49942} \quad \text{for right-hand set.} \quad \ldots \quad (11). \]

Again, by taking the sum of the balancing masses obtained in a D+S observation and a D−S observation* with the same current passing, and calling this \( m' \), we have
\[ \text{Amperes} = \sqrt{m'/29.99856} \quad \ldots \quad (12), \]
the formula employed in the great majority of the measurements.

**SECTION 10.—CALCULATION OF MUTUAL INDUCTION OF HELIX AND CIRCULAR END OF COAXIAL CURRENT SHEET.**

The formula employed is
\[ M_0 = \Theta (A+a)ck \left\{ \frac{F-E}{k^2} + \frac{c'^2}{c^2} (F-\Pi) \right\} \dagger. \quad \ldots \quad (13), \]
where
\[ \Theta = \text{angular length of helix}, \quad A = \text{radius of helix}, \quad a = \text{radius of circle}, \]
\[ x = \text{axial length of helix}, \]
\[ c^2 = 4Aa/(A+a)^2, \quad c'^2 = 1-c^2, \]
\[ k^2 = 4Aa/(A+a)^2 + x^2, \quad k'^2 = 1-k^2, \]
and \( F, E \) and \( \Pi \) are complete elliptic integrals of the 1st, 2nd and 3rd kinds respectively; \( F \) and \( E \) are to modulus \( k \), and
\[ \Pi = \int_{\phi_0}^{\frac{\pi}{2}} \frac{d\psi}{(1-c^2\sin^2\psi)(1-k^2\sin^2\psi)} \dagger. \quad \ldots \quad (14). \]

* See p. 508.
Putting \( c'/k' = \sin \beta \), the quantity \((F - \Pi)\) can be expressed in terms of complete and incomplete integrals of the 1st and 2nd kinds*; thus

\[
c^{-1}k'^2 \sin \beta \cos \beta (F - \Pi) = -\frac{1}{2} \pi - F(k') F(k', \beta) + E(k) F(k', \beta) + F(k) E(k', \beta). \quad (15)
\]

The various elliptic integrals required in equations (13) and (15) were calculated in three ways, viz.:

(a) by interpolation from Legendre’s tables;
(b) directly by successive quadric transformation;
(c) directly by series.†

Method (a) was used by two of us independently, one (F. E. S.) employing a calculating machine, and the other (T. M.) using logs. To obtain the desired accuracy, 1st, 2nd and 3rd differences were required in the interpolations.

As a check on possible misprints in the tables, one of us (T. M.) calculated all the complete integrals directly by series, and also both complete and incomplete, by method (b). When the numerical coefficients in the series had been evaluated, the method (c) proved quite expeditious. For the convenience of others who may not have access to tables, these coefficients and their logs are given in Appendix A. Successive quadric transformation, however, proved quickest when the angle \( \beta \) was well conditioned, three or four transformations being sufficient. But in the case of \( M_e \), the angle \( \beta \) was nearly \( 45^\circ \), and to obtain the seventh figure accurately ten-figure logs were used.

For any particular value of \( M_e \) the corresponding increment coefficients \( q \), \( r \), and \( s \) are given by the expressions

\[
q = \frac{\Theta c k}{M_e} \left\{ F + \frac{A - \alpha}{2\alpha} (F - \Pi) \right\},
\]

\[
r = \frac{\Theta c k}{M_e} \left\{ F - \frac{A - \alpha}{2A} (F - \Pi) \right\},
\]

\[
s = -1 - \frac{\Theta c k}{M_e} (A + \alpha) \left\{ \left(1 - \frac{2}{k^2}\right) F - \frac{2}{k^2} E \right\}. \quad (16)
\]

Denoting \( \frac{M_e}{\Theta (A + \alpha) c k} \) by \( Z \), these may be written

\[
q = \frac{A}{2\alpha Z} (F - c'\Pi), \quad r = \frac{\alpha}{2AZ} (F + c'\Pi), \quad s = -1 - P_0(k)/Z \quad . \quad (17),
\]

where

\[
P_0(k) = \left(1 - \frac{2}{k^2}\right) F + \frac{2}{k^2} E.
\]

* CAYLEY, ‘Elliptic Functions,’ § 183.
† CAYLEY, Chapter XIII.
‡ CAYLEY, Chapter III, § 77.
The mean (arithmetical) dimensions chosen for calculating the values of $M_e$, $M_{e'}$, and $M_{e''}$, respectively, were those of the left suspended coil and the lower helices on the left fixed coils, and are given in Table VIII.

**Table VIII.**

$$2\Lambda = 33'0016_6$$ centims., \quad $$2a = 20'3583_3$$ centims.

From these we get

$$A + \alpha = 26'68001, \quad \log (A + \alpha) = 1'4261860,$$

$$A - \alpha = 6'32167, \quad \log (A - \alpha) = 0'8008325,$$

$$c^2 = 0'9438574, \quad \log c^2 = 1'9749064,$$

$$c = 0'9715233, \quad \log c = 1'9874532,$$

$$c^2 = 0'0561426, \quad \log c^2 = 2'7492925,$$

$$c' = 0'2369443, \quad \log c' = 1'3746462.$$

These quantities are required for the three values of $M$ to be calculated. The remaining quantities differ according to the axial length of the helix taken, and are tabulated below.

**Table IX.**—Calculation of Mutual Induction.

<table>
<thead>
<tr>
<th>Quantities</th>
<th>Values of Quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>For $M_e$</td>
</tr>
<tr>
<td>$x$</td>
<td>6.350,</td>
</tr>
<tr>
<td>$k^2$</td>
<td>0.8932480</td>
</tr>
<tr>
<td>$k$</td>
<td>0.9451178</td>
</tr>
<tr>
<td>$k'^2$</td>
<td>0.1067520</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.3267292</td>
</tr>
<tr>
<td>$\sin B$</td>
<td>0.7252007</td>
</tr>
<tr>
<td>$\cos B$</td>
<td>0.6885375</td>
</tr>
<tr>
<td>$B$</td>
<td>46°-29'1325</td>
</tr>
<tr>
<td>$F(k)$</td>
<td>2.547390</td>
</tr>
<tr>
<td>$E(k)$</td>
<td>1.1102534</td>
</tr>
<tr>
<td>$F(k', \beta)$</td>
<td>0.8198800</td>
</tr>
<tr>
<td>$E(k', \beta)$</td>
<td>0.8029245</td>
</tr>
<tr>
<td>$k^2 \sin \beta \cos \beta (F - II)$</td>
<td>-0.7037136</td>
</tr>
<tr>
<td>$c^2$</td>
<td>-0.7629102</td>
</tr>
<tr>
<td>$F - E$</td>
<td>1.6088889</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>90\pi</td>
</tr>
<tr>
<td>$M$</td>
<td>5859.722 \times 4</td>
</tr>
<tr>
<td></td>
<td>23438.888</td>
</tr>
</tbody>
</table>
From the above table and formula (2), p. 509, the value of \( M_2 - M_1 \) for the left suspended cylinder and the lower helices on the left-hand fixed cylinders can be obtained, viz.:

\[
= 12980.562 \quad \ldots \quad \ldots \quad \ldots \quad (18).
\]

To determine the corresponding quantities for the remaining part of \( M_L \) and for those of \( M_R \) the quantities given in Table X. are required.

**Table X.**—Calculation of Increment Coefficients \( q, r, \) and \( s \) [Equations (3) and (17)].

<table>
<thead>
<tr>
<th>Quantities</th>
<th>For ( M_e )</th>
<th>For ( M_{e_1} )</th>
<th>For ( M_{e_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Pi )</td>
<td>15.373275</td>
<td>15.165695</td>
<td>9.691995</td>
</tr>
<tr>
<td>( \Pi' )</td>
<td>3.642846</td>
<td>3.593424</td>
<td>2.296368</td>
</tr>
<tr>
<td>( F - \Pi' )</td>
<td>-1.095218</td>
<td>-1.064677</td>
<td>-0.325876</td>
</tr>
<tr>
<td>( F + \Pi' )</td>
<td>6.389998</td>
<td>6.122171</td>
<td>4.266860</td>
</tr>
<tr>
<td>( Z )</td>
<td>0.845979</td>
<td>0.840184</td>
<td>0.643365</td>
</tr>
<tr>
<td>( P_e(k) )</td>
<td>-0.670387</td>
<td>-0.654965</td>
<td>-0.234772</td>
</tr>
<tr>
<td>( q )</td>
<td>-1.04931</td>
<td>-1.027088</td>
<td>-0.410543</td>
</tr>
<tr>
<td>( r )</td>
<td>2.25657</td>
<td>2.247538</td>
<td>2.045630</td>
</tr>
<tr>
<td>( s )</td>
<td>-0.20756</td>
<td>-0.220449</td>
<td>-0.635087</td>
</tr>
</tbody>
</table>

Formula (3), p. 509, Section 9, may be written

\[
dM_e = M_e \frac{q}{A} dA + M_o \frac{r}{a} da + M_o \frac{s}{x} dx \quad \ldots \quad \ldots \quad (19),
\]

and making use of the values of \( M, q, r, \) and \( s \), from Tables IX. and X., we get

\[
\begin{align*}
\frac{dM_{e_1}}{dA} &= -1490.5 \frac{dA}{dx} + 5196.7 \frac{da}{dx} - 766.0 \frac{dx}{dx} \\
\frac{dM_{e_1}}{da} &= -754.8 \frac{dA}{dx} + 2677.6 \frac{da}{dx} - 403.0 \frac{dx}{dx} \\
\frac{dM_{e_1}}{dx} &= -561.9 \frac{dA}{dx} + 4538.7 \frac{da}{dx} - 741.8 \frac{dx}{dx}
\end{align*}
\]

where

\[
M_{e_1}' = 4M_{e_1}, \quad M_{e_1}' = 2M_{e_1}, \quad M_{e_1}' = 2M_{e_1},
\]

and \( dA, \) \( da, \) and \( dx \) are increments of \( A, a, \) and \( x \) respectively.

In cases where \( dA, \) \( da, \) and \( dx \) are the same for all the windings involved in one value of \( M_2 - M_1, \) the equations (20) may be combined, thus giving

\[
d(M_2 - M_1) = -1683.4 \frac{dA}{dx} + 3335.6 \frac{da}{dx} - 427.2 \frac{dx}{dx} \quad \ldots \quad \ldots \quad (21).
\]

For the helix GH (fig. 21) and current sheet \( \alpha \alpha' \) we have

\[
\begin{align*}
dA &= -0.00053, \quad da = 0, \quad dx = 0, \\
d(M_2 - M_1) &= +1683.4 \times 53 \times 10^{-5} = 0.892.
\end{align*}
\]
Denoting by \((M_2'-M_1')\) the new value of \((M_2-M_1)\), we get
\[
(M_2'-M_1') = (M_2-M_1) + 0.892 = 12980.562 + 0.892
\]
\[= 12981.454,
\]
and therefore
\[
M_L = (M_2-M_1) + (M_2'-M_1')
\]
\[= 25962.016 \quad \ldots \ldots \ldots \ldots \ldots \quad (22).
\]

For the right-hand set of coils the increments are
\[
dA'' = 0.00111, \quad dA''' = 0.00052,
\]
for the lower and upper fixed coils respectively, and for the current sheet \(a_2a_2'\),
\[
da = 0.00027.
\]

Hence
\[
(M_2''-M_1'') = 12979.728, \quad (M_2'''-M_1''') = 12980.726,
\]
therefore
\[
M_R = (M_2''-M_1'') + (M_2'''-M_1''')
\]
\[= 25960.454 \quad \ldots \ldots \ldots \ldots \ldots \quad (23),
\]
and
\[
M_L + M_R = 51922.47 \quad \ldots \ldots \ldots \ldots \ldots \quad (24).
\]

The values obtained by the calculating machine were as follows:

\[
M_L = 25962.04 \quad \ldots \ldots \ldots \ldots \ldots \quad (22'),
\]
\[
M_R = 25960.43 \quad \ldots \ldots \ldots \ldots \ldots \quad (23'),
\]
and
\[
M_L + M_R = 51922.47 \quad \ldots \ldots \ldots \ldots \ldots \quad (24').
\]

Thus the two methods give the same result for the sum \(M_L + M_R\), although the constituent values differ by nearly 1 in 1,000,000. It should, however, be pointed out that one of us calculated the mutual inductions from the arithmetical mean dimensions of the helices concerned, and the other from the calibrated mean dimensions as obtained from the curves shown in figs. 13, 14, 15, and 16. The agreement is, nevertheless, very close.

Mr. G. F. C. Searle has calculated the force between the current in one set of fixed coils and that in the suspended coils of the system not coaxial with it. The distance between the axes of the coils is a most important factor in the calculation, the accuracy of the calculation being approximately that with which the 5th power of this distance is known. The distance was determined as 50.8 centims. approximately, and for a current of 1.018 amperes a balancing mass of 0.0427 gramme was calculated by Mr. Searle's formula. In practice the balancing mass for this current is 0.0424 gramme. The agreement is satisfactory.
Section 11.—Differential Effects of the Several Windings, and their Relation to the Linear Dimensions of the Coils.

On each fixed cylinder there are four helices, and on each suspended cylinder two helices, and the diametral dimensions of those on the same cylinder are slightly different. Let the upper helices on the left fixed cylinder be designated U1 and U2 respectively, the lower ones L1 and L2, and those on the coaxial suspended cylinder a and b; also let the helices on the cylinders to the right be represented by similar letters characterised with a dash. Then the maximum force due to a current $\gamma_a$ in the left fixed helices and a current $\gamma'$ per unit length in the current sheets equivalent to the suspended helices may be written

$$\gamma L (M_{U1} + M_{U2} + M_{L1} + M_{L2} + M_{U3} + M_{U4} + M_{L3} + M_{L4}) = 2\gamma L M = D_L \text{ (say),}$$

where $M_{U1}$ is the difference in mutual induction of the coil U1 and the circular ends of $a$ (i.e., $M_a - M_1$) of formula (1), p. 507, and $M_L$ is the difference in mutual induction of all the fixed left helices and the circular ends of the current sheet equivalent to $a$ and $b$. For the system on the right there is a similar expression which may be denoted by $D_R$, and the sum $D_L + D_R$ is conveniently written as $D$.

In addition, there are secondary forces due to the mutual action of the fixed systems and the opposite suspended ones. The maximum secondary effect due to the left fixed system and the right suspended one may be written $S_L$, and that due to the other systems $S_R$. Let $S_L + S_R = S$.

The direct and secondary forces may aid one another, in which case the total force measured by the balance is $D + S$, or they may oppose one another, the force thus becoming $D - S$. The sum $(D + S) + (D - S)$ gives $2D$. If only one-half of the whole system is used, $D_L$ or $D_R$ is obtained. In the determination of the E.M.F. of the cadmium cell, the forces $D + S$ and $D - S$ were measured in most cases.

**Estimation of Difference between Left-hand and Right-hand Systems of Coils.**—If the two forces $D_L$ and $D_R$ act in opposition on the beam of the balance, the force required to maintain equilibrium is $(D_L - D_R) + (S_L - S_R)$ or $(D_L - D_R) - (S_L - S_R)$. By reversing the current through all the coils on one side of the balance, one of these states is obtained from the other. If both of the balancing forces are measured, the mean is $D_L - D_R$, which is equal to $2\gamma L (M_L - M_R)$. Thus the mean balancing mass is $2\gamma L (M_L - M_R)/g$, and is to be accompanied by a positive sign when the force acting on it is in the same direction as $D_L$, and by a negative sign when in opposition to $D_L$. If $m_L$ is the balancing mass, $M_L - M_R = m_L g/2\gamma L \gamma_a$; a check is thus afforded on the calculated difference $M_L - M_R$. The calculated value of $M_L$ is 25962-04 centims. (see (22'), p. 514), and of $M_R$ 25960-43 centims., the difference being 1-61 centims. The mass $m_L$ was determined on five different dates, and on each occasion the current was reversed through all the fixed coils in order to reverse the direction of the force and

3 U 2
thus secure greater accuracy. The values of \(2m_1\) obtained on these occasions are as follows:—0·5, and 0·4, millimetre; 0·4 and 0·3, millimetre; 0·3, and 0·4 millimetre; and 0·4 and 0·3 millimetre, the sign being such as to indicate that \(M_L\) was the greater. The mean value of \(m_1\) is 0·21 millimetre, and the probable error of this value is about 10 per cent. A current of 1·02 amperes was used, so that \(2\gamma = 0·102 \times 14·1724\) and \(\gamma_h = 0·102\). Hence the experimental value of \(M_L - M_R\) is 0·00021g/0·147 = +1·40 centims., and is subject to a probable error of about 10 per cent. The agreement with those independently calculated by T. M. and F. E. S. from the dimensions of the coils (1·56 centims. and 1·61 centims.) is remarkably good.

*Estimation of the Difference in the Diameters of the Coils on the Fixed Cylinders.*—Suppose the current in \(U_1\) is in opposite direction to that in \(U_2\), those in \(L_1\) and \(L_2\) to be in opposite directions to each other, and that the currents in the suspended coils \(a\) and \(b\) are co-directional. Let the system on the right be inoperative. Then the force is

\[
\gamma' \gamma_h [M_{U_1a} + M_{U_1b} - (M_{U_2a} + M_{U_2b}) \pm (M_{L_1a} + M_{L_1b} - (M_{L_2a} + M_{L_2b}))],
\]

where \(\gamma'\) and \(\gamma_h\) have the same meanings as before. Here \(M_{U_1a} - M_{U_2a}\) and \(M_{U_1b} - M_{U_2b}\) are very small and practically equal; similarly \(M_{L_1a} - M_{L_2a}\) is equal to \(M_{L_1b} - M_{L_2b}\) very nearly. Hence the force may be written \(2\gamma' \gamma_h ((M_{U_1a} - M_{U_2a}) \pm (M_{L_1a} - M_{L_2a}))\). By trial this may be made a maximum. If we assume \(M_{U_1a}\) to be greater than \(M_{U_2a}\), and \(M_{L_1a}\) to be greater than \(M_{L_2a}\), the maximum force is

\[
2\gamma' \gamma_h ((M_{U_1a} + M_{L_1a}) - (M_{U_2a} + M_{L_2a})).
\]

The difference of the mean diameters of the separate helices on the upper and lower portions of the fixed cylinders was measured as 3\(\mu\) for the coils on the left and as 2\(\mu\) for those on the right (p. 488). For a mean difference in radius of 1·2\(\mu\), the value of the force for one system, as calculated by the last equation, is 0·02 dyne, and on reversal of the current through the fixed coils the necessary change in the balancing mass to maintain equilibrium should be 0·04 millimetre. If the left and right systems be made co-operative in their effect, the change in the balancing mass will be twice this, i.e., very nearly 0·1 millimetre. In experiments made to check this value, all the possible combinations of the coils on the fixed cylinders were made, subject only to the condition that the currents were in opposite directions in adjacent helices. Some small displacement of the resting point of the balance was invariably recorded on reversing the current in the fixed coils, but the change was exceedingly small and not always in the same direction. The mean of the first five observations is 0·0 millimetre as the balancing mass, and the mean of the first ten observations is 0·1 millimetre, results which are of little value except to show that the difference in diameter of the helices on the fixed cylinders is very small.
Estimation of the Difference in the Diameters of the Coils on the Suspended Cylinders.—When the currents in the a and b wires on the left suspended cylinder are in opposition, the maximum force due to the current in the left fixed helices is

$$\gamma'\gamma^2 \{(M_{Ua} + M_{Va} + M_{La} + M_{Ld}) - (M_{Ub} + M_{Vb} + M_{Lb} + M_{Ld})\}.$$  

The difference of the mean diameters of the helices on the left suspended cylinder was measured as 3.2 µ and the difference of those on the right as 2µ. For a mean difference in radius of 1.22 µ the value of the force for one system is 0.06 dyne. If the left and right systems are made to co-operate, the necessary change in mass to maintain equilibrium when a current of 1.02 amperes is passed through all the coils and reversed in the fixed coils should be 0.25 milligramme. The experimental value is 0.32 ± 0.1 milligramme; corresponding to a difference in the mean diameters of 3.5 µ ± 1 µ.

Change of Relative Azimuth of Fixed and Suspended Cylinders.—Lord Rayleigh has pointed out* that the value of the mutual induction of two coaxial helices is dependent on the relative position of the helices, and that in strictness both helices cannot be replaced by current sheets. The complication thence arising can be eliminated in experimental applications by a relative rotation, since the mean field is strictly symmetrical, and accordingly the mean mutual induction is the same as if both helices were replaced by current sheets.

The fixed and suspended coils of the ampere balance are normally arranged, so that the diametral plane containing the termini of the fixed coils on one cylinder is practically coincident with that containing the termini of the coaxial suspended coils. The mutual induction must be slightly different when these planes are at right angles, and attempts were made to estimate this difference by experiment. The difference of the forces exerted by the left and right systems was first determined in the manner indicated on p. 515. One set of fixed coils was then turned through 90° and the difference again measured; there was no certain change in the difference, and had the change in mutual induction been as great as 5 in 1,000,000 it must have been detected. The fixed coils of the other system were then turned through 90° and the difference in mutual induction of the two systems again determined; it agreed with the previous results. The angle was altered to 60° and a few more measurements made, but no change in the difference was observed. The complete set of observations lead us to conclude that the mutual induction of the helices does not vary with change in the orientation of the coils by more than 1 in 1,000,000.

Section 12.—Use of Balance and Determination of E.M.F. of Cadmium Cell.

The arrangement of the circuits employed in the determination of current strength and of the E.M.F. of the standard cell is shown diagrammatically in fig. 22, and in further detail in fig. 23. Fig. 24 gives a general view of the apparatus as used.

The current, whose value is to be determined by the current weigher, is passed through a standard resistance $R$ (figs. 22, 23) and adjusted in strength until the P.D. between the terminals of $R$ balances the E.M.F. of the cell $S$. A double commutator $C$, fig. 23, with copper contacts to reduce thermal E.M.F.'s, reverses the current in the standard resistance $R$ and simultaneously reverses the connections to the standard cell $S$. The standard resistance is described on p. 520; it is provided with current and potential leads and is immersed in a tank of insulating oil. To

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**Fig. 22. Diagram of circuit.**

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**Fig. 23. Detailed diagram of circuit.**

A represents an ammeter.  
B " a battery.  
C " a double commutator.  
E " an earthed point of battery.  
G " a galvanometer.  
M " a main commutator.  

N represents a variable resistance.  
P " a multiple commutator and plug board.  
R " a standard resistance.  
S and $S'$ represent standard cells.  
T represents a turning head for enabling either $S$ or $S'$ to be used.
avoid possible electromagnetic disturbances the oil was not stirred by a motor-driven turbine, but by a stream of air forced through it. In a few of the earlier determinations the standard cell was kept in the room containing the remainder of the apparatus; considerable variations in temperature were, however, experienced, and as there was evidence of a slight lag in the E.M.F. of the cell it was removed to

a constant-temperature room in the basement. S', fig. 23, is a second standard cell for the preliminary adjustment of the current, and the turning head T readily allows of either cell being inserted in the potentiometer circuit. B is a battery of 55 accumulators of 30 ampere hours' capacity; it is earthed at one point to eliminate electrostatic effects (see p. 525). The resistance of the circuit can be adjusted by means of a set of manganin coils and a mercury trough in N; in all there are ten 10-ohm coils,
ten 1-ohm coils, and ten 0·1-ohm coils in series with a mercury trough of resistance 0·12 ohm; a sliding short-circuiting contact provides the final adjustment, a movement of 3 millims. of the slider corresponding to a change in current of 1 in 100,000. The manganin coils are wound on long brass tubes and are immersed in paraffin oil, the capacity of the tank being 6 gallons; a very constant current was in this way ensured. Under favourable conditions, i.e., when manganin formed by far the greater part of the resistance of the circuit, a current constant to 2 in 1,000,000 could be maintained for an hour or more; when the coils of the balance were in circuit a current steady to about the same limit could be held for a few minutes only. This, however, is all that was desired.

The potential circuit included the resistance coil R, the cadmium cell S, a contact key, and a galvanometer G. The galvanometer was of the Broca type, having a resistance of 1000 ohms. The controlling field was varied from time to time and hence the sensitiveness was not the same in all of the determinations; in general a deflection of 5 millims. on the scale (1·5 metres distant) corresponded to a change of one-hundred-thousandth of an ampere in the main current. The galvanometer, commutators and all of the auxiliary apparatus belonging to the balance were made by Mr. Murfitt, the instrument maker attached to the National Physical Laboratory. Much of the fitting was also very ably done by Mr. Murfitt.

*The Resistance Coil R, fig. 23, used as a secondary standard (numbered L 87), is made of thick manganin strip, wound non-inductively on six posts and insulated therefrom by silk ribbon and shellac. The coil was built and annealed by Mr. Melsom in July, 1905, and its resistance changed very rapidly for many months afterwards; it is still rising in value. It is provided with potential points and can carry a current of 10 amperes without abnormal heating. In July, 1905, the coil was directly compared with the mercury standards of the National Physical Laboratory, and again in March, 1906; the intermediate and subsequent evaluations were made by comparing it with standard coils. The methods of comparison are described elsewhere.* The temperature coefficient was determined in 1905 and again in March, 1907; the mean coefficient for the range 10° C. − 20° C. is +0·0019 per cent. per 1° C., but for the reduction of values to a common temperature a resistance chart was used. Owing to the rapid rise in resistance with time the coil was compared with practically constant standard manganin coils on each day a determination of current was made; the secular change in resistance was thus eliminated as a source of error in the comparison of results.

*The Main Commutator (M, fig. 23) is formed of four brass quadrants of square section and an ebonite turning head carrying two springy copper contact pieces insulated from each other. Connection with the concentric cable is made by drilling two opposite quadrants, one aperture being ¼ inch in diameter and the

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other $\frac{1}{4}$ inch. Thin brass tubes, projecting outwards for $\frac{1}{2}$ inch, are fitted into these holes and hard soldered to the quadrants. To the larger of these tubes the strands comprising the outer conductor of the concentric are soldered, and to the smaller the inner strands are similarly joined. Each quadrant is drilled centrally

![Diagram](image_url)

**Fig. 25.** Multiple commutator and plug board.

with a large tapering hole; by means of conical plugs connection with other circuits—for the measurement of insulation resistance, &c.—can thus be made. The two positions of this commutator are designated hereafter by the letters A and B.

**Multiple Commutator and Plug Board** (P, fig. 23 and fig. 25).—This consists of four commutators, constructed in a similar manner to that already described, and a
plug board divided into two sections for the left-hand and right-hand sets of coils respectively. A commutator allows of the reversal of the current in all the coils on any one cylinder, and the plug board allows of the reversal of the current in any one or more helices on the fixed cylinders. The inner and outer conductors of the concentric cables, D, fig. 25, are soldered to thin brass tubes let into brass blocks and pass to the various coils of the balance. Each helix is designated by a word, a letter, and a number, which are marked on an ebonite bridge at the top of fig. 25; the turning heads are also marked so as to enable reversals of the current to be quickly made without likelihood of error. Each plug hole is numbered, and a scheme was drawn up so that any desired combination was represented by a series of numbers for the plugs and by letters for the commutators. For example, in taking a (D+S) observation, plugs are inserted in the holes 13, 2, 3, 16, 5, 18, 19, 8, 21, 10, 11, 24, and the four commutators arranged in positions represented by the diagram a, fig. 25. Here the straight lines in the circle represent the directions of the turning heads of the commutators. When the main commutator M, fig. 23, is in the A position, and the multiple commutators as shown in a, fig. 25, the whole arrangement is designated by the symbols aA. Reversing the main commutator changes it to aB. Turning the commutators connected with the suspended cylinders to the positions indicated by diagram b, fig. 25, we get an arrangement symbolised by bB, and a reversal of the main commutator gives bA. Changing from aA to bB reverses the current in the fixed coils only, as also does the change bB to aA. In fig. 25 the letters DD, &c., indicate the ten concentric cables running from the plug board to the balance.

The reversal of the current in one of the two helices on a suspended cylinder is made by a small commutator on the three-limbed spider. This has been described on p. 500, and is illustrated in fig. 17.

Balancing Masses.—The weights employed are eight in number and are made of aluminium. They are divided into two sets: four for the (D+S) observations and four for the (D−S) observations, and the masses of the weights in each set are approximately equal. The force due to one (D+S) weight very nearly balances half the total force due to the current in such observations, and it may be employed for observations of the maximum force when the current flows through all the coils of one system and through the suspended coils only of the other system. Similarly, a (D−S) weight may be used for observations of the minimum force under such conditions. For the (D+S) observations two weights are used on each side of the balance, similarly for the (D−S) observations, and the total mass of the eight weights is required for the calculations. The masses of different combinations were, however, also determined. The standard mass employed was a 100-gramme weight standardised at Sèvres, and the effective mass of the eight weights in a medium of density 0·001196 was determined as 31·12494 grammes, the four (D+S) weights being 15·73135 grammes and the four (D−S) weights being 15·39359 grammes. Aluminium is not
a very desirable material for weights, owing to its density being so small, but in our experiments the effective mass of the weights never varied by so much as 8 in 1,000,000 from the mean, and if no correction had been made for variable air displacement, the error in the measurement of the current would never have exceeded 4 in 1,000,000. Of course, the corrections were applied. The probable error of the effective mass is of the order 1 in 1,000,000.

Preliminary Difficulties.

(A) Defects in Flexible Concentric Cable.—The cable originally used consisted of an inner conductor of 30 copper wires of diameter 0.0048 inch and an outer tubular conductor of 74 strands of the same diameter. After connecting the balance coils to the multiple commutator and plug board the cable was found to be faulty, and subsequent examination showed that many of the internal strands were broken. The cable was therefore replaced by a concentric one having an inner conductor of three copper wires of diameter 0.022 inch, and an outer tubular conductor of sixteen, of diameter 0.0148 inch. This proved to be entirely satisfactory.

(B) Unsteady Current and Convection Currents of Air Produced by the Heating of the Flexible Leads.—Originally the current was led into and out of each pair of suspended coils by two silver-gilt strips, each 13 centims. long, 0.37 millim. broad, 0.035 millim. deep, and of 0.15 ohm resistance. In each pair of silver strips there was 1 calorie of heat produced every 14 seconds when a current of 1 ampere passed through them, and the maximum increase in temperature of the strips was about 20°C. The temperature coefficient of electric resistance of silver is 0.36 per cent., hence the increase in resistance of the four strips was 0.04 ohm, and a fluctuation in temperature of 1°C. corresponded to a change in resistance of the circuit (110 ohms) of 0.002 ohm. Such a change in temperature frequently resulted, as was proved by including the silver strips in a circuit containing 110 ohms of manganin; with a current of 1 ampere the fluctuations in current were of the order 5 in 1,000,000. When the strips were removed from the circuit, the corresponding changes were 1 in 1,000,000.

The energy of motion of the air particles in the immediate neighbourhood of each pair of strips was increased at the rate of about 3 \times 10^6\text{ ergs per second.} The effect of the convection currents of air thus produced was tested by passing a current of 1 ampere through one pair of the strips inside the balance case when the balance coils were not included in the circuit. After the circuit had been completed for 5 minutes the resting point of the balance changed by an amount equivalent to an added load of 9 milligrammes on that side of the balance with the heated strips; after 10 minutes the change corresponded to 24 milligrammes; 15 minutes afterwards to 39 milligrammes, after which the resting point of the balance was approximately constant. The circuit was broken for 15 seconds and the change noted; it corresponded to 0.4 milligramme; equilibrium was restored after 5 minutes. The length
of one arm of the balance is 25·4 centims., and the "equivalent arm" of each pair of strips is about 15 centims.; hence the maximum downward force on the strips was 65 dynes, equal to that produced by 66 milligrammes. It is interesting to note that the mass of the two strips was less than this—being only 36 milligrammes. The elasticity of silver changes with temperature and the control exercised by the strips must in consequence have varied with it; calculation shows, however, that the effect was negligible.

To remedy these defects, each of the four strips was replaced by 80 silver wires 1 mil (0·0025 centim.) in diameter. The surface per centimetre length of the strip was 0·80 sq. millim. and the section of the strip 0·013 sq. millim.; the corresponding values for the 80 strands are 6·0 sq. millims. and 0·04 sq. millim. The length of each strand is 10·5 centims., and the resistance of the 80 is about 0·037 ohm; the heating effect is, therefore, one-quarter of that formerly experienced, and the radiating surface over seven times as great. The sensitiveness of the balance is greater than when the strips were used, and the current through the fine wires can be kept very constant. In addition there is no drift in the resting point of the balance due to convection currents of air rising from the silver wires. Fusion of the silver did not result when a current of 0·7 ampere was passed through one strand.

(C) Heating Effect of Current in Balance Coils.—The total resistance of the fixed and suspended coils is 71 ohms at 17° C. With a current of 1 ampere the heating effect is considerable and the resistance of the coils changes comparatively rapidly. The following table (XI.) gives the resistance of the balance coils and estimated temperatures when currents of 0·70 and 1·02 amperes respectively pass through the coils until the latter are in a steady thermal state. In each case the circuit was completed for 24 hours.

<table>
<thead>
<tr>
<th>Coils</th>
<th>No current.</th>
<th>0·7 amperes.</th>
<th>1·02 amperes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>On left fixed cylinder</td>
<td>26·641</td>
<td>17·35</td>
<td>27·506</td>
</tr>
<tr>
<td>&quot; right</td>
<td>26·647</td>
<td>17·35</td>
<td>27·528</td>
</tr>
<tr>
<td>&quot; left suspended cylinder</td>
<td>8·710</td>
<td>17·35</td>
<td>9·077</td>
</tr>
<tr>
<td>&quot; right</td>
<td>8·730</td>
<td>17·35</td>
<td>9·110</td>
</tr>
<tr>
<td>Temperature of balance</td>
<td>—</td>
<td>17·35</td>
<td>—</td>
</tr>
</tbody>
</table>

Afterwards the balance case was covered with blankets and similar observations made with a current of 1 ampere. The maximum increase in temperature was 22° C., the temperature of the air within the balance case being 12° C. lower than that of the suspended coils.
An idea of the effect of the convection currents of air rising from the fixed and suspended coils was obtained from observations on the balance pointer when the forces acting on the suspended systems were in opposition. In such a case small variations in current strength have no measurable effect on the total force. With the balance case covered with blankets and practically uniform radiation in all directions (the observations were made at midnight), the mean doubled rest-point of the balance pointer was deduced from 108 readings as 206.7. These readings were taken in three sets. The first set of 36 readings gave 206.2 as the rest-point; the second set were taken immediately after the first and gave 205.9; there was an interval of half an hour between the second and third sets, the mean of the latter being 208.0. The average difference between the first 36 readings and 206.2 is 0.8, so that the mean of a few readings is associated with a large probable error. In addition there was difficulty in maintaining a very steady current through the heated coils; the rest-point of the balance was subject to drift; and the difference of temperature between the coils and marble and between fixed and suspended coils introduces serious difficulties in the calculation of the mutual induction.

The rest-point of the balance is very constant when no current is flowing through the coils and has not passed for some hours previously; it is also very constant for the first 20 minutes after the circuit has been completed. The resistance of the coils increases considerably in this period, but observations proved that a current constant to 2 in 1,000,000 and often to 1 in 1,000,000 could be maintained for four minutes, in which interval the resistance of the balance coils increases about 0.12 ohm, and the sliding contact of the mercury trough passes from the most to the least favourable position for adjustment. In this interval three readings of the balance pointer could always be taken, and experience has shown such readings to be remarkably accurate. This method was adopted.

(D) Electrostatic Effects.—Electrostatic effects of sufficient magnitude to produce a readable deflection of the balance pointer were not anticipated. The mean electrostatic potentials of the various pairs of coils are, of course, different, but the maximum variation between any part of one suspended and any part of one fixed system is less than 36 volts when a current of 1 ampere is flowing. A test was made by connecting the upper coils of one fixed system and the lower coils of the other fixed system to the + pole of a battery of 110 volts; the other coils of the balance were connected to the − pole and to earth. No difference was observed in the rest-point of the balance, and hence there could be no disturbing effect due to electrostatic attraction between the fixed and suspended coils. When, however, the balance coils were placed in series and a current of 1 ampere passed through them, a difference in the rest-point of 0.7 scale-division was always observed on reversing the current; this was found to be a measure of the difference of the electrostatic forces between the suspended coils and the metal guard-discs \( \delta \), fig. 6 (Plate 8), underneath them. The difference of mean potential of the coils on the suspended systems is 62 volts; the metal rings are about
3 millims. distant from the bases of the cylinders and are practically earth-connected. If the mean potentials of the suspended systems were +31 volts and -31 volts respectively, relatively to the earth, then the total electrostatic effect should be \textit{nil}. The resistance of the whole circuit was 110 ohms, that of the balance 71 ohms, and the E.M.F. of the battery was 110 volts. By earthing the battery between the 19th and 20th cells, counting from that end directly connected to the balance coils, the potentials were approximately as indicated and there was no measurable effect on the balance when the current was reversed. Except for the first few observations the battery was earthed at this point. No error was introduced by the omission, as the electrostatic effect occurs twice with opposite signs in the observations.

\textit{Normal Procedure.}—In making a determination of the strength of a current, the following scheme was adopted:—

(1) The commutators and plugs were set so that the current circulated through the balance coils in the order: suspended left, fixed left, fixed right, and suspended right, and so that the total force was the sum of the direct and secondary forces \((D+S)\) (see p. 508). Observations for the determination of the balancing mass were then made and repeated when

(2) the current through the fixed coils was reversed;

(3) the current through the whole of the balance circuit as typified by (2) was reversed;

(4) the current through the fixed coils was reversed, that in the suspended coils being as in (3);

(5) the current through the whole of the balance circuit as typified by (4) was reversed.

Each of these arrangements is indicated by two letters, one denoting the position of the main commutator \(M\), fig. 23, and the other that of the commutators on the multiple commutator and plug board \(P\), as described on p. 522. After these observations a similar set was made when the direct and secondary forces opposed one another, thus determining \((D-S)\). The order of making the observations in each set was rigidly adhered to, but the \((D-S)\) observations sometimes preceded and sometimes followed the \((D+S)\) observations.

After the first few determinations of E.M.F. had been made, the current which it would be necessary to pass through the circuit to balance the cadmium cell was estimated from the secular change in resistance and the temperatures of the coil and cell; the balancing mass was then calculated and the position of the rider decided on, so as to give, together with the weights, the required mass. Previous to observations of any kind being made, the circuit through the manganin coils was completed for an hour or more, after which an examination of the steadiness of the current was made by one of us, and observations of the sensitiveness of the balance and stability of the rest-point of same were made by another. In accordance with the scheme on p. 522, the multiple commutator was appropriately set, the balancing
weights placed in position, and, at a given signal, the balance coils were included in the circuit. The resistance in N, fig. 23, was rapidly adjusted until (1) the ammeter reading appeared to be the same as before, (2) balance was obtained when $S'$ was in the potentiometer circuit, and (3) the fulfilment of the latter condition when $S$ was substituted for $S'$. In general, these adjustments occupied about 10 seconds. When condition (2) held, a signal was made to the balance operator, and the beam of the balance was freed. The average duration of a complete set of observations was 20 minutes, and during this time the balance coils were included in the circuit for about 12 minutes.

General Behaviour of the Balance.—After eliminating the difficulties mentioned on pp. 523–526, the working of the balance, when cold, was most satisfactory. Under normal conditions the constancy of the rest-point of the balance is well within 0·1 scale division when no current passes through the coils, and the sensitiveness is about 8 divisions for 10 milligrammes. When a current passes through the coils for not more than 20 minutes the same constancy is in general maintained, and if the balance circuit is occasionally broken—as it is in experiments for the determination of current—this interval of constancy is prolonged to 30 minutes or more. If the current through the balance coils is maintained after this interval, approximating to 30 minutes, the balance becomes unsteady, and no very accurate observations can be made; if, however, the circuit is broken after the interval, the balance reading remains approximately constant, variations of the order of 0·2 scale division only being observed. At the end of three or four hours another determination of current is possible, with practically the same degree of accuracy as before, but soon after these observations the balance becomes unsteady, and shows variations in the rest-point, gradually increasing from 0·1 to 1·0 scale division. If the second set of observations are made within one or two hours of the first set, the balance reading is not constant, and the results obtained are not of a high order of accuracy. In general, therefore, only two determinations of current are possible within six hours, but these are associated with a very small observational error. One determination normally occupies from 16 to 25 minutes.

Our usual procedure was to make one complete set of observations in the morning and another in the afternoon, after the balance had been cooling for several hours. Attempts made on several days to make a third set were never successful.

The time which elapsed between morning and afternoon observations of E.M.F. was usually devoted to silver-deposit determinations, the standard cell $S$ and resistance $R$, fig. 23, being used for keeping the current steady at a calculable value during the deposition. In effect, therefore, the combination of cell and coil, forming a secondary standard of current, was standardised morning and afternoon by the balance, and used in the interval for measuring the current through the voltmeters. As, however, the determination of the electro-chemical equivalent of silver forms the subject of another paper, it need not be discussed here.
Below is a sample series of readings taken in the second determination on Jan. 2, 1906:

(1) Observations for constancy of resting point and of sensitiveness:

**Constancy:**

\[
\begin{array}{c|cc}
\text{reading} & 99.5 & 100.6 \\
\text{constancy} & 99.6 & 100.8 \\
\end{array}
\]

The second set of observations was made 10 minutes after the first set.

**Sensitiveness:**

\[
\begin{array}{c|cc}
\text{left} & 90.5 & 102.3 \\
\text{right} & 90.6 & 102.0 \\
\end{array}
\]

Sensitiveness = 0.77 division for 1 milligramme.

(2) Determination of current:

<table>
<thead>
<tr>
<th>Position of rider</th>
<th>-0.0060</th>
<th>-0.0050</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commutator positions</td>
<td>aA 99.85 101.05</td>
<td>aA 98.0 101.6</td>
</tr>
<tr>
<td>Weights on</td>
<td>200.9</td>
<td>L</td>
</tr>
<tr>
<td>Commutator positions</td>
<td>bB 98.7 101.9</td>
<td>bB 99.9 100.7</td>
</tr>
<tr>
<td>Weights on</td>
<td>200.6</td>
<td>R</td>
</tr>
<tr>
<td>Commutator positions</td>
<td>aB 100.0 100.9</td>
<td>aB 99.9 100.6</td>
</tr>
<tr>
<td>Weights on</td>
<td>200.9</td>
<td>L</td>
</tr>
<tr>
<td>Commutator positions</td>
<td>aA 99.1 101.75</td>
<td>aA 99.2 100.45</td>
</tr>
<tr>
<td>Weights on</td>
<td>200.8</td>
<td>L</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{Mean } \text{"a" reading} & = 200.9 \text{ difference} \\
\text{"b" reading} & = 200.6 \text{ difference} \\
\text{Effective mass of weights} & = 15.3935 - 0.0005 \\
\text{Balancing mass} & = 15.3934 - 0.0120 \\
\text{Sum of balancing masses} & = 31.1012 \text{ grammes.}
\end{align*}
\]

Mean current = \( \sqrt{31.1012/\sqrt{4 \times 7.49964}} \approx 1.01821 \) in amperes.

* Formula (12), p. 510.
The "a" and "b" positions refer to the multiple commutator and plug board, fig. 25, and the "A" and "B" positions to the main commutator M, fig. 23, as explained on p. 522. A change from "a" to "b" reverses the current in the suspended coils, and a change from "A" to "B" reverses the current in all the coils of the balance. Centigramme riders were employed, and the position $-0.0060$ in the (D–S) experiment indicates that the rider and balancing weights were on opposite sides of the beam. The correction $-0.00006$ grammme is for the difference in density of the air from $0.001196$. In all cases the sum of the balancing masses was computed to $0.1$ milligramme.

### Tables of Results

The following tables, XII. and XIII., give particulars of determinations from September, 1905, to April, 1907; no determination has been omitted, except when

#### Table XII.—(Cadmium Cell No. 2.) E.M.F. Determinations, using One Set of Coils.

<table>
<thead>
<tr>
<th>Date</th>
<th>Observation</th>
<th>Balancing mass in grammes</th>
<th>Mean temperature—</th>
<th>(R) = value of resistance coil in international ohms</th>
<th>(G) = value of current</th>
<th>(C \times R)</th>
<th>(C \times R) corrected to (17^\circ C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.9.1905</td>
<td>(D_L)</td>
<td>7.7775</td>
<td>16.1</td>
<td>16.9</td>
<td>0.999884</td>
<td>1.01834</td>
<td>1.01822</td>
</tr>
<tr>
<td>14.10</td>
<td></td>
<td>7.7833</td>
<td>9.51</td>
<td>10.35</td>
<td>74.9</td>
<td>72</td>
<td>47</td>
</tr>
<tr>
<td>14.10</td>
<td>&quot;</td>
<td>30</td>
<td>9.71</td>
<td>10.69</td>
<td>75.7</td>
<td>70</td>
<td>46</td>
</tr>
<tr>
<td>23.10</td>
<td>&quot;</td>
<td>36</td>
<td>9.0</td>
<td>8.9</td>
<td>73.5</td>
<td>74.9</td>
<td>47.0</td>
</tr>
<tr>
<td>23.10</td>
<td>&quot;</td>
<td>12</td>
<td>11.64</td>
<td>11.45</td>
<td>79.6</td>
<td>58.3</td>
<td>37.5</td>
</tr>
<tr>
<td>24.10</td>
<td>&quot;</td>
<td>23</td>
<td>11.80</td>
<td>9.55</td>
<td>74.8</td>
<td>65.2</td>
<td>39.2</td>
</tr>
<tr>
<td>24.10</td>
<td>&quot;</td>
<td>24</td>
<td>10.50</td>
<td>11.29</td>
<td>79.2</td>
<td>66.2</td>
<td>45.0</td>
</tr>
<tr>
<td>30.9.1905</td>
<td>(D_R)</td>
<td>7.7797</td>
<td>13.8</td>
<td>14.75</td>
<td>0.999842</td>
<td>1.01852</td>
<td>1.01836</td>
</tr>
<tr>
<td>14.10</td>
<td>&quot;</td>
<td>7.7836</td>
<td>9.63</td>
<td>10.53</td>
<td>75.5</td>
<td>77</td>
<td>52</td>
</tr>
<tr>
<td>23.10</td>
<td>&quot;</td>
<td>33</td>
<td>9.25</td>
<td>9.0</td>
<td>73.7</td>
<td>75.1</td>
<td>48.3</td>
</tr>
<tr>
<td>23.10</td>
<td>&quot;</td>
<td>11</td>
<td>11.60</td>
<td>11.15</td>
<td>79.0</td>
<td>60.7</td>
<td>39.2</td>
</tr>
<tr>
<td>24.10</td>
<td>&quot;</td>
<td>20</td>
<td>11.80</td>
<td>9.72</td>
<td>75.2</td>
<td>66.2</td>
<td>41.3</td>
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<tr>
<td>24.10</td>
<td>&quot;</td>
<td>20</td>
<td>10.31</td>
<td>11.12</td>
<td>78.8</td>
<td>66.2</td>
<td>45.0</td>
</tr>
</tbody>
</table>

Balancing masses for reversal of 1 ampere:—
Left-hand coils \(m_l = 7.49987\) *
Right-hand " \(m_r = 7.49942\)

* Formulæ (7) and (8), p. 510.

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Table XIII.—Cadmium Cell No. 2.

<table>
<thead>
<tr>
<th>Date</th>
<th>Observations.</th>
<th>Sum of masses = m</th>
<th>Mean temperature of cell</th>
<th>Mean temperature of coil</th>
<th>R = value of coil in international ohms</th>
<th>C = value of current = $\sqrt{m^2 / 4am^*}$</th>
<th>C × R corrected to 17° C</th>
<th>Differences from mean (1 × 10⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.9.1905</td>
<td>15·7290</td>
<td>15·3387</td>
<td>31·1177</td>
<td>14·9</td>
<td>0·999837</td>
<td>1·018481</td>
<td>1·018315</td>
<td>1·018182</td>
</tr>
<tr>
<td>29.9</td>
<td>302</td>
<td>894</td>
<td>196</td>
<td>14·3</td>
<td>15·0</td>
<td>83.9</td>
<td>5</td>
<td>139</td>
</tr>
<tr>
<td>2.10</td>
<td>310</td>
<td>913</td>
<td>223</td>
<td>12·65</td>
<td>13·3</td>
<td>81.9</td>
<td>545</td>
<td>138</td>
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<td>3.10</td>
<td>330</td>
<td>928</td>
<td>258</td>
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<td>12·3</td>
<td>79.9</td>
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<tr>
<td>3.10</td>
<td>318</td>
<td>915</td>
<td>233</td>
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<td>13·1</td>
<td>80.9</td>
<td>57.4</td>
<td>138</td>
</tr>
<tr>
<td>4.10</td>
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<td>236</td>
<td>12·3</td>
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<td>946</td>
<td>299</td>
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<td>11·0</td>
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<td>44.5</td>
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<td>338</td>
<td>934</td>
<td>272</td>
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<td>12·15</td>
<td>79.9</td>
<td>63.7</td>
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<td>240</td>
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<td>853</td>
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<td>17·00</td>
<td>90.9</td>
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<td>855</td>
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<td>11·52</td>
<td>79.9</td>
<td>37.3</td>
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<td>871</td>
<td>143</td>
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<td>10·40</td>
<td>77.9</td>
<td>42.6</td>
<td>19.5</td>
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<td>271</td>
<td>869</td>
<td>140</td>
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<td>10·60</td>
<td>77.9</td>
<td>42.7</td>
<td>19.5</td>
</tr>
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<td>860</td>
<td>117</td>
<td>16·65</td>
<td>12·12</td>
<td>81.4</td>
<td>38.2</td>
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71 observations  

Mean = 1.018197 ± 0.05

* Formula (12), p. 510.
the observations were of such a nature that a decision to disregard the result was arrived at before its computation. Such occasions were very rare.

Table XII. gives the results obtained when only one set of coils (left or right) was made use of, so that there were no secondary forces to be eliminated. They are inserted to show the order of the agreement attainable in this way, and are not considered to be so reliable as the values deduced from the \((D+S)\) and \((D-S)\) tests. When both sets of coils are operative, the balancing mass for 1 ampere is \(7.49964\) grammes—this has been denoted by \(m\) in Table XIII.

**Probable Errors.**

The mean error of a single observation in Table XIII., viz., 6 parts in 1,000,000, is surprisingly small, for this comprises the error of the balance reading, the inaccuracy of the estimation of the secular change of the secondary standard resistance coil, the variation in E.M.F. of the standard cell (including polarisation during the observations), uncertainty in temperature readings, and the error introduced by the non-maintenance of an absolutely steady current. The probable observational error of the mean value of \(C \times R\) at \(17^\circ\) C. is less than 1 in 1,000,000.

The probable error of the ratio of the diametral dimensions of the coils, viz., 5 in 1,000,000, and the uncertainty in the axial dimensions of 15 in 1,000,000 (introducing a possible uncertainty in the value of the mutual induction of about 5 in 1,000,000 and in the measurement of current of about 1 part in 100,000) have not been under-estimated. Evidence in favour of a small error is afforded by the satisfactory agreement of the calculated and observed differences of the forces due to the left and right systems when a current of 1 ampere circulates through them; in addition there is the estimate of the difference in radii of neighbouring coils from observations of the force (p. 516). These measurements lead one to suppose that the errors have been closely approximated to. The electrical method of setting the coils in position has been shown to be subject to an error not greater than 1 in 5,000,000 of the mutual induction; the magnetic susceptibility of the parts of the balance and its support is negligibly small, and the effect of the current in the leads to and from the suspended systems is too small to be measurable. The magnitudes of the errors arising from the finite thickness of the wire used, and the assumption that one of the coils is a current sheet instead of a helix, are discussed in Appendix B, and shown to be practically negligible.

The possibility of error due to the oscillation of the suspended systems has not yet been considered. For a small axial displacement of the suspended coils the force is \((1-11 \times 10^{-6} d^2)\) times the maximum,* where \(d\) is the axial displacement in mils from the plane of minimum mutual induction. One division of the pointer scale is equal to \(3.75\) mils (= 95\(\mu\)); the length of the pointer is 14.6 inches (37 centims.) and half

* See p. 502.
the length of the beam is 10 inches (25.4 centims.). A difference in doubled rest-point readings of 7.9 divisions corresponds therefore to a difference in the mean axial positions of the suspended cylinders of 10 mils (254μ). In an experiment intended as a check on the expression obtained for the change of force with small axial displacements, the doubled rest-point in a (D+S) experiment was 197.7 in one case and 189.3 in another, the latter reading being obtained by loading one end of the beam with 10 milligrammes. The correct position for maximum force corresponded to a pointer reading of 200.0. In the two experiments the difference in the balancing masses was 0.3 milligramme, corresponding to a difference in force of 0.001, per cent., and from the readings of the doubled rest-points a difference in force of 0.001, per cent. is deduced. The agreement is satisfactory. It follows that in a determination of current strength the doubled rest-point must not differ from the reading corresponding to the position of maximum force by more than 8 divisions if the error introduced by the difference in the positions is to be less than 5 in 1,000,000. When making the observations, the results of which are tabulated in Table XIII., the mean displacement of the suspended coils was always kept within 2 divisions by adjusting the position of one of the riders, and the mean displacement for all the observations is 0.5 division. The greatest error introduced on any occasion was therefore about 1 part in 3,000,000.

We have also to consider the relation between the amplitude of swing and the effective force due to the current. This relation was determined experimentally. In a particular D+S experiment the amplitude of swing was varied from 1 division to 28 divisions, but the estimated forces were identical. Other observations confirmed this result, and it was only when the amplitude was very large and the errors of observation great that any difference was observed; even these differences are of opposite signs and point to the forces being identical. It is certain that within the limits 0 to 28 divisions for the amplitude there is no measurable difference in the effective force. When determining the value of a current the amplitude was in general from 3 to 4 divisions; there is therefore no correction to be applied for the amplitude of swing.

The remaining source of error is due to an uncertainty in the value of gravity. No absolute determinations of g have been made at Teddington, and it was necessary to compare the values at Kew and Teddington by pendulum observations. Mr. E. G. Constable, of the Observatory Department of the National Physical Laboratory, made such observations in March, April, and July, 1905. The pendulums swung were half-seconds pendulums, the property of the Board of Education and used in the "Discovery" Antarctic Expedition. At Teddington two positions were chosen: one was on the concrete block on which the ampere balance stands, and the other was in a lower room maintained at a very constant temperature. At Kew the pendulums were swung in the north room of the small house to the west of the main building. The difference in period of the half-seconds pendulums was determined
to be $26 \times 10^{-7}$ second, the period at Teddington being the greater. Excluding observations made over 30 years ago, only two comparisons have been made interconnecting Kew with a station where $g$ is believed to be known in absolute measure. The first of these comparisons was made by von Sterneck in 1893, and the second by Mr. G. R. Putnam (U.S. Coast and Geodetic Survey) in 1900. The former of these observers assigned the value 981.160 to Kew and 981.200 to Greenwich; Mr. Putnam’s values are 981.199 and 981.187 respectively. It will be observed that von Sterneck makes the value at Kew less than that at Greenwich, but all other observers make it greater.* Also the differences found between Kew and Greenwich by the latest and most complete observations (those by Putnam and by Burrand, Constable and Lenox-Conyngham) are very close to that given by theory. Von Sterneck observed on only two days at Kew as against six at Greenwich; thus the probabilities of serious error are much greater for Kew than for Greenwich. Von Sterneck’s value for Greenwich exceeds Putnam’s by 0.013, but this, if we may judge from the difference 0.019 between their values for Potsdam, represents largely a difference in what answers to their base values. Helmert has accepted for Kew the value 981.200,† and it appears that no serious error is introduced by our acceptance of this value. From Mr. Constable’s observations the value of $g$ at the National Physical Laboratory would therefore appear to be 981.19 centims./sec².

The theoretical difference between Kew and Teddington may be obtained from Helmert’s formula. The places are very similarly situated with respect to surface strata and surroundings, and the only corrections it is necessary to apply are those for difference of latitude and difference of level. The latitude of Kew is 51° 28’ 6”, and of the National Physical Laboratory 51° 25’ 20” approximately; the level of Putnam’s observations at Kew was 17 feet above mean sea-level, and at Teddington the mean level of Mr. Constable’s observations was about 34 feet. The correction for difference of latitude is $-0.0044$, and for the difference of level it is $-0.0010$; the theoretical value is therefore 981.19, if Kew is 981.20. The probable error of any accepted value depends, of course, on the errors of the intercomparisons and on the error of the absolute determination at the base station. It appears that these are not very large, and that we may accept the value 981.19 centims./sec² as correct to 3 in 100,000.

The determination of current by means of the ampere balance is therefore subject to errors of the following magnitude:—

(1) Due to uncertainty of dimensions of coils: possible error about $\pm 0.001$ per cent.
(2) Due to uncertainty in the value of $g$: possible error about $\pm 0.001$, per cent.

All the other sources of error introduce uncertainties less than $\pm 0.001$ per cent., and may be disregarded. The total error of an estimation is therefore of the order $\pm 0.002$ per cent., or 2 in 100,000.

† ‘Report, Geodetic Conference of 1900,’ p. 321.
As numerous determinations of the balancing masses for \((D+S)\) and \((D-S)\) have been made, the value of \(S\) for 1 ampere can be calculated from them with considerable accuracy. By using this value a determination of current, using both sets of coils, can be made by taking the apparent change of mass produced by a single reversal of current in the fixed coils. The necessary observations can be made in less than five minutes, so that a very short time would suffice for making an absolute determination of current in this way.

*History of the Standard Cell employed.*—When the first determination of current was made, the cadmium cell chosen for insertion in the potentiometer circuit was one whose E.M.F. was lower than that of normal cells by 0·11 millivolt. Originally it was not proposed to use this cell permanently, but as its previous history indicated it to have remained very constant, it was afterwards decided to do so. The cell was compared with other standard cells on each day that a determination of current was made and on many other intermediate days. All the cells were constructed in the manner described by one of us (F. E. S.) in the *Report of the British Association,* Section A, 1905, and were set up at the National Physical Laboratory. In the first few determinations the cadmium cell was in the same room as the ampere balance, and its temperature sometimes varied from 6°C to 19°C within 24 hours. Careful observations showed that the E.M.F. of the cell did not very closely follow this rapid change in temperature, and the corrections to the value of \(C \times R\) in Table XIII., Column 9, were obtained from a curve which, though not very different from the temperature-coefficient curve of the cell, is not identical with it. This statement applies to the first twelve observations only, for on and after November 23, 1905, the cell was kept in the resistance-standards room, which is maintained at a nearly constant temperature of 17°C. After November 23, the correction to 17°C was obtained from the temperature-coefficient formula

\[
E_t = E_{17} - 3·46 \times 10^{-8} (t - 17) - 0·066 \times 10^{-4} (t - 17)^2.
\]

This formula is the result of a determination made at the National Physical Laboratory, the range of temperature during the observations being 10°C to 30°C. The coefficients are practically identical with those given by JÄGER and KAHLE. Their formula is

\[
E_t = 1·0186 - 0·000038 (t - 20) - 0·00000065 (t - 20)^2.
\]

The cell employed in the potentiometer circuit (hereafter called No. 2) was set up in January, 1905; those with which it has been compared were set up on various dates ranging from October, 1904, to April, 1907. The comparisons indicate that the cells have remained constant within a few hundred-thousandths of a volt, or have changed uniformly. The actual differences between the cells are not given here, but may be summarised by saying that with the exception of cell No. 2 the greatest

difference in E.M.F. of any cell from the mean E.M.F. of all of them is 0·03 millivolt, and the difference between the mean E.M.F. of the old cells and the new cells set up in March and April, 1907, is 0·02 millivolt. This comparison indicates constancy of the old cells; Table XIV. confirms this view. The mean difference of the "old and new cells" and cell No. 2 is 0·11 millivolt. On September 13, 1906, and on April 10 and 11, 1907, a cell representing the mean normal cell was employed in the determination of current. The results are contained in Table XIV.

The mean value of \(C \times R\) at \(17^\circ\) C. is 1·01830; the value from comparison with cell No. 2 is 1·01830. Both these values assume \(g\) to be 981·20; correcting for the difference of this and the accepted value 981·19, we obtain

\[1·01830\]

as the mean value of \(C \times R\) at \(17^\circ\) C.

It should be pointed out that the "international ohm" used in these measurements is that employed at the National Physical Laboratory, which unit does not differ by more than 3 parts in 100,000 from that of the Reichsanstalt. In absolute measure, however, its value is not known to a high degree of accuracy. Taking its ratio to the Board of Trade ohm as determined by one of us (F. E. S.) in 1903 ('B.A. Report,' 1903, and 'Phil. Trans.' A, vol. 204) as 1 international ohm = 1·0001 \(B.O.T.\) ohm, and assuming that the \(B.O.T.\) unit has remained constant since 1897, when its value in C.G.S. units was found to be 1·00026* \(\times 10^9\), we get 1 international ohm = 1·00041 \(\times 10^9\) C.G.S. units, and the E.M.F. of the normal cadmium cell at \(17^\circ\) C. becomes

\[1·0187, \times 10^8\] C.G.S. units (approximately).

This number must, however, be considered as provisional only, pending a re-determination of the international ohm in absolute measure.

It is of interest to compare our value of \(C \times R\) in terms of the international ohm with that obtained by Guthe in 1906.† He gives the number 1·01853 as the E.M.F. at \(20^\circ\) C. of the E, K, and O series of cells set up with electrolytically prepared paste, which cells are comparable with the "normal" cell used in our determination. Allowing for difference of temperature, our value of \(C \times R\) at \(20^\circ\) C. becomes 1·01819, a difference of 34 parts in 100,000.

As regards the Clark cell, the mean of a number of comparisons made at the National Physical Laboratory gives the ratio

\[\text{Clark at } 15^\circ\text{C. ÷ Cadmium at } 17^\circ\text{C. } = 1·406,\]

* "On a Determination of the Ohm, &c.," by Professor W. E. Ayrton, F.R.S., and Professor J. V. Jones, F.R.S. 'B.A. Report,' 1897.
### Table XIV.—Normal Cadmium Cell.

<table>
<thead>
<tr>
<th>Date</th>
<th>Observations.</th>
<th>Sum of masses ( = m' )</th>
<th>Mean temperature of cell.</th>
<th>Mean value of coil in international ohms.</th>
<th>( R = \frac{1}{\sqrt{m'/m} \sqrt{4m}} \times )</th>
<th>( C = \frac{1}{\sqrt{m'/m} \sqrt{4m}} )</th>
<th>( C \times R ) corrected to 17° C.</th>
<th>Difference from mean ((1 \times 10^{-6}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.9.1906</td>
<td>15.7193 gramme</td>
<td>15.3796 gramme</td>
<td>31.0989 gramme</td>
<td>17.25 °C</td>
<td>19.41 °C</td>
<td>1.000125 amperes</td>
<td>1.018174</td>
<td>1.018301</td>
</tr>
<tr>
<td>13.9</td>
<td>185</td>
<td>795</td>
<td>0980</td>
<td>17.25 °C</td>
<td>19.80 °C</td>
<td>13.0</td>
<td>15.9</td>
<td>29.1</td>
</tr>
<tr>
<td>9.4.1907</td>
<td>197</td>
<td>806</td>
<td>1003</td>
<td>17.31 °C</td>
<td>14.75 °C</td>
<td>* 9.5</td>
<td>19.7</td>
<td>29.4</td>
</tr>
<tr>
<td>10.4</td>
<td>189</td>
<td>799</td>
<td>0988</td>
<td>17.20 °C</td>
<td>16.43 °C</td>
<td>12.4</td>
<td>17.3</td>
<td>30.0</td>
</tr>
<tr>
<td>11.4</td>
<td>202</td>
<td>813</td>
<td>1015</td>
<td>17.20 °C</td>
<td>14.57 °C</td>
<td>9.2</td>
<td>21.7</td>
<td>31.1</td>
</tr>
<tr>
<td>11.4</td>
<td>190</td>
<td>799</td>
<td>0989</td>
<td>17.20 °C</td>
<td>16.90 °C</td>
<td>13.2</td>
<td>17.4</td>
<td>30.8</td>
</tr>
</tbody>
</table>

| Mean =      | 1.018309 amperes | ±0.5                     |

* Formula (12), p. 510.

[Note added January 11th, 1908.—Two determinations of the E.M.F. of the normal cadmium cell were made on January 6th and January 8th, 1908, after resetting the balance; both the tests gave the value of \( C \times R \) (corrected to 17° C.) as 1.018310, a number practically identical with the mean of Table XIV.]
and using this ratio we get
\[ C \times R \text{ for Clark cell at } 15^\circ \text{C.} = 1.4323; \]
Guthe's value of \( C \times R \) for Clark cell at 15°C = 1.43296.

The difference is in the same direction as that between the cadmium cells, but greater in proportion.

Section 13.—Conclusions.

From the measurements and observations detailed in the previous pages we may conclude that the current weigher, constructed on the lines described, is a most excellent instrument, capable of yielding results of very high precision, and worthy of acceptance as an international standard instrument for the absolute determination of the ampere. We therefore hope that other countries will make balances on similar lines, in order to realise one of the fundamental electrical units in an exact manner.

So far as we are aware, the accuracy attainable by the new balance far exceeds that secured in any previous absolute determination of any electrical unit, and we may infer that of all the electrical units the ampere is now the one best known.

Further, we may infer that cadmium cells can be set up so as to be remarkably constant in E.M.F. The observations made on cell No. 2, set up by one of us (F. E. S.), extended over a period of 19 months, and during the whole of that period its measured E.M.F. seldom differed from the mean by more than 1 part in 100,000.

Of the 71 determinations of E.M.F. made—

<table>
<thead>
<tr>
<th>Number</th>
<th>Determinations</th>
<th>Reference to Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>7 are within 1 in 1,000,000 of the mean, 14 2 1,000,000 28 5 1,000,000 53 10 1,000,000 66 15 1,000,000 70 20 1,000,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26 were made by the same pair of observers (T. M. and F. E. S.), and these show a still closer agreement, viz., of 26 determinations— 6 2 1,000,000 11 5 1,000,000 19 10 1,000,000 25 15 1,000,000</td>
<td></td>
</tr>
</tbody>
</table>

Only one determination out of the whole 71, and this one of the earliest, differs from the mean by so much as 1 part in 59,000.

It is of interest to mention that of the 71 determinations just referred to 26 were made by the same pair of observers (T. M. and F. E. S.), and these show a still closer agreement, viz., of 26 determinations—

Only the early one previously mentioned differed from the mean by more than
1 part in 70,000. The difference between the means of the 26 and the 71 determinations is 1 in 1,000,000.

These results are of considerable importance, as they show very great constancy both of current weigher and cell. In fact, the cell and balance proved to be much more constant and reliable than the standard resistance, although the latter was very carefully made and annealed with a view to ensuring permanency.

The precision of measurement attainable with the new balance exceeds the most sanguine expectations of its designers. It was intended to give the ampere to 1 in 10,000, and an accuracy of 1 in 20,000 was hoped for, but 1 in 50,000 has been attained. The instrument itself admits of a far higher accuracy, for a tenth of a milligramme can be detected with certainty, and this, in a total of 15 grammes, the balancing mass for 1 ampere, means 1 in 300,000 in the value of the current. This is a precision considered to be of a very high order, even for relative measurements. Uncertainty, however, exists as to the value of \( g \), and the axial lengths of the coils, which prevent the highest accuracy of which the balance is capable, being realised at present.

Directions in which improvements may be looked for are, therefore:

(i) A more accurate determination of the acceleration due to gravity, and
(ii) Greater precision in the means for measuring the axial lengths of the coils, or a lengthening of the coils to reduce the effect of this possible error.

As the uncertainty in \( g \) is of most consequence, we trust that an absolute determination of its value at the National Physical Laboratory will, ere long, be made.

To realise the volt to an accuracy approaching that of the ampere as now known, it is necessary that an absolute determination of resistance of corresponding precision be undertaken. At the present time the uncertainty in the absolute value of the international ohm, in terms of which our values of \( C \times R \) for the cadmium cells are expressed, approximates to 4 in 10,000, so it is of considerable importance that a better determination be made at an early date.

In conclusion, we desire to express our sincere thanks to the British Association for providing the funds with which to construct the ampere balance, and to Sir ANDREW NOBLE, F.R.S., for presenting the adjustable stand to support the instrument.

Our most hearty thanks are hereby tendered to Dr. R. T. GLAZEBROOK, F.R.S., Director of the National Physical Laboratory, for supervising the construction of the electrical portions of the balance, for the keen interest he has taken in the experiments, and also for having placed the very perfect resources of the Laboratory at our disposal. Indeed, much of the precision attained in the results is due to the facilities available at the National Physical Laboratory for such work. To Dr. T. E. STANTON we are indebted for superintending the turning of the marble cylinders used to support the coils of the balance.

Our best thanks are also due to Mr. J. P. GREGORY for valuable assistance rendered
in the design, and for the care and skill displayed in making the drawings of the instrument; to Messrs. E. Fisher and A. W. Harrold, late of the Central Technical College, for checking the initial calculations; and to Professor A. G. Greenhill, F.R.S., for advice concerning the elliptic integrals involved.

APPENDIX A.

Values of coefficients (logs of) and constant terms in series for complete elliptic integrals of the first and second kinds (F and E) when \( k \) nearly = 1. \( k' = \sqrt{1-k^2} \).

\[
F(k) = \log_{10} \frac{4}{k'} + \frac{1}{2} \frac{1}{k'^2} \left( \log_{10} \frac{4}{k'} - \frac{2}{1.2} \right)
+ \frac{1}{2} \frac{3}{2} \frac{1}{k'^2} \left( \log_{10} \frac{4}{k'} - \frac{2}{1.2} - \frac{2}{3.4} \right)
+ \frac{1}{2} \frac{3}{2} \frac{5}{2} \frac{1}{k'^6} \left( \log_{10} \frac{4}{k'} - \frac{2}{1.2} - \frac{2}{3.4} - \frac{2}{5.6} \right)
+ \text{&c.}
\]

This may be written

\[
F(k) = \log_{10} \frac{4}{k'} + A_4 k'^2 \left( \log_{10} \frac{4}{k'} - B_2 \right) + A_4 k'^4 \left( \log_{10} \frac{4}{k'} - B_4 \right)
+ A_6 k'^6 \left( \log_{10} \frac{4}{k'} - B_6 \right) + \text{&c.}
\]

Similarly the corresponding series for \( E(k) \) may be written

\[
E(k) = 1 + A'_4 k'^2 \left( \log_{10} \frac{4}{k'} - B'_2 \right) + A'_4 k'^4 \left( \log_{10} \frac{4}{k'} - B'_4 \right)
+ A'_6 k'^6 \left( \log_{10} \frac{4}{k'} - B'_6 \right) + \text{&c.}
\]

Values of \( \log A_n, \log A'_n, B_n, \) and \( B'_n \), are given below:

<table>
<thead>
<tr>
<th>( n )</th>
<th>For ( F(k) )</th>
<th>For ( E(k) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log ( A_n )</td>
<td>( B_n )</td>
<td>Log ( A'_n )</td>
</tr>
<tr>
<td>2</td>
<td>1.3979400</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>1.1480625</td>
<td>1.16</td>
</tr>
<tr>
<td>6</td>
<td>2.9897000</td>
<td>1.23</td>
</tr>
<tr>
<td>8</td>
<td>2.8737161</td>
<td>1.269047</td>
</tr>
<tr>
<td>10</td>
<td>2.7829011</td>
<td>1.291269</td>
</tr>
<tr>
<td>12</td>
<td>2.7066240</td>
<td>1.306421</td>
</tr>
<tr>
<td>14</td>
<td>2.6422546</td>
<td>1.317410</td>
</tr>
<tr>
<td>16</td>
<td>2.5861971</td>
<td>1.325743</td>
</tr>
<tr>
<td>18</td>
<td>2.5365499</td>
<td>1.332279</td>
</tr>
<tr>
<td>20</td>
<td>2.4919971</td>
<td>1.337542</td>
</tr>
</tbody>
</table>

* CAYLEY, 'Elliptic Functions,' chap. III., § 77.
APPENDIX B.

On the Forces between Coils of Wire of Finite Section.*

The formula developed by J. Vriamun Jones gives the force when the windings of the coils can be treated as infinitely fine helical filaments. In the ampere balance, however, the wires are of finite thickness, and thus small corrections may become necessary.

If the force parallel to the axis experienced by a helical filament of radius A and of fixed pitch and number of turns when carrying a current i be F, we have

\[ F = i \int_0^\theta X A \, d\theta \quad \ldots \quad \ldots \quad \ldots \quad (1), \]

where X is the magnetic force at right angles to the axis and \( \theta \) is measured round the axis. If \( y \) be the co-ordinate, parallel to the axis, of one end of the helix, the force on the helix in a magnetic field symmetrical about the axis is a function of A and \( y \), and we have

\[ \frac{d^2F}{dA^2} + \frac{d^2F}{dy^2} = i \int_0^\theta A \left( \frac{d^2X}{dA^2} + \frac{d^2X}{dy^2} + \frac{2}{A} \frac{dX}{dA} \right) \, d\theta \quad \ldots \quad \ldots \quad \ldots \quad (2). \]

Now, if \( V \) be the magnetic potential of the magnetic field, \( V \) is symmetrical about the axis, and hence satisfies Laplace's equation

\[ \frac{d^2V}{dA^2} + \frac{d^2V}{dy^2} + \frac{1}{A} \frac{dV}{dA} = 0 \quad \ldots \quad \ldots \quad \ldots \quad (3). \]

But \( X = - \frac{dV}{dA} \), and hence, differentiating (3) with respect to A,

\[ \frac{d^2X}{dA^2} + \frac{2}{A} \frac{dX}{dA} = \frac{1}{A} \frac{dX}{dA} + \frac{X}{A^2}. \]

Thus

\[ \frac{d^2F}{dA^2} + \frac{d^2F}{dy^2} = i \int_0^\theta \left( \frac{dX}{dA} + \frac{X}{A} \right) \, d\theta = \frac{1}{A} \frac{dF}{dA} \quad \ldots \quad \ldots \quad \ldots \quad (4). \]

This is similar to Maxwell's theorem† for mutual induction.

Distribution of Current in the Wire.—In default of any accurate knowledge of the variations of specific resistance over the cross-section of the wire forming a helical coil, it is impossible to accurately determine the distribution of current in the wire. We shall, however, examine the case in which the specific resistance is uniform and shall call the corresponding distribution of current the "natural" distribution. The current density at any point may be taken as inversely proportional to the length of

* For the major portion of the following treatment we are indebted to Mr. G. F. C. Searle, F.R.S.
one turn of the line of flow through that point. Hence, if the distance of the point from the axis is \(A + h\), the current density is equal to \(Ki[(A + h)^2 + p^2]^{-1/2}\), where \(K\) is a constant, \(2\pi p\) is the pitch of the helix, and \(i\) is the total current through the wire.

To find \(u\), the current per unit area of the section by a plane containing the axis of the helix, we must multiply the current density by \(\cos \alpha\), where \(\alpha\) is the slope of the line of flow. Hence

\[
u = Ki (A + h)/((A + h)^2 + p^2)\]  

(5).

The constant \(K\) is to be determined from the condition that the total current in the wire is \(i\). When, as in the case of the coils of the ampere balance, \(p\) is small compared with \(A + h\), it will be sufficient to take the first two terms of the expansion of (5) in powers of \(p^2\), and to write

\[
u = Ki \left\{ \frac{1}{A + h} - \frac{p^2}{(A + h)^3} \right\}\]  

(6).

If \(h, y\) be the co-ordinates of the point relative to axes through the centre of the section parallel and perpendicular to the axis, we can write

\[
u = \rho \cos \phi, \quad y = \rho \sin \phi\]  

(7).

Thus, if \(R\) is the radius of the wire,

\[
i = \int_0^R \int_0^{2\pi} u \rho \, d\rho \, d\phi = Ki \int_0^R \int_0^{2\pi} \left\{ \frac{1}{A + \rho \cos \phi} - \frac{p^2}{(A + \rho \cos \phi)^3} \right\} \rho \, d\rho \, d\phi\]

Now, since \(\rho\) is less than \(A\),

\[
\int_0^{2\pi} \frac{d\phi}{A + \rho \cos \phi} = \frac{2\pi}{(A^2 - \rho^2)^{1/2}},
\]

and two applications of the reduction formula

\[
\int_0^{2\pi} \frac{d\phi}{(A + \rho \cos \phi)^{m+1}} = \frac{1}{A} \left( 1 + \frac{\rho \, d}{m \, d\rho} \right) \int_0^{2\pi} \frac{d\phi}{(A + \rho \cos \phi)^m}
\]

give

\[
\int_0^{2\pi} \frac{d\phi}{(A + \rho \cos \phi)^3} = 2\pi \left\{ \frac{3A^2}{2 (A^2 - \rho^2)^{3/2}} - \frac{1}{2 (A^2 - \rho^2)^{5/2}} \right\}.
\]

On integrating with respect to \(\rho\), we find

\[
\frac{1}{K} = 2\pi \left\{ A - (A^2 - R^2)^{1/2} - \frac{p^2 R^2}{2 (A^2 - R^2)^{3/2}} \right\}
\]

\[
= \frac{\pi R^2}{A} \left( 1 + \frac{R^2 - 2p^2}{4A^2} \right)
\]
as far as terms involving \( R^4 \) or \( R^2 p^2 \). Hence, to the same order,

\[
K = \frac{A}{\pi R^3} \left(1 - \frac{R^2 - 2p^2}{4A^2} \right).
\]

(8)

If \( F_0 \) be the force parallel to the axis, experienced by the helical filament defined by \( h = 0, y = 0 \), and if \( F' \) be the force on the helical wire when carrying the same current, we have

\[
F' = \frac{1}{2} \int_0^{2\pi} u \left( F_0 + h \frac{dF}{dx_0} + y \frac{dF}{dy_0} + \cdots \right) \rho \, d\rho \, d\phi
\]

(9)

where the force on the helix \( h, y \) is expanded by Taylor's theorem. On integration the first term yields \( F_0 \) exactly, since the total current is \( i \). For the other terms we may use (6), and may replace \((A + h)^{-1} - hA^{-2} + h^2A^{-3} \) and \( p^2(A + h)^{-3} \) by \( p^2A^{-3} \). When we substitute for \( h \) and \( y \) from (7) and integrate, we obtain

\[
F' = F_0 + \frac{\pi K R^4}{A} \left\{ \frac{1}{8} \left( \frac{d^2F}{dx_0^2} + \frac{d^2F}{dy_0^2} \right) \frac{1}{4A} \frac{dF}{dx_0} + \frac{1}{A^2} \frac{d^2F}{dx^2} \left( \frac{R^2 - p^2}{48} - \frac{p^2}{8} \right) + \frac{1}{A^2} \frac{d^2F}{dy_0^2} \left( \frac{R^2}{16} - \frac{p^2}{8} \right) \right\}.
\]

Using (4), and inserting the value of \( K \), we find

\[
F' = F_0 - \frac{R^4}{8A} \left(1 - \frac{R^2 - 2p^2}{4A^2} \right) \left\{ \frac{dF}{dx_0} \left( -1 + \frac{R^2 - 2p^2}{2A^2} \right) - \frac{R^4}{3A} \frac{d^2F}{dx_0^2} \right\},
\]

or, as far as the terms involving \( R^4 \) or \( R^2 p^2 \),

\[
F' = F_0 - \frac{R^4}{8A} \left(1 - \frac{3(R^2 - 2p^2)}{4A^2} \right) \frac{dF}{dx_0} - \frac{R^4}{24A^2} \frac{d^2F}{dx_0^2}.
\]

This expression includes all the terms up to \( R^4 \) or \( R^2 p^2 \) arising from the differential coefficients of not greater than the second order in the Taylor expansion in (9).

In the case of the ampere balance it is unnecessary to go beyond terms involving \( R^2 \). To this order we have

\[
F' = F_0 - \frac{R^2}{8A} \frac{dF}{dx_0}.
\]

(10)

It is easy to give a physical interpretation to this result. For, if we take a helical filament of radius \( A-z \), with its ends in the same planes as the centres of the terminal sections of the helical wire, the force on it is

\[
F_0 - z \frac{dF}{dx_0} + \frac{1}{2} z^2 \left( \frac{d^2F}{dx_0^2} \right) - \cdots
\]

The first two terms of this series will be the same as the terms shown in (10) if \( z = R^2/8A \). Hence, as far as correcting terms involving \( R^2 \), \( F' \) is the force on a helix of radius \( A-R^2/8A \). Thus, the force experienced by a wire helix of mean radius \( A \) is the same as that experienced by a filamentary helix of radius \( A-R^2/8A \). It is
noteworthy that, to this approximation, no correction is to be applied to the axial length of the coil. The argument applies also to the fixed coils of the balance.

For "natural" distribution of current in the coils of the ampere balance, the force $F$ calculated on p. 509 is too great. The corrected value of the force is

$$F - \frac{R^2}{8a} \frac{dF}{da} - \frac{R^2}{8A} \frac{dF}{dA} \ldots \ldots \ldots \ldots$$

where $a$ and $A$ are the mean radii of the suspended and fixed coils. We may write (11) in the form

$$F \left(1 - \frac{R^2}{8a} r - \frac{R^2}{8A} q\right),$$

where

$$r = \frac{a dM}{M da} = \frac{a}{F} \frac{dF}{da} \quad \text{and} \quad q = \frac{A dM}{M dA} = \frac{A}{F} \frac{dF}{dA}.$$

Inserting the values of $R$, $q$, $r$, $A$, and $a$, tabulated on pp. 488, 512, 513, we obtain a correction to the force of 17 parts in 10,000,000 for the complete system of coils. The sign of the correction is negative.

If we assume the current density to be uniform, the force in this case is found by making $u = i/\pi R^2$ in (9), and the corrected value of the force is

$$F + \frac{R^2}{8a} \frac{dF}{da} + \frac{R^2}{8A} \frac{dF}{dA}.$$

The correction is of the same value as before, but of opposite sign. As the distribution of current is uncertain, the value of the force stated on p. 509 has been used throughout our work.
XIII. The Silver Voltameter.

PART I.—By F. E. Smith, A.R.C.Sc., and T. Mather, F.R.S.


(Communicated by R. T. Glazebrook, F.R.S.)

Received July 22,—Read November 21, 1907.

(From the National Physical Laboratory.)

[Plate 9.]

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Introduction.

It has been known for several years that the measurement of electric quantity by
the electro-deposition of silver is liable to inaccuracies which appear to be dependent
on the condition of the anode, kathode, and electrolyte of the voltameter (or coulo-
meter) employed. In 1884 Lord Rayleigh* and Mrs. Sidgwick found that a small
quantity of silver acetate added to a solution of silver nitrate or of silver chlorate
apparently increased the mass of silver deposited per ampere-second, and in 1895
Rodger and Watson† showed that the silver voltameter was liable to give results
varying by as much as 1 part in 1000 when the same solution of silver nitrate was
repeatedly used. The latter effect was thought to be due to the formation of a
complex silver salt, and in 1899 Richards, Collins, and Heimrod‡ practically
confirmed this view. A new form of silver voltameter was suggested by the latter
observers, and this has been frequently used for observations of precision. In 1898
Kahle§ made a very large number of measurements, using platinum and silver bowls
as kathodes and silver nitrate solutions, treated in various manners and from many
sources, as electrolytes. He found that the deposit of silver per coloumb was greater
on a silver surface than on one of platinum; that it increased with the continued use

* Rayleigh and Sidgwick, 'Phil. Trans.,' 175, p. 411, 1884.
† Rodger and Watson, 'Phil. Trans.,' A, 186, p. 631, 1895.
of a solution, and that the nature of the deposit also varied with the solution employed. In 1892 Schuster and Crossley* discovered that the mass of silver deposited was related to the pressure and also to the size of the silver anode; the pressure effect was verified by Kahle,† Richards,‡ and Myers,§ and the latter observer found an increase when the liquid was saturated with nitrogen, but a decrease when the dissolved gas was carbon dioxide. Merrill‖ repeated the pressure experiments and found no effect due to change of pressure alone. Lord Rayleigh and Mrs. Sidgwick observed an increase of deposit with increase of temperature; Richards, Collins, and Heimrod obtained greater deposits at 60°C and at 0°C than at 20°C. Leduc‖ found a decrease with increasing temperature, and Merrill‖ suggests that the mass is independent of the temperature.

In more recent years Guthie** and van Dijk†† have made a special study of various forms of voltameters. The form suggested by Richards was found by him to give a smaller deposit of silver than the form originally devised by Lord Rayleigh. The difference between the two forms found by Richards in 1899 was 80 parts in 100,000; in 1902 he found 44 parts in 100,000; Watson,‡‡ in 1901, obtained a difference of 26; Guthie, in 1904, found 48, and in the same year van Dijk observed a difference of 23. Van Dijk also compared the syphon and Rayleigh types and found a mean difference of 8 parts in 100,000, the latter form giving the heavier deposit; if a very doubtful observation is excluded, the mean difference is 18 parts in 100,000. In addition, van Dijk observed a difference due to the size of the platinum bowls, the smaller one invariably containing the lighter deposit for the same form of voltameter. There are many other interesting differences which need not now be enumerated; sufficient has been written to show that the silver voltameter could not be regarded as an instrument of high precision. The international ampere is, however, defined in terms of the deposit of silver, and the Conference on Electric Units at Charlottenburg in October, 1905, reaffirmed this definition, but expressed the opinion that the information before it was not sufficient to enable it to lay down exact directions in respect to the silver voltameter to be employed. Hence the necessity for an enquiry to ascertain the possibility of specifying a voltameter which is easily reproducible and in which an ampere-second always deposits the same mass of silver.

¶ Leduc, 'Journ. de Phys.,' 1, p. 561, 1902.
‡‡ Watson, 'Phil. Trans.,' 1898, p. 445, 1902.
MR. F. E. SMITH, MR. T. MATHER, AND DR. T. M. LOWRY

For convenience this communication is divided into two parts. In some of the very early experiments it was found that the mass of the deposit was dependent on the mode of preparation of the silver nitrate. A considerable quantity of the crystallised salt was necessary for the observations, and for economy and experience the salt was recovered from the used solutions by recrystallising. The first products gave very remarkable results, both as regards the deposited mass and its appearance, but on further purification the normal salt giving normal deposits was obtained. The abnormal results were found to be due to impurities hitherto unsuspected, and which are not usually contained in the salt purchased as pure in the ordinary way; they appear to arise in the manipulation of the solution, the fusion of the salt, and its long exposure to the air. These impure solutions are dealt with in the second part of this communication. In the measurements discussed in the first part the pure salt only was used.

PART I.

A Comparison of Various Forms of Silver Voltameters, by F. E. Smith, A.R.C.Sc.;

and a Determination of the Electrochemical Equivalent of Silver,

by F. E. Smith, A.R.C.Sc., and T. Mather, F.R.S.

Description of the Voltameters.

Eleven platinum vessels and two silver ones have been used for the kathodes of the voltameters. The dimensions, approximate masses, capacities, &c., of these vessels are given in the following table. We are indebted to Messrs. Johnson, Matthey and Co. for the loan of the vessels A, B, C, D, L, and M.

<table>
<thead>
<tr>
<th>Letter by which the vessel is indicated in Table I.</th>
<th>Shape.</th>
<th>Approximate mass in grammes.</th>
<th>Diameter at mouth, in centimetres.</th>
<th>Depth, in centimetres.</th>
<th>Maximum capacity, in cubic centimetres.</th>
<th>Convenient volume of electrolyte, in cubic centimetres.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Bowl</td>
<td>80</td>
<td>10</td>
<td>8.2</td>
<td>570</td>
<td>300–450</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>80</td>
<td>10</td>
<td>8.2</td>
<td>570</td>
<td>300–450</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>83</td>
<td>10</td>
<td>8.2</td>
<td>570</td>
<td>300–450</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>87</td>
<td>10</td>
<td>8.2</td>
<td>570</td>
<td>300–450</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>78</td>
<td>10</td>
<td>3.8</td>
<td>250</td>
<td>150–200</td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>30</td>
<td>10</td>
<td>4.5</td>
<td>280</td>
<td>150–200</td>
</tr>
<tr>
<td>G</td>
<td></td>
<td>30</td>
<td>10</td>
<td>4.5</td>
<td>280</td>
<td>150–200</td>
</tr>
<tr>
<td>(Silver) HS</td>
<td></td>
<td>85</td>
<td>10</td>
<td>6.5</td>
<td>450</td>
<td>300–400</td>
</tr>
<tr>
<td>(Silver) KS</td>
<td></td>
<td>90</td>
<td>10</td>
<td>6.5</td>
<td>450</td>
<td>300–400</td>
</tr>
<tr>
<td>L</td>
<td></td>
<td>65</td>
<td>6.3</td>
<td>5.7</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>M</td>
<td>Ring</td>
<td>65</td>
<td>7.7</td>
<td>4.1</td>
<td>75</td>
<td>50</td>
</tr>
<tr>
<td>N</td>
<td>Bowl</td>
<td>39</td>
<td>6.0</td>
<td>5.0</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>O</td>
<td>Crucible</td>
<td>39</td>
<td>4.1</td>
<td></td>
<td>50</td>
<td>40</td>
</tr>
</tbody>
</table>
L, M, and N are platinum vessels with lateral projecting ears to support them during electrolysis. L is nearly cylindrical in shape, M is a cylindrical ring only, and N is hemispherical. The vessels N and O were very kindly lent to the National Physical Laboratory by Professor G. van Dijk; N is the small bowl referred to as B in Professor van Dijk’s papers,* and O is one of the crucibles indicated by I and II. For the vessel E we are indebted to Professor Ayrton.

**The Anodes.**

An anode usually consisted of a pure silver plate, $5.0 \times 5.0 \times 0.4$ centims., held by a silver rod riveted through its centre. The silver was obtained from Messrs. Johnson, Matthey and Co. Before employing it for a determination of the electrochemical equivalent of silver, about 10 grammes of silver were deposited electrically on the plate, and on these occasions a platinum bowl with a deposit of silver on its inner surface was generally used as the anode. In this way the silver was always removed from the platinum bowls, but not from those of silver. When new, the surface of a platinum vessel is free from scratches, and silver deposited on it adheres much better than to a scratched surface; it is important, therefore, to avoid the use of a spatula. The electrical method removes the deposit, cleans the platinum, and at the same time prepares the anode. Shortly before using, the latter was washed with distilled water and dried in an electric oven. The platinum bowls were rinsed with distilled water and strong nitric acid, and if much of the dark silver salt Ag₃NO₃ adhered to the platinum the washing with nitric acid was repeated. Distilled water was finally used and the bowls dried in an electric oven at 160°C.

For the Richards form of voltameter silver rods of two sizes were used; some of the rods were 1 centim. in diameter and the others 2.5 centims. These rods were also coated with electrically deposited silver.

**The Electrolyte.**

For the comparison of various types of voltameters the electrolyte was usually a 15 per cent. solution of pure silver nitrate in water. The silver nitrate was sometimes purchased and sometimes recovered from used solutions. A description of the preparation of the pure salt is given in Part II., p. 585, of this communication.

**Form of Voltameters.**

The following types were used:

1. *The Rayleigh Form* (fig. 1).—In this the kathode was usually a platinum bowl and the anode a silver plate or rod coated with electrically deposited silver. The anode was inserted in a cup made of filter paper, the folds in the paper being secured

---

with a little sealing-wax. The silver plate was immersed in the solution just below the surface, and the sealing wax which secured the folds of the filter paper was at least 2 centims. above the surface of the electrolyte. The filter cup was supported by three platinum wires from an ebonite ring.

(2) The Richards Form (fig. 2).—A platinum bowl was in general used for the kathode, and the anode was of the same form as that of the Rayleigh voltameter. It was, however, surrounded by a fine-grained porous pot instead of a filter paper, and the electrolyte inside the pot was maintained at a lower level than the electrolyte in contact with the kathode. Usually no appreciable change in the difference of level resulted during an experiment, but a small syphon was frequently employed to ensure an approximately constant difference. Two of the porous pots were made by the Akron Insulator and Marble Company, of the United States of America, and were obtained for us by Dr. Guthe; several were made by Pukal, of Berlin; and others were from an unknown source.

(3) The Syphon Form (fig. 3).—The kathode was a platinum bowl and the anode a silver plate or silver bowl coated with electrically deposited silver. When a silver plate was used, it was contained in a glass dish, the electrolyte in the latter being connected with that in the platinum bowl by a glass syphon. Two sizes of syphon were used; one was 30 sq. centims. in its narrowest part and 30 centims. in axial length, the other was 8 sq. centims. section and 20 centims. in axial length.

(4) The Pot-Syphon-Bowl Form (P.S.B.) (fig. 4).—In this the liquid in the syphon was separated from that in the anode vessel by a porous pot. Any advantages of the Richards form were thus combined with those of the syphon.
(5) The Syphon-Pot-Bowl Form (S.P.B.) (fig. 5).—In this the liquids in the syphon and kathode vessel were separated by a porous pot. Any disadvantages of the Richards form were thus introduced without eliminating any advantage of the syphon.

Fig. 5. Fig. 6.

(6) The Elevated Kathode Form (fig. 6).—A silver bowl with electrically deposited silver formed the anode, and a platinum ring, or platinum bowl of smaller diameter than that of the silver bowl, formed the kathode. If a heavy anode liquid was formed, it would not come into such intimate contact with the kathode as in the Rayleigh form.

(7) Several Modifications of the above. — (a) The silver anode in the Rayleigh type was replaced by a platinum anode; (b) for the filter paper of the Rayleigh form a porous pot drilled with fine holes was substituted, and purified asbestos was placed in the pot to prevent any anode slime reaching the kathode; (c) in addition to the filter paper a china filter cup with very fine holes surrounded the anode of the Rayleigh form. The internal resistance was thus increased 100 times, and the potential difference between anode and kathode was correspondingly increased.

In all of the forms the platinum bowls used as kathodes were supported on brass rings mounted on ebonite, and the silver rods supporting the anodes were clamped to a metal arm projecting from a rod similarly mounted. From 300 to 400 cub. centims. of solution were used in the large bowls and about 30 to 40 cub. centims. in the small crucible loaned to us by Professor Van Dijk. The solution was introduced by means of a pipette and was similarly removed after the required amount of silver was deposited. The liquid was carefully examined for loose silver, and if any was found, the solution and the water used for washing the deposit were filtered through a hard filter paper, the particles of the silver washed to the lowest part of the paper, and the latter dried in an electric oven. By the aid of a pointed glass rod the loose silver was transferred to the bowl. The main portion of the deposit was washed by rinsing three or four times with distilled water, after which the bowl was filled with water and left overnight. This last wash-water rarely showed more than the faintest bluish colour on addition of neutral NaCl solution. Two more rinsings with water followed, and then the bowl was dried by heating in an electric oven at 160° C.
Electrical Arrangements.

With the exception of that portion of the circuit which included the silver voltameters, the apparatus and its arrangement was the same as that used in the determination of current in absolute measure by the British Association (Ayrton-Jones) Ampere Balance.* The current which it was necessary to pass through a standard resistance at a known temperature in order that the potential difference on its terminals just balanced the E.M.F. of a Weston cadmium cell at a constant temperature, was determined by the balance, and for other slightly different temperatures of the coil and cell the change of current was calculated from their temperature coefficients. Neither cell nor coil was assumed to remain constant except over very short periods of time, and as the change in E.M.F. of the cell was determined to be not greater than 1 part in 100,000 in eighteen months and the secular change of the resistance coil was easily determined by comparison with the National Physical Laboratory Standards, no appreciable error was thus introduced. The probable error of the measure of the current in absolute units is shown in the communication dealing with the ampere balance to be about 2 parts in 100,000, and the mass of silver deposited per ampere-second in the silver voltameter is subject to the same error.

The arrangement of the apparatus is represented by fig. 7. The current was furnished by a battery $B$ of 55 accumulators of 30 ampere-hours capacity, and in series with it were placed a three-dial adjustable resistance $R_1$ of 111 ohms, a double-groove mercury trough $M$ for fine adjustment of the current, a standard resistance $R$ of manganin strip built to carry a current of 10 amperes, an ammeter $A$, and the voltameters $V$. The latter were put in and out of the circuit by the switch $K$. This was specially designed to close the circuit of a chronograph at the same time as that of the voltameters and to close it again when the latter circuit

* AYRTON, MATHER, and SMITH, ' Phil. Trans.,' A 207, p. 518, 1908.
was opened. The precision with which this was secured was tested by placing a second chronograph and battery in place of the silver voltameters and noting the difference in the intervals of time recorded by the two instruments. The mean of 20 readings indicated a difference of a little less than one-hundredth of a second, which is equivalent to an error of 1 part in 600,000 in the observations made with the voltameters. The time was measured by the standard clock presented to the National Physical Laboratory by Lady Galton. The rate of the clock was determined by means of signals from Kew and Greenwich. The battery was earthed at such a point, E, that the mean difference of potential between the voltameters and the earth was very nearly zero, but the insulation of all the apparatus from earth was also very carefully attended to. The switches C and C' were on one board and could not be separately operated; C reversed the current through the standard resistance, and C' reversed the connections of the standard cell to the potential points of the resistance. C'' is a switch for placing either of two cells S, S' in the potentiometer circuit; S' was employed for the adjustment of the current before including the voltameters in the circuit, and S continually afterwards. No secondary potentiometer circuit was used. The resistance coils of R1 were of manganin and were immersed in a large bath of paraffin oil. The double mercury trough M was bridged by a copper sliding piece which shunted a portion of the resistance of the trough and allowed of a fine adjustment. A change in current of 1 part in 1,000,000 was easily detected, and sometimes a current constant to this amount could be maintained for an hour or more. G was a galvanometer of the Broca type of 1000 ohms resistance.

The circuit was at first closed so as to exclude the voltameters, and remained closed for 1 hour or more before any adjustment for constancy of current was made. On many occasions a determination of current in absolute measure preceded the deposition of silver. This usually occupied 20 minutes; immediately afterwards R1 was diminished by an amount comparable with that of the voltameters and the latter switched into the circuit. With the Rayleigh form of voltameter a current steady to 1 part in 100,000 was secured within 20 seconds after closing the circuit; a slightly longer time was necessary for the Richards type and longer still for the largest of the syphons.

Owing to the difficulty of maintaining a steady current through the syphon and other modified forms of voltameters, some of the observations are relative only. In these latter cases the standard is the Rayleigh form, but the constancy of this had been well established before any relative observations were made. In order to distinguish between the relative and the absolute values, we have placed an asterisk against all absolute determinations.

When Lord Rayleigh* determined the electrochemical equivalent of silver, the current that passed through the voltameters also passed through the standard current balance, and was thus directly determined in absolute measure. We also might have

* Rayleigh and Sidgwick, 'Phil. Trans.,' 175, p. 411, 1884.
adopted this method, but, owing to the ampere balance being less steady when a current passes through it for more than half an hour, the measurement of the current through the voltmeters would have been subject to a comparatively large error. By frequently standardising a combination of resistance coil and cadmium cell (as already described) and employing these for the measurement of current through the voltmeters, the probable error was appreciably reduced.

**Mass of Deposits.**

The large bowls were weighed on a balance by L. OERTLING, sensitive to one-fiftieth of a milligramme; the small bowls were weighed on a more sensitive balance by OERTLING, and very kindly lent by Mr. OERTLING for this work, or on a balance by RUPRECHT, which was loaned to the National Physical Laboratory by Dr. SCOTT, of the Davy-Faraday Laboratory. All weighings were made by the method of GAUSS, a similar vessel being used as a tare. The mass of silver usually deposited was about 7 grammes in the large bowls and a single weight of 7 grammes was used to counterpoise; the difference was obtained by means of a rider. The weight employed was standardised by comparison with a 100-gramme weight from Sèvres. For difference determinations the four bowls A, B, C, D were largely used.

To reduce the error of weighing we have found it convenient to compare the masses of the bowls when empty and again with the deposits of silver. The following example is one with the bowls containing silver, and gives an idea of the error introduced:

<table>
<thead>
<tr>
<th>Observation</th>
<th>Bowls</th>
<th>Difference in mass in grammes</th>
<th>Calculated from observations</th>
<th>Difference in mass. Mean value in grammes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A and B</td>
<td>+0.49678</td>
<td>2 and 4</td>
<td>+0.49679</td>
</tr>
<tr>
<td></td>
<td></td>
<td>682</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>676</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>A (), C</td>
<td>-3.94383</td>
<td>1 (), 4</td>
<td>-3.94386</td>
</tr>
<tr>
<td></td>
<td></td>
<td>387</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>389</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>A (), D</td>
<td>-6.58421</td>
<td>1 (), 5</td>
<td>-6.58418</td>
</tr>
<tr>
<td></td>
<td></td>
<td>419</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>415</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>B (), C</td>
<td>-4.44065</td>
<td>1 (), 2</td>
<td>-4.44064</td>
</tr>
<tr>
<td></td>
<td></td>
<td>061</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>065</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>B (), D</td>
<td>-7.08097</td>
<td>1 (), 3</td>
<td>-7.08098</td>
</tr>
<tr>
<td></td>
<td></td>
<td>099</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C (), D</td>
<td>-2.64032</td>
<td>2 (), 3</td>
<td>-2.64034</td>
</tr>
<tr>
<td></td>
<td></td>
<td>038</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>032</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It is of interest to state that the diminution in mass of these four bowls from June, 1906, to June, 1907, is 0.8 milligram only. The electrical method of removing the deposit from the bowl does not take the platinum into solution, and the mass of any one bowl in a series of five or six experiments remains constant to 0.1 milligramme. We observed this constancy and found it a most useful check on our weighings of the empty vessels.

As the results of our observations differ very materially from those of nearly all other workers on the same subject, we include particulars of the kathode, anode, solution, current and deposit in Table I. These results are in chronological order and include the measurements discussed in Part II. of this paper.

When two or more voltimeters were placed in series and the same current passed through each, the results of the observations are indicated by the same number, but by different letters. For those observations in which the current was maintained steady throughout the time of the deposit, the value of the current in amperes (10⁻¹ C.G.S. unit) is stated to 1 part in 1,000,000. This is for the accurate comparison of results; the error of this measure is about 2 parts in 100,000. The time is recorded to one-hundredth of a second and is probably correct to 0.1 second. When the observations were made merely for the comparison of different forms of voltimeters and the current was not maintained steady, the approximate value of the current only is given. Except in four special cases (43a, b, c, d) the electrochemical equivalent is calculated to 1 part in 100,000.

Under the heading of solution, letters are given which indicate the source of the silver nitrate crystals; H, M, G, and W are samples of silver nitrate purchased from four different manufacturing chemists, and when more than one sample was purchased from the same firm a number accompanies the letter. LR indicates that the salt was recrystallised by Lowry, and SR that the same process was conducted by Smith. WS is a solution from Professor Watson, and the VD solutions were prepared from salt recrystallised by Professor van Dijk. The degree of electrolysis of the solution, i.e., the ratio of the silver previously deposited by the passage of an electric current through the solution to that present in the solution is stated in column 8, and some brief notes on the appearance of the deposits appear in the last column. The pressure to which the electrolyte was subjected and its temperature are also stated, but only when these differed from the pressure and temperature of the air of the room in which the observations were made.

In column 4, R denotes the Rayleigh form of voltameter, P the Richards (porous pot) form, S the syphon form, P.S.B. and S.P.B. the arrangements we have called the pot-syphon-bowl, and syphon-pot-bowl forms, respectively, and ELK. the elevated kathode form.
<table>
<thead>
<tr>
<th>Observation</th>
<th>Date</th>
<th>Kathode bowl</th>
<th>Form of voltmeter</th>
<th>Source of crystals</th>
<th>Concentration</th>
<th>Added impurities</th>
<th>Degree of electrolysis</th>
<th>Mass of silver deposit in grammes</th>
<th>Time in seconds</th>
<th>Current in amperes</th>
<th>Milligrammes of silver per coulomb</th>
<th>Remarks on deposit, pressure, temperature, etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2.12</td>
<td>F</td>
<td>P</td>
<td>percent.</td>
<td>15</td>
<td>—</td>
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*Observations to get an idea of reproducibility of Rayleigh form.

Coarse texture.

Pot, W. and J. George.
| 46a | 11.10 | A | R | Hg | 15 | | | | 7-00382 | 7000 | 0° variable | 1° 113° | Pot, Akron Cruc. Co. |
| 46b | 11.10 | B | P | Hg | 15 | | | | 25 | 345 | 340 | 0° | 8 | 7900 | 9° | 30 |
| 46c | 11.10 | C | R | Hg | 15 | | | | 7-00421 | 7000 | 0° variable | 1° 113° | Pot, W. and J. George. |
| 46d | 11.10 | P | R | Hg | 15 | | | | 7-00297 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 46e | 11.10 | R | Hg | 15 | | | | 7-00297 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47a | 21.10 | C | C | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47b | 21.10 | D | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47c | 25.10 | C | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47d | 25.10 | D | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47e | 25.10 | E | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47f | 25.10 | F | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47g | 25.10 | G | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47h | 25.10 | H | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47i | 25.10 | I | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47j | 25.10 | J | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47k | 25.10 | K | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47l | 25.10 | L | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47m | 25.10 | M | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47n | 25.10 | N | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47o | 25.10 | O | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47p | 25.10 | P | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47q | 25.10 | Q | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47r | 25.10 | R | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47s | 25.10 | S | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47t | 25.10 | T | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47u | 25.10 | U | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47v | 25.10 | V | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47w | 25.10 | W | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47x | 25.10 | X | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47y | 25.10 | Y | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |
| 47z | 25.10 | Z | R | Hg | 15 | | | | 7-00554 | 6150 | 5° | 20 | 25° | 6120 | 5° | 20 |

**Very striated.**

**Chlorate solution. Striae.**

Liquor 30 c. in pot (see p. 566). 30 c. in anode vessel (see p. 566). Chlorate solution.
Table I. (continued).

<table>
<thead>
<tr>
<th>Observation</th>
<th>Date</th>
<th>Kathode bowl</th>
<th>Form of Volta-meter</th>
<th>Source of Crystals</th>
<th>Concentration</th>
<th>Added Impurities</th>
<th>Degree of Electrolysis</th>
<th>Solution</th>
<th>Mass of Silver Deposit in Grammes</th>
<th>Time in Seconds</th>
<th>Current in Amperes</th>
<th>Milligrams of Silver per Coulomb</th>
<th>Remarks on Deposit, Pressure, Temperature, &amp;c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>59a</td>
<td>23.1</td>
<td>A</td>
<td>R</td>
<td>H₂</td>
<td>15</td>
<td>—</td>
<td>0.50</td>
<td>10·10753</td>
<td>6147</td>
<td>1·0 variable</td>
<td>1·11827</td>
<td>(B and C in parallel. Resistance in circuit with C.)</td>
<td></td>
</tr>
<tr>
<td>59b</td>
<td>23.1</td>
<td>B</td>
<td>C</td>
<td>H₂</td>
<td>15</td>
<td>—</td>
<td>0.50</td>
<td>768</td>
<td>6147</td>
<td>0·1 &quot;</td>
<td>30</td>
<td>300 cub. centims. electrolyte.</td>
<td></td>
</tr>
<tr>
<td>59c</td>
<td>23.1</td>
<td>B</td>
<td>B</td>
<td>H₂</td>
<td>15</td>
<td>—</td>
<td>0.50</td>
<td>6·21520</td>
<td>2400</td>
<td>2·3 &quot;</td>
<td>50</td>
<td>100 &quot;</td>
<td></td>
</tr>
<tr>
<td>60a</td>
<td>25.1</td>
<td>A</td>
<td>B</td>
<td>W₅</td>
<td>7·5</td>
<td>—</td>
<td>?</td>
<td>234</td>
<td>2400</td>
<td>2·3 &quot;</td>
<td>27</td>
<td>125 &quot;</td>
<td></td>
</tr>
<tr>
<td>60b</td>
<td>25.1</td>
<td>B</td>
<td>B</td>
<td>H₂</td>
<td>7·5</td>
<td>—</td>
<td>0</td>
<td>7·14259</td>
<td>2294</td>
<td>0·75 and 0·25 &quot;</td>
<td>37</td>
<td>(B and C in parallel.) From A and D.</td>
<td></td>
</tr>
<tr>
<td>61a</td>
<td>26.1</td>
<td>A</td>
<td>B</td>
<td>H₂</td>
<td>7·5</td>
<td>—</td>
<td>0</td>
<td>7·00867</td>
<td>6147</td>
<td>1·0 &quot;</td>
<td>27</td>
<td>From B and C.</td>
<td></td>
</tr>
<tr>
<td>61b</td>
<td>26.1</td>
<td>B</td>
<td>B</td>
<td>H₂</td>
<td>7·5</td>
<td>—</td>
<td>0</td>
<td>7·10653</td>
<td>12294</td>
<td>0·75 and 0·75 &quot;</td>
<td>1·11829</td>
<td>Base of bowl protected.</td>
<td></td>
</tr>
<tr>
<td>62a</td>
<td>30.1</td>
<td>A</td>
<td>B</td>
<td>H₂</td>
<td>15</td>
<td>—</td>
<td>0·75</td>
<td>882</td>
<td>17</td>
<td>0·1 &quot;</td>
<td>27</td>
<td>Sides of bowl protected. Normal.</td>
<td></td>
</tr>
<tr>
<td>62b</td>
<td>30.1</td>
<td>A</td>
<td>B</td>
<td>H₂</td>
<td>15</td>
<td>—</td>
<td>0·75</td>
<td>7·01348</td>
<td>6147</td>
<td>1·0 variable</td>
<td>27</td>
<td>Pot, Pukal.</td>
<td></td>
</tr>
<tr>
<td>63a</td>
<td>1.2</td>
<td>A</td>
<td>A</td>
<td>H₂</td>
<td>15</td>
<td>—</td>
<td>0</td>
<td>358</td>
<td>17</td>
<td>0·1 &quot;</td>
<td>30</td>
<td>0·1 per cent. acid. 1 per cent. acid.</td>
<td></td>
</tr>
<tr>
<td>63b</td>
<td>1.2</td>
<td>A</td>
<td>A</td>
<td>H₂</td>
<td>15</td>
<td>—</td>
<td>0</td>
<td>358</td>
<td>17</td>
<td>0·1 &quot;</td>
<td>30</td>
<td>0·1 per cent. acid. 1 per cent. acid.</td>
<td></td>
</tr>
<tr>
<td>64a</td>
<td>22.2</td>
<td>A</td>
<td>B</td>
<td>H₂</td>
<td>15</td>
<td>—</td>
<td>0</td>
<td>358</td>
<td>17</td>
<td>0·1 &quot;</td>
<td>30</td>
<td>0·1 per cent. acid. 1 per cent. acid.</td>
<td></td>
</tr>
<tr>
<td>64b</td>
<td>22.2</td>
<td>B</td>
<td>B</td>
<td>H₂</td>
<td>15</td>
<td>—</td>
<td>0</td>
<td>358</td>
<td>17</td>
<td>0·1 &quot;</td>
<td>30</td>
<td>0·1 per cent. acid. 1 per cent. acid.</td>
<td></td>
</tr>
<tr>
<td>66a</td>
<td>28.2</td>
<td>A</td>
<td>A</td>
<td>H₂</td>
<td>15</td>
<td>—</td>
<td>0</td>
<td>7·00061</td>
<td>6147</td>
<td>1·0 &quot;</td>
<td>27</td>
<td>Solution in pyridine. Copper also added. Ferric nitrate also added.</td>
<td></td>
</tr>
<tr>
<td>66b</td>
<td>28.2</td>
<td>B</td>
<td>B</td>
<td>M₅</td>
<td>15</td>
<td>—</td>
<td>0</td>
<td>652</td>
<td>6147</td>
<td>1·0 &quot;</td>
<td>27</td>
<td>Mother liquor.</td>
<td></td>
</tr>
</tbody>
</table>

Temperature = 15°C. Pressure = 2·4 centims. mercury. Temperature = 05°C.
ON THE SILVER VOLTAMETER.

561

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Discussion of the Results.

Observations 1 to 13 were made with solutions which are now known to have been impure. Apart from the electrolytes, the observations are also very unsatisfactory, for in these early experiments the silver deposits were partly removed with the aid of a platinum spatula, and the remainder with warm nitric acid; the bowls were much scratched in consequence, and many of the deposits were very loose. In addition, we were not so expert in the manipulation of the voltameters as in the later experiments, although the errors introduced on this account are regarded as very much smaller than the differences in the electrochemical equivalent which we found from day to day. As the electrolytes were not pure we have deferred the discussion of the first 13 sets of observations to Part II. (pp. 582, 595).

The Rayleigh Form of Voltameter.

Table II. summarises the results obtained with the Rayleigh form. In all, there are 52 independent observations; the mean value of the electrochemical equivalent is

TABLE II.—Rayleigh Form. Absolute Determinations.

<table>
<thead>
<tr>
<th>No.</th>
<th>Milligrammes per coulomb</th>
<th>Difference from mean</th>
<th>No.</th>
<th>Milligrammes per coulomb</th>
<th>Difference from mean</th>
<th>No.</th>
<th>Milligrammes per coulomb</th>
<th>Difference from mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>14a</td>
<td>1.11827</td>
<td>0</td>
<td>22c</td>
<td>1.11825</td>
<td>-2</td>
<td>43a</td>
<td>1.11826</td>
<td>0</td>
</tr>
<tr>
<td>14b</td>
<td>25</td>
<td>-2</td>
<td>23d</td>
<td>32</td>
<td>+5</td>
<td>43b</td>
<td>26</td>
<td>-1</td>
</tr>
<tr>
<td>15a</td>
<td>26</td>
<td>-1</td>
<td>24a</td>
<td>27</td>
<td>0</td>
<td>43c</td>
<td>25</td>
<td>-2</td>
</tr>
<tr>
<td>15b</td>
<td>22</td>
<td>-5</td>
<td>24b</td>
<td>25</td>
<td>-2</td>
<td>43d</td>
<td>27</td>
<td>0</td>
</tr>
<tr>
<td>16a</td>
<td>25</td>
<td>-2</td>
<td>25d</td>
<td>28</td>
<td>+1</td>
<td>44a</td>
<td>27</td>
<td>0</td>
</tr>
<tr>
<td>16b</td>
<td>22</td>
<td>-5</td>
<td>27a</td>
<td>28</td>
<td>+1</td>
<td>44b</td>
<td>26</td>
<td>-1</td>
</tr>
<tr>
<td>17a</td>
<td>22</td>
<td>-5</td>
<td>27c</td>
<td>28</td>
<td>+1</td>
<td>44c</td>
<td>16</td>
<td>-11</td>
</tr>
<tr>
<td>17b</td>
<td>33</td>
<td>+6</td>
<td>27d</td>
<td>30</td>
<td>+3</td>
<td>46b</td>
<td>32</td>
<td>+5</td>
</tr>
<tr>
<td>17c</td>
<td>27</td>
<td>0</td>
<td>28a</td>
<td>33</td>
<td>+6</td>
<td>46c</td>
<td>30</td>
<td>+3</td>
</tr>
<tr>
<td>17d</td>
<td>25</td>
<td>-2</td>
<td>28b</td>
<td>28</td>
<td>+1</td>
<td>47a</td>
<td>25</td>
<td>-2</td>
</tr>
<tr>
<td>18a</td>
<td>38</td>
<td>+11</td>
<td>28c</td>
<td>26</td>
<td>-1</td>
<td>51a</td>
<td>23</td>
<td>-4</td>
</tr>
<tr>
<td>18b</td>
<td>40</td>
<td>+13</td>
<td>29a</td>
<td>27</td>
<td>0</td>
<td>79b</td>
<td>25</td>
<td>-2</td>
</tr>
<tr>
<td>18c</td>
<td>26</td>
<td>-1</td>
<td>29b</td>
<td>29</td>
<td>+2</td>
<td>84a</td>
<td>25</td>
<td>-2</td>
</tr>
<tr>
<td>19</td>
<td>29</td>
<td>+2</td>
<td>30a</td>
<td>27</td>
<td>0</td>
<td>84b</td>
<td>28</td>
<td>+1</td>
</tr>
<tr>
<td>20</td>
<td>25</td>
<td>-2</td>
<td>30b</td>
<td>27</td>
<td>0</td>
<td>86a</td>
<td>26</td>
<td>-1</td>
</tr>
<tr>
<td>21a</td>
<td>34</td>
<td>+7</td>
<td>30d</td>
<td>23</td>
<td>-4</td>
<td>86b</td>
<td>26</td>
<td>-1</td>
</tr>
<tr>
<td>21b</td>
<td>29</td>
<td>+2</td>
<td>31a</td>
<td>28</td>
<td>+1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21c</td>
<td>30</td>
<td>+3</td>
<td>31b</td>
<td>28</td>
<td>+1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mean = 1.11827₃ milligrammes per coulomb.

1.11827₃ milligrammes per coulomb, and the mean observational error is 2.4 parts in 100,000. The greatest differences from the mean occur with 18a, 18b, and 44c, and it is possible that the solution used on the occasions 18a and 18b was impure owing to
its prolonged contact with the atmosphere. If we exclude these results the mean is 1.11826. The mean difference of 24 parts in 100,000 must not be taken as the figure indicating the reproducibility of the Rayleigh form, for the errors of time, of current determination, of weighing, and of manipulation, are factors in this, as well as the possible changes which ensue due to slight variations in anode, kathode and electrolyte, and which jointly constitute the error associated with the voltameter. If we exclude all of the errors except those due to the voltameter and faulty manipulation, the mean difference is very small; this is well illustrated in observations 43a, b, c, d, the results of which are given to 1 part in 1,000,000. The mean of these four results is 1.11826, and the mean difference is only 7 parts in 1,000,000, which is probably much lower than the usual error of manipulation. We feel justified, therefore, in regarding the Rayleigh form of voltameter, as employed by us, to be reproducible within 1 part in 100,000.

The Richards Form of Voltameter.

The results obtained with the Richards form were at first more variable and always lower than when the Rayleigh form and the syphon form were employed. For some time we were at a loss to understand why the Richards value should be lower than that of the syphon, for both forms do, to a considerable extent, exclude the anode liquid from the kathode vessel, and the changes in concentration of the kathode liquids are also comparable. We eventually found the discrepancy to be due to the porous pots, of which we had three kinds:—(1) From the Akron Insulator and Marble Company of the United States of America; (2) from Pukal of Berlin; (3) from an unknown source. Dr. Gütth kindly obtained the pots (1) for us, and they are similar to those used by him in his research on the Silver Voltameter at the National Bureau of Standards.* The second type of pot is larger, but presumably of the same kind of ware as the pots used by Richards. The third class of pot is from an unknown source; they were made from large porous pots obtained through the agency of Messrs. W. & J. George, Ltd.

We cleaned the pots with aqua regia, potassium cyanide, nitric acid, and hot distilled water before using in the voltameter. After a few runs they became stained, and further cleaning with potassium cyanide, nitric acid, and water was necessary. In our earlier experiments the pots were soaked in several lots of distilled water for 24 hours before using, and in neutral silver nitrate solution for 3 or more hours before the erection of the voltameter. The water in which the pots were finally soaked was invariably free from acid sufficient to redden very sensitive blue litmus paper, but we were forced to conclude that the pots were not acid-free, for on electrolysis of silver nitrate with a pot interposed between anode and kathode the solution in contact with the kathode became sufficiently acid to affect litmus. An

acid solution usually gives a lower deposit of silver than a neutral one (p. 595), and in consequence the results with the porous pot form were at first more variable and lower than with the Rayleigh form. In addition, some cyanide may have been present in solution. More consistent results were obtained on prolonged soaking, but we found the most satisfactory treatment was to place the pot in an electric furnace for a few hours. This procedure was adopted in our later observations, and the mean of the values resulting from these is given separately (Tables III. and IV.). The final result, 1.11828, is practically the same as that obtained for the Rayleigh form, and we conclude that the porous pot in our form of voltameter is of no advantage.

**Table III.—Richards Form. Absolute Determinations.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Milligrammes per coulomb</th>
<th>Difference from mean</th>
<th>No.</th>
<th>Milligrammes per coulomb</th>
<th>Difference from mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>22a</td>
<td>1.11797†</td>
<td>−8</td>
<td>46d</td>
<td>1.11831*</td>
<td>+3</td>
</tr>
<tr>
<td>34c</td>
<td>809†</td>
<td>+4</td>
<td>79a</td>
<td>26*</td>
<td>−2</td>
</tr>
<tr>
<td>34d</td>
<td>05†</td>
<td>0</td>
<td>79c</td>
<td>30*</td>
<td>+2</td>
</tr>
<tr>
<td>44d</td>
<td>00†</td>
<td>−5</td>
<td>79d</td>
<td>25*</td>
<td>−3</td>
</tr>
<tr>
<td>46a</td>
<td>16†</td>
<td>+11</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mean of * observations = 1.11828 milligrammes per coulomb.
Mean of † " = 1.11805 " " "

* Porous pots baked in electric furnace after soaking in water.
† Porous pots soaked in acid and afterwards in water for several days.

**Table IV.—Comparison of the Richards Form with the Rayleigh Form.** The latter is taken as the Standard (1 Coulomb deposits 1.11827 Milligrammes of Silver).

<table>
<thead>
<tr>
<th>No.</th>
<th>Milligrammes per coulomb</th>
<th>Difference from mean</th>
<th>No.</th>
<th>Milligrammes per coulomb</th>
<th>Difference from mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>32a</td>
<td>1.11813†</td>
<td>−7</td>
<td>49c</td>
<td>1.11827*</td>
<td>−1</td>
</tr>
<tr>
<td>39b</td>
<td>20†</td>
<td>0</td>
<td>57b</td>
<td>27*</td>
<td>−1</td>
</tr>
<tr>
<td>41a</td>
<td>20†</td>
<td>0</td>
<td>64c</td>
<td>30*</td>
<td>+2</td>
</tr>
<tr>
<td>41d</td>
<td>20†</td>
<td>0</td>
<td>69b</td>
<td>28*</td>
<td>0</td>
</tr>
<tr>
<td>42a</td>
<td>22†</td>
<td>+2</td>
<td>69c</td>
<td>28*</td>
<td>0</td>
</tr>
<tr>
<td>42c</td>
<td>22†</td>
<td>+2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45b</td>
<td>21†</td>
<td>+1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45c</td>
<td>20†</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mean of * observations = 1.11828 milligrammes per coulomb.
Mean of † " = 1.11820 " " "

* Porous pots baked in electric furnace after soaking in water.
† Porous pots soaked in acid and afterwards in water for several days.
That the porous pots were sufficiently close-grained to keep the anode and cathode liquids apart is shown on p. 566. The results obtained with pots soaked in nitric acid, and afterwards in several lots of distilled water for about 2 to 4 days, are given in 22a, 34c, 34d, 44d, 46a, 32a, 39b, 41a, 41d, 42a, 42c, 45b, and 45c. These values are in fairly good agreement with one another, but all are lower than the figure obtained for the Rayleigh form.

The Syphon, Pot-Syphon-Bowl (P.S.B.), and Syphon-Pot-Bowl (S.P.B.) Forms (Table V.).

The results for the syphon form and for the P.S.B. and S.P.B. types are mainly comparative, the Rayleigh form being taken as the standard. The P.S.B. and S.P.B. types give the effect of the porous pot and clearly indicate that the low results of the early experiments with the Richards form were due to contamination of the solution.

| Table V.—Comparison of the Syphon, Pot-Syphon-Bowl, and Syphon-Pot-Bowl Voltameters with the Rayleigh Form. The latter is taken as the Standard (1 Coulomb deposits 1.11827 Milligrammes of Silver). |
|---|---|---|
| **Syphon.** | **P.S.B.** | **S.P.B.** |
| 32c | 1.11825 | -2 | 33b | 1.11825 | -3 | 35a† | 1.11819 |
| 39e | 28 | +1 | 35b | 31 | +3 | 36a† | 01 |
| 43d | 29 | +2 | 36b | 31 | +3 | 37a* | 25 |
| 49d | 29 | +2 | 37b | 27 | -1 | 40b* | 28 |
| 51c‡ | 25 | -2 | 40c | 24 | -4 | | |
| 55c | 31 | +4 | 45d | 30 | +2 | | |
| 57c | 25 | -2 | | | | | |
| 58b | 28 | +1 | | | | | |
| 69d | 27 | 0 | | | | | |

Mean = 1.11827

Mean = 1.11828

Mean of * = 1.118264
Mean of † = 1.11810

* Porous pots baked in electric furnace after soaking in water.
† Porous pots soaked in acid and afterwards in water for several days.
‡ Absolute determination.

by the liquid included in the pot. The result of observation 51c is not comparative (see Table I.), the very large syphon being used on this occasion. The mean value of the electrochemical equivalent is practically the same for the three forms, and agrees also with the values obtained with the Rayleigh and Richards types of voltameter.
Elevated Kathode Type.

The results are given below (Table VI.) and call for no comment. No difference from the usual type was anticipated, for the Rayleigh and syphon forms had been found to agree before the first of the observations in Table VI. had been made.

Table VI.—Comparison of the Elevated Kathode Voltameter with the Rayleigh Voltameter (1‘11827).

<table>
<thead>
<tr>
<th>No.</th>
<th>Milligrammes per coulomb</th>
<th>Difference from mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>516*</td>
<td>1‘11829</td>
<td>+3</td>
</tr>
<tr>
<td>512*</td>
<td>26</td>
<td>0</td>
</tr>
<tr>
<td>82c</td>
<td>24</td>
<td>-2</td>
</tr>
</tbody>
</table>

Mean = 1‘11826
* Absolute determinations.

Efficiency of Porous Pots and of Syphons.

Nearly all previous researches have led to the conclusion that a source of trouble exists at the anode, and the porous pot voltameter was designed by Richards to prevent the anode liquid having access to the cathode. Novak* was the first to suggest the possible existence of a complex silver salt in the electrolyte; Rodger and Watson† independently made the same suggestion; Richards‡ experiments strengthened the view, and the work of Kahle,§ Guthe,|| Van Dijk¶ and others supports the theory of anode complications. When the very excellent work of these observers is reviewed the results of our observations are astonishing, and we deem it necessary to give evidence of the reliability of our porous pots and syphons.

When the porous pots of classes (1) and (2) were filled with water and allowed to stand for 12 hours, about 40 per cent. of the liquid appeared to pass through their walls. When pots of class (3) were similarly treated, less than 5 per cent. of the liquid passed through the pots. In one of the pots of class (3) 50 cub. centims. of the electrolyte used in observation 30c, which gave a deposit of 1‘12055 milligrammes per coulomb, were used for the anode liquid in observation 49c, the cathode liquid being normal AgNO₃ solution. The result is 1‘11827, showing that very little of the

† Rodger and Watson, ‘Phil. Trans.,’ A, 186, p. 631, 1895.
abnormal liquid could have diffused through the walls of the pot. An analysis of the strength of the anode and kathode solutions before and after electrolysis was made in other experiments and led to the conclusion that the pots were efficient. The syphon was tested by placing the electrolyte used in observation 30c in the anode bowl and a normal solution in the syphon limb and kathode bowl; the result, 1·11829 (49d), shows that no appreciable quantity of the anode liquid could have diffused into the kathode vessel.

Deposit on Platinum and on Silver.

Table VII. gives the results when silver bowls were employed as kathodes. Our successful employment of these bowls is in a large measure due to the use of an electric oven for drying purposes.

Table VII.—Comparison of Results with Platinum and Silver Kathodes. The Mean Value of the Results with Platinum Bowls is 1·11827 Milligrammes of Silver per Coulomb.

Results with Silver Bowls as Kathodes.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>14b</td>
<td>1·11825</td>
<td>- 3</td>
<td>22c</td>
<td>1·11825</td>
<td>- 3</td>
<td>30a</td>
<td>1·11827</td>
<td>- 1</td>
</tr>
<tr>
<td>15a</td>
<td>26</td>
<td>- 2</td>
<td>23d</td>
<td>32</td>
<td>+ 4</td>
<td>30b</td>
<td>27</td>
<td>- 1</td>
</tr>
<tr>
<td>16a</td>
<td>25</td>
<td>- 3</td>
<td>25d</td>
<td>28</td>
<td>0</td>
<td>31a</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>17a</td>
<td>22</td>
<td>- 6</td>
<td>26a</td>
<td>30</td>
<td>+ 2</td>
<td>32c</td>
<td>25</td>
<td>- 3</td>
</tr>
<tr>
<td>17b</td>
<td>33</td>
<td>+ 5</td>
<td>26b</td>
<td>27</td>
<td>- 1</td>
<td>34b</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>18b</td>
<td>40</td>
<td>+ 12</td>
<td>27a</td>
<td>28</td>
<td>0</td>
<td>64d</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>21c</td>
<td>30</td>
<td>+ 2</td>
<td>28a</td>
<td>33</td>
<td>+ 5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Mean = 1·11828

It is apparent that the deposit on a clean platinum surface is the same as that on a silver surface. This result is in agreement with Van Dijk’s* observations.

Gore, Kahle,† and Richards and Heimrod‡ found a somewhat larger deposit when the kathode of the Rayleigh form was of platinum with silver deposited on it than when the kathode at the commencement of the observation was platinum only. Richards found that the deposit on a silver kathode was 1 part in 10,000 heavier

than that on one of platinum when the Rayleigh form of voltameter was used, but that the masses were equal for the porous pot form. Guthe* confirmed the latter result.

Influence of Pressure.

In testing for a pressure effect, one of the voltameters was placed under a glass bell jar in which the gaseous pressure could be varied from 2·5 centims. of mercury to atmospheric pressure. The voltameter was supported on a cast-iron plate through which the leads passed, the latter being well insulated from the plate by ebonite and rubber, and tests made before and after each experiment proved the efficiency of the insulation. In two cases the solution under diminished pressure was made with silver nitrate and distilled water which was boiled a few minutes before setting up the voltameter; in the remaining cases the solution was prepared in the ordinary way. For obtaining a continuous low pressure a large filter pump was used and proved satisfactory. The mass of silver deposited per coulomb is practically the same as before and there is, therefore, no pressure effect in the Rayleigh form of voltameter if set up and used in the manner specified in this communication. Schuster and Crossley† found

Table VIII.—Pressure Effect. Rayleigh form of Voltameter used.

<table>
<thead>
<tr>
<th>No.</th>
<th>Pressure in centimetres of mercury.</th>
<th>Milligrammes per coulomb.</th>
<th>Difference from mean.</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>8</td>
<td>1·11820††</td>
<td>+3</td>
</tr>
<tr>
<td>20</td>
<td>8</td>
<td>25††</td>
<td>−1</td>
</tr>
<tr>
<td>21b</td>
<td>2·5</td>
<td>29††</td>
<td>+3</td>
</tr>
<tr>
<td>70b</td>
<td>2·4</td>
<td>28††</td>
<td>+2</td>
</tr>
<tr>
<td>75b</td>
<td>2·4</td>
<td>20††</td>
<td>−6</td>
</tr>
</tbody>
</table>

Mean = 1·11826

†† Absolute determinations.
†† Rayleigh voltameter at atmospheric pressure taken as the standard (1·11827).

that the amount of silver deposited, when their voltameter was subjected to a gaseous pressure of about 2·8 centims. of mercury, was 4 parts in 10,000 greater than when in air, and Dr. Kahle‡ verified this result. Myers§ who repeated these experiments, found the difference between deposits in air and in vacuo to be as much as 1 part in 1000, and also found an excess of 5 parts in 10,000 if the deposit was made in an

† Schuster and Crossley, 'Roy. Soc. Proc.,' 50, p. 344, 1892.
atmosphere of nitrogen. Richards and Heimrod* verified these results. Merrill† varied the pressure from 1 to 103 atmospheres and found no pressure effect for this range—he did not make observations at less than atmospheric pressure.

**Temperature Coefficient.**

In order to investigate the effect (if any) of temperature upon the silver deposits, we first compared the deposit in two Rayleigh forms maintained at different temperatures, but in the same circuit. The lower temperature was that of the room in which the observations were made and averaged about 16°C. The higher temperature was that of an electric oven and was varied from 40°C to 95°C. Sufficient distilled water was taken to fill the voltameters and was warmed until its temperature was comparable with that of the electric oven. The solution was made and divided into two parts, that portion for the voltameter at the normal temperature being cooled to 16°C and the other portion inserted in the kathode vessel of a voltameter and the whole placed in an electric oven. The results were as follows:

<table>
<thead>
<tr>
<th>grammaes. °C.</th>
<th>grammes. °C.</th>
<th>(a=)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.00401 15 (70a)</td>
<td>7.00483 65 (70c)</td>
<td>(+2.4 \times 10^{-6})</td>
</tr>
<tr>
<td>7.01085 16 (71a)</td>
<td>7.01210 92 (71b)</td>
<td>(+2.4 \times 10^{-6})</td>
</tr>
<tr>
<td>7.05431 16 (72a)</td>
<td>7.05500 46 (72b)</td>
<td>(+3.5 \times 10^{-6})</td>
</tr>
</tbody>
</table>

The values are fairly consistent, but we were not satisfied. The mean temperature coefficient appears to be positive and about 2 or 3 parts in 1,000,000 per degree, but it appeared to us that there were sufficient disturbing influences at work to account for the higher deposits at the higher temperatures. The filter paper cup, the folds of which were secured with platinum wire and not with wax, turned a very dark brown colour on exposure to the atmosphere of the electric oven, and we felt that we were not justified in using filter paper at temperatures much higher than that of the room. The same thing happened to the exposed portions of a porous cup, and we resolved, therefore, to use a syphon at both high and low temperatures. In addition, we placed sheets of glass over the kathode bowl, so that, together with the limb of the syphon which entered the vessel, they shielded the electrolyte from currents of air. The following results were obtained:

<table>
<thead>
<tr>
<th>grammaes. °C.</th>
<th>grammes. °C.</th>
<th>(a=)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.98703 16 (77b)</td>
<td>6.98754 90 (77a)</td>
<td>(+1.9 \times 10^{-6})</td>
</tr>
<tr>
<td>7.00301 15 (82b)</td>
<td>7.00342 92 (82a)</td>
<td>(+0.9 \times 10^{-6})</td>
</tr>
</tbody>
</table>

These indicate that the temperature coefficient over the range 15°C to 92°C is either nil or negligibly small. Unfortunately, we could not pass a current of 1 ampere.

through the electrolyte in the syphon at high temperatures. The heat produced by
the passage of such a current raised the temperature of the liquid sufficiently to
vaporise a portion of it and so break the circuit at the bend of the tube.

Our results are not in agreement with those of most other observers. Lord
Rayleigh* found a higher deposit at 50° C. than at 15° C., and a higher deposit at
15° C. than at 4° C. The temperature coefficient was therefore positive and averaged
about 0.001 per cent. per 1° C. for the range 4° C. to 50° C. Leduc found a negative
coefficient. Richards, Collins, and Heimrod obtained at 60° C. and also at 0° C. a
larger deposit than at 20° C. They state, however, that the apparent gain at 0° C.
was undoubtedly due to the difficulty in washing the deposited silver. The tempera-
ture coefficient obtained from their results is about 0.0017 per cent. per 1° C. for the
range 20° C. to 60° C.

Merrill,† who experimented with fused silver nitrate and solutions at normal
temperatures, concluded that temperature has no effect on the mass of the deposit.

Liquid Inclusions in the Deposit.

The appearance of the deposits in the platinum bowls varied with the solutions
used, but with pure solutions they were generally of very open texture. The
deposits were usually dried in an electric oven at 160° C., but in eight cases we
reheated at 240° C. without observing any loss in weight, and on three other occasions
some deposits in silver bowls were heated to over 400° C. In no case was there a
diminution in weight, but in two of the latter experiments a gain of 3 parts in 100,000
was recorded. This was possibly due to the formation of silver sulphide.

Lord Rayleigh and Mrs. Siddwick* sometimes found no loss on a second heating,
but more often a slight decrease. Richards‡ found a mean loss of 18 parts in 100,000
when the deposits were reheated over an alcohol flame to constant weight. The most
extensive observations have been made, however, by van dijk,§ who after washing
and drying at 150° C. reheated in an electric furnace to 500° C., and in some cases to
600° C. No loss in weight was observed. van dijk used smaller bowls and
crucibles than Richards, but the amounts of silver deposited by him are comparable
with those deposited by Richards; it is apparent, therefore, that the texture of the
deposits must have been different or that something in addition to silver was
derived in Richards’ experiments.

Size of Kathodes.

In general the area of the kathode surface in our experiments was 200 sq. centims.,
but in observation 58d the bowl L of 100 sq. centims. kathode surface was used, and

* Rayleigh and Siddwick, ‘Phil. Trans.,’ 175, p. 411, 1884.
in 58e one of the bowls (N) belonging to Professor van Dijk was employed. The area of the kathode surface of this last bowl was 40 sq. centims. only, and this is the smallest kathode area employed by us for currents of nominal value 1 ampere. The results of observations 58a, b, d, and e are in remarkable agreement (1·11827, 1·11828, 1·11827, and 1·11827), and it appears that within the limits stated above the area of the kathode has no influence on the deposit, conditionally, of course, that the concentration of the electrolyte is within certain limits, and that the current density is not too great. In some of our earlier experiments we used rotating kathodes; the large platinum bowls were rotated about 40 times per minute and stationary glass vanes were inserted in the kathode liquid to prevent its uniform rotation. The steadiness of the current was not appreciably affected by this motion, and had more satisfactory deposits been obtained in the rotating bowls than in the stationary ones we should have no hesitation in recommending the method. The deposits were much the same in texture, however, and there was no difference in their masses. As an example we may refer to 38a, b, and c. 38a and 38b were rotated; 38c was not. The masses of the deposits were 7·03110, 7·03096 and 7·03108 grammes respectively.

Size of Anodes.

In most of our experiments it was impossible to estimate the extent of the anode surface owing to the outer coating of the electrically deposited silver. The silver plates generally used as anodes were about 5 × 5 × 0·4 centims., and the current density at an anode was therefore comparatively small. In observations 25a, 26c and 41b the anodes were very small silver discs, having a total area of about 2·5 sq. centims. at the commencement of the deposit, and about 1 sq. centim. at the conclusion; they were not coated with electrolytic silver. On one occasion the mass of the anode disc at the commencement was 12 grammes only, and 7 grammes of silver were deposited. This is an extreme case. The results of the "small anodes" observations are as follows:—

25a 1·11825.
26c 37.
41b 27.

According to Schuster and Crossley,* a small anode may give a deposit which is too small. Leduc† states the opposite of this, and Merrill‡ observed no difference due to variation in the size of the anode. In the porous cup form Guthe§ found the size of the anode to be immaterial, but states that the drop of potential

† Leduc, 'J. de Phys.,' 1, p. 561, 1902.
from anode to kathode should not be large enough to allow of a decomposition of water. We have made experiments to test this, and give the results obtained when the potential difference was varied from 0·03 volt to 30 volts. The effect of using a platinum anode is discussed in Part II., p. 588.

**Effect of Potential Difference between Anode and Kathode (56a and 56b).**

When a syphon form of voltameter and a Rayleigh form were placed in series and a current of 1·02 ampere passed through them, the drop in potential on the syphon form (small syphon) was of the order of 30 volts and on the Rayleigh form about 1 volt. It has already been shown that the mass of silver deposited on these occasions is the same. Comparison observations were also made with a very high resistance Rayleigh voltameter and one of the usual type. The voltameters were placed in series and the kathode bowls of each contained 350 cub. centims. of a 15 per cent. solution of silver nitrate. The high-resistance voltameter was one in which the filter paper was enclosed in a glass funnel perforated with small holes, and the funnel was enclosed in a second similarly perforated. With a current of 0·03 ampere the difference of potential on the high-resistance voltameter was 3·0 volts, and that on the usual form was 0·03 volt. The deposits were very loose and markedly striated. The mass of silver deposited in 50 hours in the usual form was 7·10382 grammes (56a), and in the high-resistance form 7·10411 grammes (56b). These results are interpreted as indicating that in all ordinary cases the potential difference produces no disturbing effect.

**Variable Concentration of Electrolyte.**

The extreme range in the concentration of the electrolyte has been from 1·5 parts to 50 parts of silver nitrate in 100 parts of the solution, the intermediate values being 5, 10, and 15 parts in the same quantity of solution. The chief difference in the deposits was that of texture, the solutions of higher concentration giving less adherent and more striated deposits than the weak solutions when the current employed was between 0·1 and 1·0 ampere, but from 1·0 ampere upwards the striae were faint even for the concentrated solutions. When the 1·5 per cent. solution was used, only 3·3 grammes of silver were present in the electrolyte, and the degree of the electrolysis at the end of this experiment was therefore 7·1/3·3 = 2·15.

The masses of silver in milligrammes per coulomb recorded as deposited from the various solutions are as follows:—

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Mass Deposited</th>
</tr>
</thead>
<tbody>
<tr>
<td>1·5 per cent. solution</td>
<td>1·11823 (64b).</td>
</tr>
<tr>
<td>5·0    </td>
<td>1·11825 (40a, 40c).</td>
</tr>
<tr>
<td>10·0    </td>
<td>1·11827 (33a, b, c).</td>
</tr>
<tr>
<td>15·0    </td>
<td>1·11827 (large number of observations).</td>
</tr>
<tr>
<td>50·0    </td>
<td>1·11827 (30b).</td>
</tr>
</tbody>
</table>
ON THE SILVER VOLTAMETER.

The differences from the mean value are within the limits of error, and there is, therefore, no certain change in the mass of silver deposited per coulomb from electrolytes containing from 1.5 to 50 parts of silver nitrate in 100 parts of solution.

We think it necessary, however, to point out that a current of 0.1 ampere was used to electrolyse the 1.5 per cent. solution; when strong currents were used the silver was deposited as long, needle-shaped crystals, and on one occasion it was precipitated in a spongy form. It is insufficient, therefore, to state the range in the concentrations of the electrolyte without also specifying the quantity of the electrolyte, the extent of the kathode surface, and the current to be used.

Variation of Current Density.

We believe that one of the objections to the silver voltameter is that the ordinary size of voltameter possibly allows only of currents of the magnitude of 1 ampere to be measured. It was of some importance, therefore, to decide whether or not currents of the order of half an ampere and others of the order of 10 amperes deposited exactly the same mass of silver per coulomb in our form of the Rayleigh voltameter. This might have been tested by evaluating the currents, noting the times, and determining the masses, but a much simpler and more accurate way was a comparison of the masses of silver deposited, similar to the calibration of a box of weights. This latter method was adopted by us. In our first experiment we compared the masses of the bowls A and B and of C and D. B and C were then placed in parallel and A in series with them, and a current of 1 ampere passed through A for 2.4 hours. A mass of silver, weighing about 10 grammes, was thus deposited in A. The bowl D was then substituted for A and the same current passed through it for the same time. At the conclusion of the experiment there were about 10 grammes of silver in each bowl, but the silver in A and D had been deposited with a current of 1 ampere, and that in B and C with a current of half an ampere. A was again compared with B, and C with D. The difference \((A-B)-(C-D)\) should be the same as before if the change in current had no effect. Similar observations were made for currents in the main circuit of 2, 4, and 8 amperes. The masses of silver deposited and the difference \((A-B)-(C-D)\) before and after the depositions are given in Table IX., p. 574.

We conclude from these results that the voltameter employed by us can be used for the determination of currents as great as 8 amperes and as small as 0.5 ampere, and that these currents will deposit the same mass of silver per coulomb. With a current of 4 amperes the electrolyte was warm to the hand after the experiment, and with 8 amperes the temperature rose from 18° C. to 35° C. The deposits with high current densities are firm and of a matt surface, while with very low current densities the silver is loose and the deposit striated.

We have made one observation which connects the deposits obtained with 1 ampere
with those obtained with 0.75 and 0.25 ampere. In this case a resistance was added to that portion of the branch circuit containing C for one-half of the time of the experiment and to B for the other half. A current of 1 ampere was passed through A and D, and through B and C currents of 0.75 and 0.25 ampere passed. The total mass of silver deposited in A and D was 14.02215 grammes and in B and C it was 14.02246 grammes, a difference of 0.0022 per cent. (62a, b, c, d).

**Effects of Electrolysis on the Concentration of the Electrolyte.**

When the current first leaves the anode it spreads out in the approximately homogeneous electrolyte which surrounds it, and, if the normal distance from the anode to the kathode is everywhere the same, the current density over the anode surface is uniform, and the same is true for the kathode surface. Immediately, the layers of liquid in contact with each electrode become changed in concentration and density: around the silver anode a film of dense liquid of high concentration is formed and about the kathode a film results the density of which approximates to that of water and is of very small concentration. In the Rayleigh form of voltameter the heavy anode liquid descends, and since it constitutes a path of high conductivity, more silver per unit area is deposited on the base of the bowl than on the sides if the anode surface is everywhere at the same normal distance from the kathode surface. This descending column of heavy anode liquid gives rise to the star-shaped deposit on the base of the bowl which has been so frequently noticed by other observers and by ourselves (fig. 8, Plate 9). If the distance of the anode from the base of the bowl is appreciably greater than the distance from the sides, the path of least resistance is not necessarily that of the descending column, and the deposit per unit area on the base is less than on portions of the sides. This latter condition holds for the Rayleigh voltameter as we have generally used it.

It follows that the lowest point of the anode is in contact with a thin layer of electrolyte of greater concentration than the solution at the surface. A concentration cell is thus produced and normally a current would flow through the electrolyte from
the highest point of the anode to the lowest. This, however, only holds good for a few seconds after the cessation of the current in the main circuit. The superposition of the effect on the main current effect results in the current density being greatest at the point where the anode enters the electrolyte, and this is, in general, the first portion of the anode which becomes noticeably thin. If the current is very feeble, diffusion tends to keep the liquid more homogeneous. Observations show that when silver rods are used as anodes there are other effects of electrolysis which produce vertical grooves in them.

If the concentration of the electrolyte is diminished, the ratio of the concentration of the anode film to that of the main electrolyte is increased and that of the kathode film to the liquid is probably diminished. There is, however, a similarity with respect to the action of the current on the surfaces of separation of these films and the electrolyte. In both cases the current in its passage through the voltameter flows from a liquid of high concentration into a mass of liquid of lower concentration, and hence, if there is a marked surface of separation of anode liquid and electrolyte, and kathode liquid and electrolyte, any effect of the current on these surfaces will be similar. Godef* has shown that when a solution of small concentration rests on one of high concentration and a current is passed downwards, the surface of separation of the liquids becomes indistinct, but if the current is reversed the surface of separation becomes more marked. By using silver anodes and kathodes of platinum foil in electrolytes contained in glass vessels we were able to see the heavy anode liquid in its descent from the anode and the light liquid in its ascent from the kathode. Even when at a distance of a few millimetres from the electrode these liquids appeared to be quite distinct from the main body of the electrolyte, and we are justified therefore in assuming the existence of even more distinct surfaces of separation around the anode and kathode when the current is flowing.

An interesting question is whether the properties of these films of liquids are very different from the main portion of the electrolyte. Observation shows that as they leave the electrodes they break up into cylindrical columns, but whether or not they are in the form of uniform thin films when in contact with the electrodes direct observation does not show, but a number of experiments with currents of different intensities and electrolytes of different concentrations enable an opinion to be formed. When weak electrolytes are used (e.g., 1\% per cent. solutions) a current of 0.1 ampere produces a deposit having a matt surface, but with a 15 per cent. solution the deposit is markedly striated (figs. 9† and 10, Plate 9). We interpret these results in the following manner. The film of liquid in contact with the kathode has a greater mean thickness in the 1\% per cent. solution than in the 15 per cent. solution. This follows because the rate of deposition of silver is the same in each voltameter. If the film is very thin, it is unstable and breaks up into cylindrical columns of liquid. Hence in

† Fig. 9 represents a portion of a deposit which was stripped from the side of a platinum bowl.
contact with the kathode surface there are columns of liquid of low concentration, and in between these the electrolyte is of approximately normal concentration. The latter has the higher conductivity, and since in addition there is an E.M.F. acting from the columns of low concentration towards the main body of the electrolyte, the current will pass into the kathode through the liquid in between the columns. Immediately the concentration falls and possibly the resultant liquid of small density is pulled into the columns of low concentration. If our assumptions are correct, an increase in the current should result in the kathode film becoming thicker and more stable, and when it is sufficiently stable to remain as a film a striated deposit should not be formed. This was tested by experiment and found to be so.

The following table indicates the results. All the solutions were pure, and the same volume of electrolyte (350 cub. centims.) was taken in each case.

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<tbody>
<tr>
<td></td>
<td>per cent.</td>
<td>amperes</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>0.1</td>
<td>No striae</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>0.7</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>1.0</td>
<td>&quot; &quot;Marked striae.</td>
</tr>
<tr>
<td>4</td>
<td>15.0</td>
<td>0.1</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>5</td>
<td>15.0</td>
<td>0.3</td>
<td>&quot; Striae, but not so marked as in (4).</td>
</tr>
<tr>
<td>6</td>
<td>15.0</td>
<td>0.7</td>
<td>Very faint striae at bend of bowl.</td>
</tr>
<tr>
<td>7</td>
<td>15.0</td>
<td>1.0</td>
<td>No striae</td>
</tr>
<tr>
<td>8</td>
<td>15.0</td>
<td>2.0</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>9</td>
<td>15.0</td>
<td>4.0</td>
<td>&quot; fine matt surface.</td>
</tr>
<tr>
<td>10</td>
<td>15.0</td>
<td>8.0</td>
<td>Striae.</td>
</tr>
<tr>
<td>11</td>
<td>50</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

It appears that for solutions of all concentrations striated deposits are obtained for small current densities at the kathode, and matt deposits for very large current densities.

We may now compare the changes in the Rayleigh and Richards forms of voltameter. In the latter case there is no descending anode liquid, and there will be, therefore, less tendency for a star-like deposit to be formed on the base of the bowl. In our own form of Richards' voltameter the volume of kathode liquid was in general about 250 cub. centims., and during electrolysis the mean concentration of the solution must have diminished from 15 to $10^{-6}$ per cent. The mean concentration of the electrolyte in the Rayleigh form remains constant and, in consequence, for the same current density strie were produced in the Rayleigh form when they were absent in the Richards form. This effect has also been observed by Guthe* and by van Dijk†. In the Richards form, as employed by the latter observer, the kathode

---

liquid consisted of about 30 cub. centims. of a 20 per cent. solution, and at times nearly 3 grammes of silver were deposited, the concentration being thus reduced to about 4·3 per cent. Professor Van Dijk observed little or no striae in the Richards form, but marked striae in the Rayleigh form.

In the Rayleigh form the process of intermixing of the anode and kathode liquids is considerably accelerated by their ascent and descent respectively. We have made observations on the currents of liquid thus produced and find that they may be approximately represented by fig. 11. The electrolyte which is above the horizontal plane containing the sheet of silver which forms the anode is certainly of lower concentration than that below this plane when electrolysis has proceeded for a short time. It therefore appears that the kathode film may be stable in the upper portion of the electrolyte when it is unstable in the lower portion. In other words, it should be possible to produce striae at the base and bend of the bowl when the upper portion of the deposit presents a matt surface (see fig. 9). Probably this has been observed by other workers besides ourselves, but we have found no reference to the phenomenon. Our own deposits at low current densities were often markedly striated at the bend of the bowl and gradually merged into the matt surface which existed above the point A. The portion B of the electrolyte, which is partly enclosed by the curved surface of the liquid, is in a most unfavourable position for the renewal of its original concentration, and it is probably of smaller density than any other part of the solution. Because of this the conductivity is small, and an appreciable E.M.F. acts from B towards the main body of the electrolyte; in consequence, the quantity of silver precipitated by the passage of electricity through B is very small. In most of our experiments we have closely observed the deposit and the electrolyte, and in about six instances have found a distinct gap between the line of contact of electrolyte and platinum and the edge of the deposited silver. In these cases a few crystals of silver were sometimes
deposited in the form of a thin ring where the electrolyte was at its highest point, and one or two millimetres below this ring the edge of the main deposit was formed. A photograph of such a ring deposit is given in fig. 13 (Plate 9).

Another interesting question is whether the kathode and anode films can be easily scattered by agitation of the liquid. We have made experiments with the kathode only, for there were no means of detecting whether the anode film was disturbed or not. Our solutions were such (solutions used in Observations 1 to 13) that striae were readily produced, and the method of investigation was to rotate the kathode and insert stationary glass vanes in the electrolyte to prevent a uniform motion. We were astonished to find the striae as distinct as ever, but instead of being vertical they were in the form of a spiral. This is well shown in figs. 12 and 13, which are from photographs. Examination of the inclination shows (1) that the kathode liquid moved upwards; (2) that on the assumption that the kathode alone rotated and the whole of the electrolyte remained stationary, the vertical velocity was 21 centims. per second.* The electrolyte was not stationary, however, and we judged the kathode film to rotate at very nearly the same rate as the kathode; had it been at exactly the same rate the striae would have been vertical. It is evident, therefore, that the vertical velocity of the kathode film was not very great; it was possibly of the order of 1 centim. per second. The stability of the liquid columns is, however, astonishing.

It is well to point out that the Richards voltameter is a concentration cell after electrolysis commences. The anode liquid within the porous pot is of higher concentration than the kathode liquid, and in consequence any short-circuiting of the voltameter after the main circuit has been broken will diminish the mass of silver on the kathode bowl. A steady current may thus be produced for some time, and is easily measured by an ammeter.

Another point investigated by us was the possibility of silver being deposited from a concentrated solution of silver nitrate at the bottom of a platinum bowl when a second solution of much lower concentration rests on it. We employed solutions containing 50 per cent. and 1 per cent. of silver nitrate, but neither in platinum bowls nor in silver ones was any increase observed.

Other effects have been observed, but it is not easy to suggest an explanation of them. The most remarkable occurs when a kathode bowl is half filled with an electrolyte, left for an interval of about 10 minutes, and the remaining portion of the electrolyte added just prior to the completion of the electric circuit. If about 5 grammes (or less) of silver are deposited, the level of the electrolyte when the bowl was half filled is clearly indicated in the deposit, the density of the latter being appreciably greater below the original level of the solution, and the change in the density is marked by a clear line running round the bowl.

* The bowl rotated clockwise at the rate of 40 turns per minute: its maximum diameter was 10 centims., and the inclination of the striae was almost exactly 45° C.
The Electrochemical Equivalent of Silver.

The mean of the values for the mass of silver deposited by the passage of 1 coulomb of electricity through any of the normal voltameters described in this communication is 1.11827 milligrams.

The quantity of electricity which passed through a voltameter in any experiment was determined by a measurement of time, to which measure no appreciable error can be attached, and by an evaluation of a current in absolute measure through the medium of the Ayrton-Jones ampere balance. It is shown elsewhere* that the error in such a determination of current is of the order of 2 parts in 100,000, and this also is the probable error of the value stated above for the mass of silver deposited per coulomb.

The value has been obtained not from one solution, nor with one voltameter, but with many solutions and many forms, as well as many voltameters. It has, moreover, been shown that the value is the same whether a current of half an ampere is passed through a voltameter, or a current of 8 amperes; whether the pressure is atmospheric or equivalent to that of a few centimetres of mercury; and if the temperature is 90°C instead of 15°C, it is probable that the value is still the same.

The remarkable consistency of our results is probably due to the large kathode bowls, the purity of our anodes, the small mass of filter paper in the Rayleigh form, and most of all to the purity of the electrolyte. With very small bowls, a small quantity of electrolyte, a small anode, a relatively large mass of filter paper, and current densities which are very high or very low, the estimated mass of silver deposited in the passage of 1 coulomb may be different from the value given by us. Secondary reactions may then occur which never happened in our experiments, or if they did the large volume of electrolyte masked their effects and rendered their detection impossible by any means tried by us.

Comparison of Results with those of other Observers.

Professor van Dijk very kindly forwarded to Dr. Glazebrook two of his voltameters together with a considerable quantity of silver nitrate which he had recrystallised, and which was comparable with that employed in his investigations. We here express our hearty thanks to Professor van Dijk. Solutions were prepared from the salt which was sent, and they were found to be abnormal. In one case the value found for the electrochemical equivalent was 1.11847 (52b), and in a second experiment 1.11860 (76b) resulted. The solutions, as originally prepared, were slightly turbid and had to be filtered, and the deposits with a current of 1 ampere were noticeably striated. If different quantities of an abnormal electrolyte are contained in

two similar voltameters in series, the one containing the least quantity of solution does in general give the smaller deposit. This is well illustrated in 77c and d. In one of these, 450 cub. centims. of an abnormal electrolyte gave 1.12007 as the value of the electrochemical equivalent, while the other, which contained 150 cub. centims., gave 1.11923. With an abnormal electrolyte a large bowl will therefore give a heavier deposit than a small one, but although there is an appreciable difference in the size of the Rayleigh bowl and the Richards crucible which Professor Van Dijk used, we do not think that the differences which he observed are to be entirely attributed to this cause.

Professor Watson also sent a silver nitrate solution used by him in 1895. This gave 1.11872 (23a) for the electrochemical equivalent, and when diluted to a 7½ per cent. solution it gave 1.11850 (60a) with a current of 2.3 amperes, and 1.11837 (61a) on a second electrolysis with a current of 0.1 ampere.

In view of these facts and the great difference in the size of the voltameters, &c., used by other observers, it appears that no very useful purpose would be served by an attempt to explain the results of other experimenters without first reproducing as nearly as possible the conditions under which they worked. This we shall endeavour to do.

It is of some interest, however, to compare the results obtained by absolute methods, since a form of voltameter practically identical with that used by Lord

<table>
<thead>
<tr>
<th>Observer</th>
<th>Year</th>
<th>Value</th>
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<tbody>
<tr>
<td>Mascart*</td>
<td>1884</td>
<td>1.1156</td>
</tr>
<tr>
<td>Fr. and W. Kohlrusch†</td>
<td>1884</td>
<td>1.1183</td>
</tr>
<tr>
<td>Rayleigh and Sidgwick‡</td>
<td>1884</td>
<td>1.1179</td>
</tr>
<tr>
<td>Pellat and Potier§</td>
<td>1890</td>
<td>1.1192</td>
</tr>
<tr>
<td>Kahle</td>
<td></td>
<td>§</td>
</tr>
<tr>
<td>Patterson and Guthie¶</td>
<td>1898</td>
<td>1.1192</td>
</tr>
<tr>
<td>Pellat and Leduc**</td>
<td>1903</td>
<td>1.1182</td>
</tr>
<tr>
<td>Van Dijk and Kunst†</td>
<td>1904</td>
<td>1.1182</td>
</tr>
<tr>
<td>Guthie‡‡</td>
<td>1906</td>
<td>1.1182</td>
</tr>
</tbody>
</table>

‡ Rayleigh and Sidgwick, 'Phil. Trans.,' 175, p. 411, 1884.
§ Pellat and Potier, 'J. de Phys.,' 3, p. 381, 1890.
** Pellat and Leduc, 'C. R.,' 136, 1649, 1903.
Rayleigh has been employed on most occasions. We are unaware of the exact conditions of the experiments, but it will be seen that the differences between the values and the mean value are not appreciably greater than the probable errors of many of the current determinations. It must be remembered that in the very early observations great precision was not claimed.

Patterson and Guthe used a type of voltameter in which the electrolyte was saturated with silver oxide, and their result is not therefore comparable with the others. Guthe and van Dijk employed the Richards and the Rayleigh forms; the values given in Table X. are those obtained by them for the Rayleigh pattern.

Conclusions.

(1) The Rayleigh, the Richards, the Syphon, the Pot-Syphon-Bowl, the Syphon-Pot-Bowl, and the Elevated Kathode forms of voltameter give identical values within 1 or 2 parts in 100,000 for the electrochemical equivalent of silver, subject to easily attained conditions with respect to the size of the voltameter and the purity of the electrolyte. (The purity of the electrolyte is dealt with in Part II.)

(2) The mass of silver deposited is independent of the pressure to which the voltameter is subjected, and also independent of the temperature, except that at high temperatures the filter paper of the Rayleigh form may interact with the silver nitrate solution, and give rise to a very slightly abnormal value for the electrochemical equivalent of silver.

(3) The current through the Rayleigh form of voltameter* may vary from 0.5 ampere to 8 amperes, and possibly beyond these limits without producing any appreciable disturbing effect.

(4) The electrochemical equivalent of silver is

\[1.11827 \, \text{milligrammes of silver per coulomb (10}^{-1} \, \text{C.G.S.)}.
\]

This value is subject to a probable error of about 0.002 per cent.

PART II.

The Chemistry of the Silver Voltameter;

A. Preparation of Pure Silver Nitrate.

In the earlier experiments (1 to 13) on the electrochemical equivalent of silver considerable difficulty was experienced in obtaining concordant figures when different samples of silver nitrate were electrolysed under apparently identical conditions. Many

* The size of the voltameter is assumed to be the same as that described in this communication.
of the solutions used had been prepared from silver nitrate recovered from previous electrolyses, purified by adding nitric acid, boiling down to dryness, and fusing in a platinum basin; the fused mass was dissolved in water, filtered from the black residue which was always left after fusion, and was often used for electrolyses without further purification. On a few occasions silver nitrate was crystallised from the filtrate and a 15 per cent. solution made from this recovered salt. The values for the electrochemical equivalent of silver varied from 1·11832 to 1·11886 milligrammes per coulomb (mean of 14 determinations = 1·11857) when the Rayleigh voltameter was used, and from 1·11786 to 1·11854 (mean of 21 determinations = 1·11825) when the porous pot voltameter was used.

Before a definite figure could be established for either form of voltameter it was necessary first to demonstrate the possibility of preparing again and again from silver nitrate of different origins solutions which should give identical weights of silver when electrolysed under identical conditions. The following experiments were therefore made in order to test the constancy of the electrochemical equivalent of a range of silver nitrate samples of different origins.

I. Silver Nitrate from Electrolytic Silver.—185 grammes of electrolytic silver recovered from previous electrolyses were dissolved in a mixture of equal volumes of “commercial pure” nitric acid and water. The resulting solution was filtered, by means of a small Gooch crucible, from a small residue of insoluble matter,* and evaporated on a water-bath (since it was not thought to be desirable to fuse the product) during 50 hours, water being added from time to time. A crop of crystals was then drained off and dried overnight in the oven. When recrystallised the product was found to be neutral, but yellow in colour. After three further recrystallisations the electrochemical equivalent of the sample was tested. The solution for electrolysis was prepared by dissolving 90 grammes of the purified salt in 600 cub. centims. of water of low conductivity, and when electrolysed in a Rayleigh voltameter gave a deposit of 1·11825 milligrammes per coulomb (24b).

II. From Recovered Silver Nitrate.—850 grammes of strongly acid crystals, recovered from previous electrolyses by acidifying and concentrating the solutions, were purified by repeated crystallisation only, without any attempt to remove the acid by evaporating on the water-bath, by drying in an oven, or by fusing. After four crystallisations the nitrate was found to be neutral to litmus, and after one further crystallisation it was dissolved in water (113 grammes AgNO₃ in 750 cub. centims. of water of low conductivity) and electrolysed. The electrochemical equivalent of the sample was found to be 1·11827 milligrammes per coulomb (24a).

* The insoluble residue referred to was suspended in very minute particles in the liquid, to which it imparted a red colour suggestive of a colloidal metal. It was found to be platinum, and 0·0136 gramme was obtained from 185 grammes of electrolytic silver. The impurity, therefore, was probably not a product of electrolysis, but may have been derived from the platinum bowls or from the platinum spatula which was used to remove the electrolytic silver.
III. The strongly acid mother-liquors from II. were evaporated on the water-bath and dried in the oven until free from acid. The dry salt was further heated until the blue colour of the copper nitrate had disappeared, and was then dissolved in water, filtered, and recrystallised until colourless. After one further crystallisation a solution was prepared as before, and the electrochemical equivalent determined. Three determinations gave the values

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<tr>
<td>III.</td>
<td>1.11827</td>
<td>(26b)</td>
</tr>
<tr>
<td></td>
<td>1.11830</td>
<td>(27d)</td>
</tr>
<tr>
<td></td>
<td>1.11827</td>
<td>(29a)</td>
</tr>
<tr>
<td>Mean</td>
<td>1.11828 milligrammes per coulomb.</td>
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Other samples of recovered silver nitrate purified by this method gave the values

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<tr>
<td>IV.</td>
<td>1.11826</td>
<td>(28c)</td>
</tr>
<tr>
<td>V.</td>
<td>1.11831</td>
<td>(35b)</td>
</tr>
<tr>
<td></td>
<td>1.11827</td>
<td>(35c)</td>
</tr>
<tr>
<td>VI.</td>
<td>1.11816 (?)</td>
<td>(44c)</td>
</tr>
<tr>
<td></td>
<td>1.11830</td>
<td>(46c)</td>
</tr>
<tr>
<td>VII.</td>
<td>1.11830</td>
<td>(65b)</td>
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whilst a 50 per cent. solution prepared by dissolving recovered silver nitrate (purified as above) in its own weight of water gave the value

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<td>VIII.</td>
<td>1.11827</td>
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IV. *Silver Nitrate from Commercial Samples.*—As a further test of the possibility of preparing silver nitrate of constant properties, two commercial samples were procured, one from an English and one from a German firm, and these were purified by recrystallising two or three times from water. One of these samples was of especial interest, as it gave initially a lower value for the electrochemical equivalent than any of the samples I. to VIII. which we had purified for ourselves, and we were uncertain at first whether a higher standard of purity might not perhaps be attained by a works-recrystallisation on a large scale than when smaller quantities were dealt with. The recrystallised samples gave, however, entirely normal values, and the low value of one of the commercial samples was therefore due to an impurity which could be removed by recrystallising (see later p. 595). The values obtained for the electrochemical equivalent were:

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<tbody>
<tr>
<td>IX.</td>
<td>1.11830</td>
<td>(26a)</td>
</tr>
<tr>
<td></td>
<td>1.11828</td>
<td>(27c)</td>
</tr>
<tr>
<td></td>
<td>1.11828</td>
<td>(28b)</td>
</tr>
<tr>
<td>X.</td>
<td>1.11827</td>
<td>(44a)</td>
</tr>
<tr>
<td>XI.</td>
<td>1.11826</td>
<td>(44b)</td>
</tr>
</tbody>
</table>
It will be seen that with one exception all the eleven solutions gave, when electrolysed under similar conditions, values for the electrochemical equivalent lying between 1·11826 and 1·11831, the mean value being 1·11828 milligrammes per coulomb. The average error for the nine concordant solutions is 0·00001, and is of about the same magnitude as that observed in the case of duplicate determinations with the same sample of nitrate.

The only discordant value in the above series (No. VI.) gave on a first electrolysis the figure 1·11816, but this may possibly have been due to some accident of manipulation, e.g., to the loss of a trace of loose silver from the bowl; a redetermination of the electrochemical equivalent gave the value 1·11830, a figure which differs only by 0·00003 from the mean. One solution prepared subsequently for use in a comparative test gave the value 1·11836 (52c), but the nitrate used for making the solution had been exposed to the air for a long time and was considered not to be sufficiently pure for an absolute determination.

B. Tests of Commercial Silver Nitrate.

Having established a definite figure for the weight of deposit obtained from highly purified samples of silver nitrate when electrolysed under standard conditions, it was desirable to ascertain how far commercial "pure" silver nitrate could be relied upon to give a correct weight of deposit. The result was encouraging in so far as with one exception all the samples examined gave figures agreeing with those obtained in the preceding section A. The values for the different samples were as follows:

\[
\begin{align*}
H_1 & \quad 1\cdot11827 \\
H_2 & \quad (1\cdot11827) \\
H_3 & \quad 1\cdot11827 \\
W_1 & \quad 1\cdot11819 (22b, 23b, 25a, 25b, 31b). \\
G_1 & \quad 1\cdot11827 (30a). \\
M & \quad 1\cdot11829 (30d). \\
G_2 & \quad 1\cdot11827 (38a). \\
W_2 & \quad 1\cdot11826 (48a). 
\end{align*}
\]

The abnormal specimen \(W_1\) gave a normal deposit (IX.) when recrystallised and was therefore considered to contain a removable impurity. When the 15 per cent. solution was tested with neutral litmus paper it did not show any acid reaction; but a more concentrated solution tested with blue litmus showed a marked acidity which was absent from the solutions which gave normal deposits. The acidity of the specimen was further established by precipitating the solution with neutral sodium chloride and testing with methyl orange. The makers subsequently stated that the nitrate had been crystallised from a slightly acid liquid in order to secure the formation of clear crystals, and there can be little doubt that a trace of acid mother-liquor
had been retained, and that this was the cause of the abnormal character of the deposit. The makers forwarded a second sample which was crystallised from a neutral liquid, and normal results (W_3) were obtained with this.


It is now possible to state the conditions that should be complied with in preparing silver nitrate solutions for use in the voltameter.

1. If commercial "pure" silver nitrate is used, a part of it should be purified by recrystallising twice from water and the deposit compared with that from the original sample. If the values agree, this can be used without purification; if not, the whole of the sample should be twice recrystallised. For rough work in which an error less than 0.1 per cent. may be neglected the commercial nitrate may be used directly without testing or purifying.

2. If recovered silver nitrate is used it should be freed from acid by evaporating to dryness and heating in the oven at 140° C. until the blue colour of the copper nitrate (if present) is destroyed, then dissolved, filtered and recrystallised until the mother-liquor drained from the crystals is colourless, then once again recrystallised before being used for electrolysis.

3. In crystallising the nitrate it is desirable to effect the dissolution of the crystals by heating on a water-bath, rather than over a bare flame, so as to avoid all risk of overheating the solution, and to dissolve in a conical flask of Jena glass rather than in a beaker, so as to reduce the risk of contamination by exposure to the air.

4. For filtering the hot solution we prefer to use a Hirsch porcelain funnel, the perforated plate of which is covered by two discs of filter paper. The funnel is attached to a filter pump and warmed by pouring boiling distilled water through it; there is then but little risk that the hot solution will crystallise in the filter. The filtered solution is allowed to crystallise in the pump-flask, so as to avoid unnecessary exposure to the air. If the flask is cautiously cooled and shaken it is generally possible to secure the separation of the nitrate in small crystals; these can subsequently be drained much more effectively than the larger crystals, which separate when the solution is allowed to cool slowly and without disturbance. As an alternative the filtered solution may be left to deposit large crystals from which the mother-liquor can be poured off, but in this case the separation of the mother-liquor is much less complete and a larger number of crystallisations is required. Towards the end of the crystallisation the flask may be cooled in ice, so as to reduce the amount of material left behind in the mother-liquors.* A porcelain filter funnel may be used without filter paper for collecting and draining the crystals; when these are well pressed down in the funnel, most of the mother-liquor can be removed by means of a

* 100 grammes of water dissolve 115 grammes AgNO_3 at 0°, 160 grammes at 10°, and 215 grammes at 20° C.
filter pump, but if the liquors contain much impurity it is advisable to rinse the crystals cautiously with a few cubic centimetres of iced distilled water.

(5) If it is desired to dry the crystals, the best method is to make use of a Hempel's vacuum desiccator charged with stick potash, and cautiously heated over a water-bath to accelerate the drying. As a rule, however, it is best to use the moist crystals for preparing solutions, the exact strength of which can, if necessary, be determined by evaporating a known weight of the solution.

(6) The water used in the earlier experiments for the final crystallisation of the nitrate and for the preparation of the solutions was a specially pure sample prepared at Hendon by Mr. W. R. Bousfield, by a process of continuous fractional distillation, and stored in a large Welsbach bottle. Its electrical conductivity had been measured and found to be only 1 reciprocal megohm per centimetre cube. Subsequent experiments showed that commercial distilled water could generally be used without introducing any error.

D. Effects produced by Repeated Electrolysis.

That an increase in the value obtained for the electrochemical equivalent of silver may result from repeated electrolysis of a silver nitrate solution was first observed by Novak,* and later by Rodger and Watson,† Kahle,‡ Van Dijk§ and Guthe.|| Rodger and Watson record as successive relative values the numbers

9983, 9987, 9990, 9999, 9995, 9995, 9995, 10002, 10005, 10006, 10002.

In an attempt to confirm these observations we repeatedly electrolysed two solutions of silver nitrate, the one being contained in a platinum bowl and the other in a silver bowl. The resulting values of the electrochemical equivalent were,

when the platinum kathode was used:—— and when a silver kathode was used:——

\[
\begin{align*}
1.11827 \ (14a) & \quad 1.11825 \ (14b) \\
1.11822 \ (15b) & \quad 1.11826 \ (15a) \\
1.11822 \ (16b) & \quad 1.11825 \ (16a) \\
1.11827 \ (17c) & \quad 1.11833 \ (17b) \\
1.11838 \ (18a) & \quad 1.11840 \ (18b) \\
1.11834 \ (21a) & \quad 1.11830 \ (21c)
\end{align*}
\]

It thus appears that there may be a small increase, but nothing comparable with that observed by Rodger and Watson.

† Rodger and Watson, 'Phil. Trans.,' A, 186, p. 631, 1895.
In a final experiment a current of 1 ampere was passed through a solution during 200 hours until the solution was blue with copper from the "pure" silver anode. During this interval the mass of silver transferred through the solution amounted to no less than 820 grammes, or more than 100 times as much as in a normal electrolysis. The values obtained for the electrochemical equivalent were:

Before electrolysis . . . . . . 1.11827 (solution H)
After 100 hours . . . . . . 1.11822 (17a)
After 200 hours . . . . . . 1.11832 (23d)

We were therefore driven to the conclusion that the mere act of electrolysis is not sufficient to produce the effects recorded by Rodger and Watson and others.

The only change which we have been able to detect in the properties of the solution after repeated electrolysis is that it gives somewhat more coherent and very slightly striated deposits. Kahle* has pointed out that the filter paper may have an effect on the electrolyte, and this view is adopted by van Dijk† in explanation of the increase which he observed. In our experiments the volume of the electrolyte was exceptionally large, and the mass of filter paper‡ immersed was small; contamination of the solution by the paper would therefore not be likely to produce any marked effect in the course of a few electrolyses at ordinary temperatures; at higher temperatures we have reason to think that important effects may be produced by the action of the filter paper on the electrolyte. No filter paper was used in the 200-hour electrolysis except during the actual determination of the electrochemical equivalent.

E. The Question of Anodic Impurities.

It has been generally assumed that the high values obtained on repeated electrolysis were due to the introduction of impurities at the anode during electrolysis. It was to overcome the supposed effects of such impurities that the porous pot voltameter was introduced by Richards. We were at first inclined to agree with this view; it is well known that when silver nitrate is electrolysed with a platinum anode, crystals are formed of a "peroxynitrate," Ag$_2$NO$_3$. This substance was discovered by Ritter§ in 1804; its composition has been established by repeated analysis,|| and it is known to be decomposed when warmed with water at temperatures from 25° upwards according to the equation

$$\text{Ag}_2\text{NO}_3 = \text{AgNO}_3 + 3\text{Ag}_2\text{O}_3 + \text{O}_2$$

‡ Schleicher and Schull, No. 595.
and this affords the only general method of preparing silver peroxide. It was possible that whilst this compound does not crystallise out when a silver anode is used, and does not occur in the anode slime, it might be produced in small quantities and pass into solution, especially if high current densities are used at the anode. It was found, however, that no increase in the electrochemical equivalent resulted when the area of the silver anode of the Rayleigh voltameter was made very small and when high current densities were employed (pp. 571 and 573, Part I.).

In further experiments it was shown that this action at the anode, which is accompanied by a liberation of acid, actually lowers the value of the electrochemical equivalent instead of raising it. An apparatus was arranged with a platinum crucible as an anode, and between it and the cathode a large filter paper cup was suspended to prevent any crystals of Ag₃NO₃ falling on the platinum bowl. The solution was very acid after electrolysis, and the resulting values of the electro-chemical equivalent were 1.11779 (34a) and 1.11811 (55b). The abnormally high equivalents are therefore not due to the formation of peroxynitrate at the anode.

Richards* found that the anode liquid was so changed during electrolysis that it deposited silver on prolonged contact with silver crystals. We have been unable to confirm this in our voltameters.

The following experiment was performed so that the anode liquid should come into contact with the silver surface a few seconds after its formation. The anode and cathode liquids were contained in two silver bowls (fig. 14) connected by a syphon, and the anode was a silver plate which dipped into a glass funnel fitted with a filter paper. On electrolysis, the dense liquid descended to the bottom of the bowl and thus came into contact with silver. The anode bowl was weighed both before and after electrolysis, but no gain in weight was recorded in any of the experiments, even though on one occasion 20 grammes of silver were deposited on the cathode bowl. In the first experiment the silver plate was surrounded with filter paper only, but this led to complications, owing to part of the current entering and leaving the

bowl surrounding it. The glass funnel largely prevented such a distribution of current.

The experiments recorded in Part I. indicate further that, under normal conditions of working, the exclusion from the kathode vessel of the anode liquid by means of a porous pot is without influence on the deposit, and we therefore conclude that the cause of the abnormal values in our voltameter (Observations 1 to 13) is to be sought in the contamination of the solution, but that this is not due to any change which is inseparably connected with the conditions of electrolysis.

F. Examination of the Mother-Liquors from Recovered Silver Nitrate.

Although it was not found possible to obtain appreciably higher values for the electrochemical equivalent by repeated or prolonged electrolysis, or by bringing the anode liquid into contact with the kathode, it was known that high values could readily be obtained by using recovered silver nitrate that had been cleared with acid and rendered neutral by fusion, but not otherwise purified. It was therefore thought to be desirable to investigate these solutions in order to determine the nature of the impurity which they contained. For this purpose the mother-liquors left behind during the purification of the recovered nitrate, as described in § A II. and III., were collected and examined. After recovering in a pure state the greater part of the 850 grammes of nitrate there remained a yellowish liquid containing about half its weight of silver nitrate. On dilution with water the liquid became turbid and a thick brown cloud was formed which ultimately settled down as a black precipitate.* The diluted solution, which contained 14·4 per cent. AgNO₃, was then electrolysed and gave the extraordinary value

\[ 1.12141 \text{ milligrammes per coulomb (27b)} \]

for the electrochemical equivalent. A second electrolysis gave the value

\[ 1.12055 \text{ (30c),} \]

and a third electrolysis, after the addition of 1 gramme of crystallised ferric nitrate to about 400 cub. centims. of the mother-liquor, gave the value

\[ 1.12171 \text{ (74d).} \]

As it appeared that the impurities were largely precipitated by diluting to 15 per cent., an electrolysis was carried out with a more concentrated mother-liquor containing 43 per cent. AgNO₃. The value obtained for the electrochemical equivalent was 1·12252 (47b), which is no less than 0·00425, or 0·36 per cent., higher than the normal, and is possibly the highest yet recorded.

* A slight cloudiness had already been noticed when the fused nitrate referred to at the beginning of the section was dissolved in water and diluted after filtration instead of before.
The impurity present in the mother-liquor evidently consists, then, to a considerable extent of substances which are insoluble in water, but soluble in silver nitrate solutions of moderate concentration. These impurities are partially precipitated on diluting the solutions, but a certain amount remains in solution. The property of dissolving in silver nitrate appears to be possessed by a large range of silver salts which are insoluble in water, and many of these possess the property of increasing the weight of the deposit obtained on electrolysis of the solution. The removal of silver at the kathode leads, as is well known, to the formation of a film of dilute solution which (owing to its small density) flows upwards towards the surface of the solution. The film immediately in contact with the kathode may be regarded as almost pure water, and the dilution from 15 per cent. to nearly 0 per cent. (by removal of silver nitrate instead of by addition of water) probably causes a precipitation of impurity similar to that which results from the dilution from 50 per cent. to 15 per cent. In this direction we believe an explanation may be sought of the abnormally high equivalents obtained from impure silver nitrate solutions.

In the course of the later work several centigrammes of the precipitate formed on diluting the silver nitrate mother-liquors were collected and fractionated as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Gramme.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble in dilute nitric acid (Ag₂O, &amp;c.)</td>
<td>0·0231</td>
</tr>
<tr>
<td>&quot; ammonia (AgCl, &amp;c.)</td>
<td>0·0664</td>
</tr>
<tr>
<td>Undissolved (Ag₂S, &amp;c.)</td>
<td>0·0274</td>
</tr>
<tr>
<td></td>
<td>0·1169</td>
</tr>
</tbody>
</table>

From the first fraction there was recovered 0·0113 gramme AgCl, equivalent to 0·0091 Ag₂O; from the second fraction 0·0567 gramme AgCl. It appears, therefore, that about half the residue consisted of silver chloride, whilst the remaining part contained sufficient oxide and sulphide to give the precipitate a black colour, and so disguise to a large extent the chloride which was its chief constituent.

G. Striation of the Deposit.

It was noticed very early in the investigation that high values for the electrochemical equivalent were almost invariably accompanied by a characteristic striation of the deposit, whilst normal equivalents were almost always obtained from unstriated deposits with currents of 1 ampere; it was in fact possible to guess roughly what the weight of the deposit would be by noting the appearance of the silver deposited in the bowl. The impurity which causes the high values is evidently characterised by the property of producing marked striations, and this property was for some time the only qualitative test for the presence or absence of the substance in the silver solutions. It was also considered to be of importance in seeking to determine
nature of the impurity; thus if high values could be obtained with a variety of added
impurities, that one which most readily gave striated deposits was the most likely to
be the characteristic impurity of the actual solutions used for electrolysis.

The deposits from the mother-liquors showed an exceedingly marked striation, although the silver was dull in appearance.

II. Influence of Oxide, Carbonate and Chloride.

The influence of silver oxide on the silver voltameter has been investigated by
Patterson and Guthe,* Guthe,† Richards,‡ and Kahle.§ Patterson and Guthe
used a solution saturated with silver oxide, and Guthe's comparison of it with the
Rayleigh type showed the two to agree. Richards, however, found his form of
voltameter to give a deposit lower by 0.1 per cent. when compared with Patterson
and Guthe's type, and Kahle§ found the effect of silver oxide was to increase the
deposit by 0.05 per cent. From the point of view to which we have referred it was
probable that any silver salt which was insoluble in water would, if dissolved in the
nitrate solution, give an abnormally heavy deposit. Two experiments made with
solutions containing silver oxide gave confirmation to this view. Pure sodium
hydroxide was prepared by the action of water-vapour on metallic sodium and was
added to a 50 per cent. solution of silver nitrate; the filtered solution gave a
slight brown precipitate on diluting to 400 cub. centims, and on electrolysis it
gave for the electrochemical equivalent the value

1.11852 (50\(d\)),

0.021 per cent. higher than the normal figure. A later experiment carried out in the
same way gave the value

1.11842 (80\(c\)).

These results are not directly comparable with those of other observers owing to the
difference in the size of the voltameters, but may be regarded as substantially in
agreement with that of Kahle.

Very similar results were obtained on adding sodium carbonate, which raised the
electrochemical equivalent by about two parts in 10,000 (Observation 53\(b\)).

Addition of potassium chloride gave the values

1.11840 (50\(c\)), 1.11847 (80\(b\)).

The chloride is freely soluble in concentrated silver nitrate solutions, especially when
hot, and is copiously precipitated on dilution; its effect on the electrochemical

The above results go far to justify the view that the majority of silver salts which are insoluble in water dissolve to a slight extent in concentrated silver nitrate solutions, and that the increase in the electrochemical equivalent which usually results may be related to this difference in solubility, which probably acts by causing a precipitation of the sparingly soluble salt from the impoverished solution at the kathode.

I. Influence of Sulphide.

In view of the readiness with which metallic silver blackens on exposure to air, it was evident that silver sulphide was likely to be a frequent impurity in the nitrate solutions. The blackening of the bottles in which silver nitrate solutions are kept is a universal experience in the laboratory, and in voltameter work the blackening of the porous pots has constantly proved a source of trouble. The sediment from the silver nitrate mother-liquors undoubtedly contained sulphide, and it was therefore very important to determine the influence of this substance on the electrochemical equivalent.

(1) A solution of 60 grammes of silver nitrate in an equal weight of water was prepared in a wide test-tube, and a small volume of hydrogen sulphide gas was delivered into the tube above the surface of the solution. The first effect of the sulphuretted hydrogen was to produce on the surface of the solution a yellow film which turned black where the gas was present in largest quantities. On shaking the solution a granular precipitate of a canary-yellow colour became distributed throughout the solution, and the black sulphide disappeared. It was evident that where the nitrate was in excess the precipitate was stable in a yellow form, and became black only when the proportion of sulphuretted hydrogen to nitrate was increased. When a considerable quantity of the yellow precipitate had been formed the solution was filtered. On diluting with distilled water to 400 cub. centims., a brown cloud appeared which slowly settled to a black precipitate at the bottom of the colourless solution. The behaviour of the sulphide solution was thus essentially similar to that of the silver nitrate mother-liquors. The diluted solution was filtered and transferred to a voltameter. It gave a normal electrochemical equivalent

\[1.11828 \text{ milligrammes per coulomb (87b).}\]

Three other solutions (85b, 85c, 86c), prepared by somewhat similar methods, also gave normal values,

\[1.11829, \ 1.11828, \ 1.11828.\]

We are therefore driven to the conclusion that although many of the heavy deposits were obtained from solutions which were undoubtedly contaminated with sulphide (mother-liquors 27b, 47b), the presence of this substance alone is not sufficient to account for the production of these abnormally high values.
ON THE SILVER VOLTAMETER.

Our experiments have shown that the abnormally heavy deposits cannot be explained as due to sulphide acting in presence of copper or of iron.

Two solutions were prepared by dissolving 60 grammes of silver nitrate in 60 grammes of water, and to each of these was added 0.12 gramme of commercial pure copper foil; this was left in contact with the solution until the copper had dissolved as nitrate by displacing an equivalent quantity of metallic silver. Hydrogen sulphide was then added and the solution filtered and diluted as before; very little sulphide was precipitated by diluting, and the electrochemical equivalent was found to be in the case of the first solution

1.11850 (67c);

in the case of the second solution, to which hydrogen sulphide had beenlavishly added, a nearly normal value was obtained,

1.11824* (74a).

Similar experiments were made with iron. This could not be introduced in the same way as the copper, for the metal appeared to become passive in contact with the strong nitrate solution and refused to dissolve. Two solutions were prepared by adding 1 gramme of crystallised ferric nitrate to 60 grammes of silver and adding sulphuretted hydrogen as before. The first solution gave the perfectly normal electrochemical equivalent

1.11825 (67d),

and the second, to which much more hydrogen sulphide was added, gave the value

1.11834 (74c),

also substantially normal. The ferric nitrate was strongly acid, and this fact must be taken into account in discussing the above result, but it is clear that the extraordinarily high electrochemical equivalent of the mother-liquors cannot be attributed to the presence either of iron or of copper. Addition of ferric nitrate to the mother-liquor produced no marked change in the electrochemical equivalent, the value obtained being 1.12141 (27b) and 1.12055 (30c) before and 1.12171 (74d) after the addition of 1 gramme of ferric nitrate to about 400 cub. centims. of 15 per cent. mother-liquor.

J. Influence of Nitrite and Hyponitrite.

The abnormally high deposits obtained with the silver voltameter have usually been attributed to anodic impurities. Such impurities would normally be oxidised substances comparable with the persulphuric acids, with lead peroxide, or with silver peroxynitrate. Richards has, however, made the suggestion that reduction may

* The fact that this figure is somewhat lower than the normal may be due to the trace of acid which is liberated by the sulphide 2AgNO₃ + SH₂ = Ag₂S + 2HNO₃. The solution did not, however, appear acid to litmus.
take place at the anode with formation of silver nitrite. It was therefore of interest to determine the effect of this substance on the electrochemical equivalent.

Richards* prepared silver nitrite by boiling silver nitrate solution with finely divided silver, and obtained with a nitrate solution saturated with it a value identical within 1 part in 200,000 with that found with a pure nitrate solution. He also prepared nitrite from pure potassium nitrite and silver nitrate and concluded, from voltameter experiments made with a nitrate solution saturated with the salt so prepared, that the nitrite caused an increase in the deposit of between 30 and 80 parts in 100,000.

A first experiment, in which a solution of pure silver nitrate was saturated with silver nitrite (purchased as pure) by making a saturated solution of the latter and dissolving the requisite quantity of silver nitrate in it, gave 1.11832 (24d) as the equivalent. That the solution was saturated with nitrite was evident from the copious precipitate of this salt which resulted when the silver nitrate crystals were dissolved in it.

A second experiment, in which a 50 per cent. solution of silver nitrate was saturated with nitrite by the addition of KNO₂ and then diluted and filtered, gave the value 1.11837 (52d) for the electrochemical equivalent. In this case the saturation of the solution was evidenced by the fact that needles of silver nitrite actually crystallised out from the solution on standing in a cool place.

The above experiments show clearly that silver nitrite even when present in considerable quantity does not raise the electrochemical equivalent by more than one part in 10,000 and can only be an unimportant impurity. In view of the yellow tint of the nitrite crystals, which should be colourless when pure, we are by no means certain that the slight increase which we have observed may not be due to hyponitrite (vide infra) and not to the nitrite itself.

The influence of hyponitrite on the deposit does not appear to have been determined. The salt was prepared by reducing sodium nitrite with sodium amalgam, neutralising with acetic acid and precipitating with dilute silver nitrate solution. The yellow precipitate of silver hyponitrite was drained on a filter, thoroughly washed with water and shaken up with 120 grammes of a 50 per cent. solution of silver nitrate. The strong saturated solution was then filtered and diluted to 400 cub. centims. with water. A slight cloud was produced which was removed by filtration and the solution was then electrolysed. The deposit was strongly striated and gave the value 1.11873 (88b). An earlier preparation gave a higher figure, 1.11930 (47c), but we do not wish to lay stress on this.

K. Influence of Acids.

It has been shown that there are a considerable number of impurities which raise the electrochemical equivalent of a silver nitrate solution—oxide, carbonate, chloride

and nitrite increasing the value by about one part in 10,000 and hyponitrite by about one part in 2000. Occasionally, however, abnormally low values are obtained, as, for instance, in the case of the commercial sample \( W_1 \), which gave the mean value 1·11818, and in a large number of the earlier porous pot experiments 1·11786 (4a), 1·11810 (5a), 1·11818 (6a), 1·11815 (7b), &c.\(^*\)

These low values we were able to associate in most cases with the presence of acid, but if acid was responsible for the low values the quantity required to lower the electrochemical equivalent by one part in 10,000 appeared to be very small and could not easily be detected by litmus and other indicators. The commercial sample \( W_1 \) had admittedly been crystallised from an acid solution and showed a trace of acid when carefully tested with blue litmus paper. Finally it was found that the porous pots which had been cleaned with nitric acid but soaked in water for a fortnight until all the acid had apparently been removed, gave up acid to the solutions when a current was passed through them, and this in sufficient quantity to be detected by litmus. It was thought, however, to be desirable to make direct experiments on the influence of acids.

Our own experiments have shown that the addition of nitric acid to silver nitrate solutions produces very irregular results. The normal effect appears to be a small decrease in the electrochemical equivalent, but this never exceeds about two parts in 10,000, and there is very little difference in the effect produced by a mere trace of acid which can only be detected with difficulty by means of litmus and that produced by the addition of acid corresponding to 1 per cent. of the silver nitrate present in the solution. On the other hand we have found that addition of diluted nitric acid may produce an increase in the electrochemical equivalent; this we attribute to the presence in the nitric acid of oxides of nitrogen or other substances which, like the hyponitrite, may raise the electrochemical equivalent to such an extent as to mask completely the small decrease due to the acid.

The irregular effects obtained may be seen from the following summary\(^\dagger\):

<table>
<thead>
<tr>
<th>I. Normal solution</th>
<th>II. Normal solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·1 per cent. ( \text{HNO}_3 ) 1·11841 (65c).</td>
<td>0·1 per cent. ( \text{HNO}_3 ) 1·11860 (66c).</td>
</tr>
<tr>
<td>1·0 per cent. ( \text{HNO}_3 ) 1·11836 (65d)</td>
<td>1·0 per cent. ( \text{HNO}_3 ) 1·11840 (66d).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>III. Normal solution</th>
<th>IV. Normal solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·2 per cent. ( \text{HNO}_3 ) 1·11812 (73b).</td>
<td>1·0 per cent. ( \text{HNO}_3 ) 1·11814 (58c).</td>
</tr>
<tr>
<td>1·0 per cent. ( \text{HNO}_3 ) 1·11814 (73c).</td>
<td>1·0 per cent. ( \text{HNO}_3 ) 1·11810 (75c).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>IIIa. 1·0 per cent. ( \text{HNO}_3 ) 1·11829 (73d).</th>
<th>1·0 per cent. ( \text{HNO}_3 ) 1·11819 (78b).</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·1 per cent. ( \text{HNO}_3 ) 1·11822 (78c).</td>
<td>0·1 per cent. ( \text{HNO}_3 ) 1·11822 (78c).</td>
</tr>
</tbody>
</table>

\(^*\) There was, however, a considerable quantity of loose silver in most of the early determinations.

\(^\dagger\) One series, No. 53, has been omitted, as the unacidified solution (53c) gave a high value and the nitrate was therefore not pure.
In all cases but IV. the nitric acid was purified by distillation from silver nitrate; in series III. and IIIα the acid was added in a concentrated form, in the others it was diluted and titrated. Leduc found a diminution in the mass of the deposits of 2 parts in 10,000 when free acid was present.

We conclude, therefore, that whilst the abnormally low values which are observed from time to time can only be explained by the presence of acid, it may be very difficult in practice to add nitric acid without at the same time introducing other impurities which may more than counterbalance the effects produced by the acid itself.

I. Effect of Heating Silver Nitrate.

It has been shown above that the mere act of electrolysis does not cause any increase in the electrochemical equivalent of a silver nitrate solution, and that in our experiments no contamination appears to be produced by the changes which take place at the anode. For a considerable time we were of opinion that atmospheric contamination with sulphide might in some way produce an alteration in the electrical behaviour of the solution, but finally we were unable to uphold this explanation of the heavy deposits. We believe, however, that a clue to the origin of the abnormal deposits may be found in the behaviour of the nitrate when heated, and, on the other hand, in the action of the nitrate on the filter paper, to which we have referred above, but which in our own experiments we have only been able to detect at high temperatures.

Very early in the course of the investigation we noticed that the fusion of the nitrate caused an increase in the weight of the deposit. A perfectly normal salt (H₁) was fused, dissolved in water, and its electrochemical equivalent was found to be 1·11838 (24c), an increase of 1 part in 10,000. A second similar experiment with a slightly acid salt (W₁) showed an increase in the electrochemical equivalent from 1·11819 (mean of several) to 1·11835 (25c), the latter value being again 1 part in 10,000 higher than the normal. It was further noticed that the mother-liquors which gave such high deposits were all obtained from samples of nitrate which had been fused or strongly heated at some stage of their treatment.

In order to test the effect of heat alone on the nitrate a quantity of the purified salt was heated to incipient fusion for several hours, and the greater part of the nitrate was removed by crystallisation. The colourless mother-liquor was electrolysed, and gave for the electrochemical equivalent the value of 1·11972 (88c). We therefore feel justified in suggesting that whilst other causes (action of light, action of filter paper, &c.) may contribute to the production of heavy deposits, the heating of the nitrate appears to be one of the most effective ways of producing this effect. It is possible that traces of hyponitrite may be formed both by the action of heat and by the reducing action of filter paper, but we do not wish to commit ourselves to the view that the hyponitrite is the only, or even the main, source of the disturbances.
which have been noticed by ourselves and others. We hope at some future date to enquire more closely into the nature of the impurities which affect so strongly the weight of the deposit from the silver nitrate mother-liquors.

M. Other Electrolytes.

(1) Silver Acetate.—Lord Rayleigh* found that the addition of a small quantity of silver acetate to a solution greatly improved the texture of the deposit, but that the mass of silver deposited per coulomb was considerably increased thereby. We prepared a saturated solution of silver acetate and electrolysed in the usual manner; the deposit was of very fine texture, and the resulting electrochemical equivalent was 1.12154 (31c) or 0.3 per cent. higher than the normal. There was evidence, however, that the deposit was not silver alone, for on stripping a portion of it from the platinum bowl a yellowish-white film was plainly visible on both silver and platinum where they had been in contact.†

(2) Silver Chlorate.—Lord Rayleigh* also employed silver chlorate as an electrolyte, independent of the nitrate, and obtained very satisfactory results from it, and if the mean value of the electrochemical equivalent is deduced from the chlorate observations alone, it is higher than the value obtained with the nitrate solutions by only 6 parts in 100,000. In our first attempt to use silver chlorate as an electrolyte we used a 10 per cent. solution and obtained 1.11839 (49a) for the electrochemical equivalent. It was apparent, however, that the electrolyte also contained silver chloride, for a white precipitate had to be filtered from the original solution, and the effect of silver chloride in solutions of silver chlorate is possibly the same as in nitrate solutions. The chlorate was recrystallised to free from chloride and a 5 per cent. solution used to minimise the effect of any remaining impurity. The resulting deposit had a matt surface and its mass was 2 parts in 100,000 greater than that from a 3 per cent. solution of the nitrate, but less by 1 part in 100,000 than that from a 15 per cent. solution (81a, b, c). The electrochemical equivalent may therefore be taken as 1.11827, and confirms Lord Rayleigh’s view that a solution of silver chlorate gives the same mass per coulomb as one of silver nitrate.

(3) Silver Perchlorate.—Carhart, Willard and Henderson‡ have suggested the use of silver perchlorate as an electrolyte. They found the deposits from such a solution to be striated and firmly attached to the bowl, but heavier than the deposits from the nitrate by about 0.007 per cent. It appears, however, that silver chloride may also have been present in the perchlorate, as instructions are given by them for this to be filtered out. A small quantity of perchlorate was prepared for us by some

* Rayleigh and Sidgwick, ‘Phil. Trans.,’ 175, p. 411, 1884.
† Van Dijck found a diminution in the mass of a silver deposit from an acetate solution when it was heated to a high temperature in an electric oven.
manufacturing chemists, but it was far from pure, and our results are not therefore comparable with those of Carhart. The chloride was filtered out, and when a 5 per cent. solution was used, the value 1·11860 (81d) milligrammes per coulomb resulted; subsequently we used a 10 per cent. solution and obtained 1·11840 (83b). We infer that pure perchlorate of silver will give the same value as pure nitrate, but it is much more difficult to prepare.

(4) Acting on a suggestion of Mr. W. C. D. Whetham, we prepared an electrolyte by dissolving silver nitrate in pyridine. Considerable heat was evolved during dissolution, but the liquid was quite clear. On electrolysis the deposited silver was of a brownish-red tint, but when washed with very hot water the intensity of the colour was considerably reduced. It was apparent, however, that the mass was not pure silver, and the result (1·11890) (67b) is not of very great interest.

(5) Fused Silver Nitrate.—Merrill* was successful in obtaining coherent deposits from fused silver nitrate, and compared them with deposits obtained from solutions of the same salt. He concluded that the masses were identical. We have on several occasions deposited about 7 grammes of silver on platinum bowls and obtained very coherent deposits, but errors introduced in the manipulation have so far prevented us from making a satisfactory comparison with deposits obtained in the usual way.

Summary.

1. It is possible to prepare again and again samples of silver nitrate which give in the voltameters described in Part I. of this communication values for the electrochemical equivalent which do not vary by more than 3 parts in 100,000 on either side of the mean figure.

2. A standard method of purification is described. Commercial samples are usually pure, but cannot be absolutely relied on.

3. High values are obtained for the electrochemical equivalent if the solution contains oxide, carbonate, chloride, nitrite or hyponitrite. Low values are caused by the presence of acid.

4. Impurities which increase the mass of the deposit per coulomb are usually substances which are insoluble in water, but soluble in silver nitrate solutions; they are therefore precipitated from the impoverished solution at the kathode.

5. Silver chlorate and silver perchlorate appear to give normal deposits, but are more troublesome in use and have no advantage over the nitrate.

6. There may be slight changes in the electrolyte due to its interaction with filter paper, but the mass of the deposit is not seriously affected thereby in our size of voltameter in the course of one electrolysis at ordinary temperatures. It is inadvisable, however, in measurements of precision, to use an electrolyte more than once.

We desire to thank the Committee of the British Association for grants of money for the purchase of materials; Messrs. Johnson, Matthey and Co. for the loan of several platinum vessels; Mr. L. Oertling and Dr. Scott for the loan of sensitive balances; and Professor G. van Dijk for the loan of apparatus used by him in his researches. Our thanks are also due to Lord Rayleigh and Dr. Glazebrook for much advice during the progress of the investigation.
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NINE AUTOMATIC EXPOSURES ON ONE PLATE.

(Figures in first line = exposure; in second line = ratio of focal-length and equivalent diameter of lens.)
MICROPHOTOGRAPHS OF CRYSTALS OF MERCUROUS SULPHATE.

Magnification = 250.

Figs. 1, 5, 8. Steinwehr's method of preparation.
. . 6, 7. Electrolytic method of preparation.
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Fig. 1. Large high-pressure furnace (vertical position).

Fig. 2. Large high-pressure furnace (horizontal position).
Fig. 2. Complete current weigher (sides of case removed).
Fig. 6. General view of physical balance (without coils).

Fig. 7a. End view of current weigher.